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Referencia: Solicitud de PCT Patente de Invención denominada
Producción de Redes de Estructura Cristalina de Carbono.

Asunto: Respuesta al Requerimiento No. 5417 del 16 de abril de 2021.

Expediente No. NC2018/0014109

Juan Carlos Cuesta Quintero, mayor de edad, identificado como aparece al pie de mi firma, obrando en mi calidad de apoderado de la sociedad **Carbonx IP 3 B.V.**, doy respuesta al Oficio No. 5417 del 16 de abril de 2021, bajo los siguientes términos:

1. Reivindicaciones relativas a un uso:

La reivindicación 10 ha sido eliminada del nuevo capítulo reivindicatorio.

2. Reivindicaciones:

- En el nuevo juego de reivindicaciones (adjunto), la reivindicación 1 se ha modificado para incluir que el reactor es un reactor de negro de carbón de horno (base en la página 7, líneas 20-21; Figura 1A y descripción de la Figura 1A (página 4, líneas 22-29) de la solicitud original.
- Las reivindicaciones anteriores 1 y 2 (nuevas reivindicaciones 1 y 4) se modifican para incluir que la microemulsión también comprende aceite de materia prima de negro de carbón (base en la página 2, líneas 35-37 de la solicitud PCT presentada).
- Todas las reivindicaciones se han redactado en dos partes. En la reivindicación 1, el uso de la microemulsión específica con las nanopartículas metálicas forman la parte caracterizante.
- Se modifican las reivindicaciones anteriores 1-4 y 7-8 (nuevas reivindicaciones 1, 4, 7, 9, 13 y 14, respectivamente) para eliminar las características preferidas; Algunas de estas características se incluyen ahora en las nuevas reivindicaciones dependientes 2-3, 5-6, 8, 10, 15 y 16. La característica preferida en la nueva reivindicación 8 también se modifica para aclarar que la referencia a "superior" cuando se hace referencia a un porcentaje es equivalente a un máximo del 100%.

- Se modifica la reivindicación 4 anterior (nueva reivindicación 9) para incluir un límite superior a la concentración de nanopartículas de catalizador metálico (en base a la solicitud presentada, página 11, líneas 20-23).
- La reivindicación anterior 6 (nueva reivindicación 12) se modifica a rangos específicos cerrados para cada una de las propiedades de la red (según la solicitud presentada, página 13, líneas 1-11).
- Se modifica la reivindicación 8 anterior (nueva reivindicación 14) para eliminar cualquier referencia a un resultado a alcanzar.
- Las reivindicaciones independientes anteriores 11 y 12 (nuevas reivindicaciones 18 y 19) se hacen dependientes de la reivindicación 1.
- Hemos sustituido los verbos en gerundio en la reivindicación 1 por verbos en infinitivo, según la sugerencia del Examinador.
- El término “composite” se ha sustituido por “material compuesto” a lo largo de la descripción y las reivindicaciones.
- Con respecto a las objeciones al uso de la “emulsión aromática o alifática” y “polímeros” en las reivindicaciones 3 y 8 anteriores (nuevas reivindicaciones 7 y 14), nos gustaría defender que estas declaraciones están soportadas por los Ejemplos y representan una generalización aceptable del alcance de protección sin necesidad de restringir indebidamente el alcance de las reivindicaciones. Evidentemente, está claro que la naturaleza de la fase oleosa y el tipo de polímeros no tienen un efecto limitante sobre la invención, la cual se basa en la formación de redes de carbono utilizando estas microemulsiones específicas con nanopartículas metálicas en un negro de carbón de horno.
- Con respecto a las objeciones sobre la reivindicación 5 de “product by process” (nueva reivindicación 11), nos gustaría aclarar al Examinador que la estructura de la red de estructura cristalina de carbono de la reivindicación 11 es una consecuencia directa del proceso, que es novedoso e implica un nivel inventivo como se explica a continuación. El solicitante estaría indebidamente limitado al tener que restringir la estructura del producto tal como se fabrica mediante el proceso más allá de la definición de la reivindicación 11; Es imposible y poco práctico caracterizar las redes en características estructurales, o en este caso, usando características funcionales, manteniendo un alcance justo de protección asociado con el concepto inventivo de usar microemulsiones específicas con nanopartículas metálicas en un negro de carbón de horno. Por lo tanto, rogamos amablemente al Examinador que reconsidere su postura.

3. Examen de Patentabilidad:

2.1. Nivel Inventivo

Observamos que el Examinador considera que las reivindicaciones anteriores 1-12 carecen de nivel inventivo en vista de las enseñanzas de los documentos D1 y D2. El solicitante aporta un nuevo juego de reivindicaciones defendiendo que las nuevas reivindicaciones 1-19 implican méritos inventivos sobre estos documentos en base a los siguientes argumentos:

La presente solicitud se refiere a la producción de redes estructuradas cristalinas de carbón, donde las características clave de la invención son el uso de microemulsiones (termodinámicamente estables), ya sean bicontinuas o de tipo w/o, donde las microemulsiones comprenden nanopartículas de catalizador metálico, donde las microemulsiones que contienen catalizador se someten a alta temperatura para producir redes de estructura cristalina de carbono. El nuevo juego de reivindicaciones también especifica que el proceso para lograr estas estructuras debe realizarse en un reactor de negro de carbón de horno y que las microemulsiones comprenden aceite de materia prima de negro de carbón.

D2 enseña un método para fabricar redes de nanotubos de carbono (CNT) (párrafo [0001]) utilizando un proceso de deposición química en fase de vapor (CVD) que es común a la fabricación de CNT. Se hace referencia al párrafo [0010] en D2, y por lo tanto el producto producido por los diferentes procesos es diferente.

Se llama la atención del Examinador sobre el hecho de que los CNT son estructuras de carbono de una forma muy específica y estas formas son las que hacen que estas estructuras sean atractivas para su uso en la adición de resistencia mecánica y conductividad en D2. Si bien el uso de microemulsiones tiene un efecto sobre estas estructuras específicas derivadas de CNT así obtenidas con CVD, esto no le da al experto en la materia ninguna indicación de que, en un proceso de fabricación completamente diferente, es decir, no el de CNT sino de negro de carbón, se obtienen redes de nanoestructuras cristalinas de carbono con propiedades mejoradas en comparación con el negro de carbono. El negro de carbón se produce en grandes cantidades en todo el mundo. Sus partículas esféricas de carbono elemental, que se agregan para formar estructuras complejas amorfas que agregan negrura, resistencia al caucho o conductividad a muchos productos. En ocasiones, los CNT y el negro de carbón son a veces tecnologías en competencia. Esto tiene poco que ver con la fabricación, que no presenta similitudes en absoluto.

Deshmukh (2010) proporciona una revisión de diferentes métodos para producir diferentes estructuras y formas de materiales de carbono; se adjunta una copia de este documento

para conveniencia del Examinador. El segundo párrafo menciona que los tubos de carbono y las esferas son diferentes: “*En particular, los nanotubos de carbono (CNT) se han estudiado ampliamente y esta área ha proporcionado un fuerte enfoque para muchos trabajos en el estudio de SCM.* El otro tipo de estructura que tiene una larga historia de estudio, y se ha convertido de nuevo en un foco de atención reciente, es el material de carbono de forma esférica”. Por lo tanto, ya en términos de producto, hay una clara distinción entre estos tubos y esferas. La siguiente tabla resume las principales (¡no exhaustivas!) diferencias entre CVD y un proceso de negro de carbón:

	CVD	Negro de horno
Tiempo de residencia	>1 min	10-1000 ms
Temperatura de reacción	<1200C	>1300C
Lote / continuo	Lote / semicontinuo	Continuo
Rendimiento máximo	Gramos	Toneladas / hora
Ambiente	Inerte	Presencia de oxígeno
Distribución de tamaño de partícula	Monodisperso	Muy amplio

D1 describe un proceso en el que se inyecta simplemente una solución acuosa o una emulsión de fase única en la zona de reacción. La columna 6, líneas 1 - 19, menciona la opción de usar agua o una emulsión; sin embargo, no se menciona una microemulsión, y mucho menos una microemulsión del tipo w / o o bicontinua. Además, D1 describe específicamente la incorporación de aditivos de níquel, vanadio, hierro o cobalto en la materia prima antes de la reacción del negro de carbón, para tratar los depósitos de coque u otros materiales carbonosos y, por lo tanto, no para su uso como catalizadores. Debido a que D1 solo se refiere generalmente a "metal", D1 no describe la característica de "nanopartículas de catalizador de metal" según la invención, es decir, nanopartículas de catalizador de metal con las siguientes características: uniformidad de las partículas de metal (página 11, línea 3) obtenidas por una sal de complejo metálico capaz de reducirse hasta las partículas metálicas definitivas (página 11, líneas 5-6).

El proceso descrito en la nueva reivindicación 1 independiente difiere por lo tanto de D1 en, al menos, las características de "*una microemulsión de agua en aceite o bicontinua*" que comprende "*aceite de materia prima de negro de carbón y nanopartículas de catalizador metálico*". El efecto de estas características combinadas se puede derivar directamente de las redes obtenidas que tengan las características descritas en la página 15, líneas 8-12 (Ejemplo 1A), es decir, un N2SA y OAN de 350 m2 / gy 170 cc / 100 g, respectivamente. En contraste, el proceso descrito en D1 da como resultado negro de carbón tradicional, que tiene un área superficial de N2 y absorción de aceite (N2SA y OAN) de aproximadamente 79 m2 / g y 111 - 117 cc / 100 g, respectivamente. Las redes de acuerdo con la invención también son distintas en términos de estructura según se derivan de SEM.

Los ejemplos 4 - 6 de la solicitud evidencian además los efectos de las redes de estructura cristalina de carbono, en términos de resistencia y conductividad, en comparación con el negro de carbón, como resultado de las diferencias en la fabricación, es decir, la microemulsión de agua en aceite o bicontinua, que comprende nanopartículas de catalizador metálico, y estas características esenciales son parte de las reivindicaciones. El ejemplo 3 de la solicitud proporciona evidencias de que no se forman redes sin la presencia de estas nanopartículas de catalizador metálico.

Por tanto, el problema resuelto por la presente invención no es cómo modificar el método de D1 para obtener un método alternativo, como cree el Examinador, sino cómo proporcionar nuevas redes de nanoestructuras de carbono con propiedades mejoradas en términos de propiedades de absorción y / o resistencia mecánica y conductividad en un proceso de negro de horno.

El experto en la materia no encontraría ningún incentivo para aplicar las enseñanzas de D2 al proceso tradicional de negro de carbón de D1 para llegar al objeto de la nueva reivindicación 1. Dado que D2 está dirigido sólo al proceso de CVD, que es diferente al proceso de negro de carbón empleado en la invención, el experto en la materia no consideraría las enseñanzas de D2, y mucho menos las emplearía en D1. En primer lugar, no hay evidencia de que la ECV sea siquiera un campo vecino. Además, incluso si se encontraran efectos específicos en dicho proceso de CVD, la persona experta no habría tenido expectativas razonables de que se tuviera que aplicar lo mismo si partes del proceso de CVD se implementaran en una línea de tecnología completamente diferente.

Es un claro conocimiento retrospectivo argumentar que la persona experta podría haber aplicado el conocimiento sobre la formación de redes con CVD para CNT (usando un catalizador) como se describe de D2 al proceso de negro de horno de D1 con sus propios tiempos y temperaturas de reacción específicos. De hecho, con las condiciones de fabricación del negro de carbón se pueden producir redes con propiedades mejoradas en comparación con las de CVD en D2. Por lo tanto, el problema de proporcionar nuevas redes de nanoestructuras de carbono con propiedades mejoradas en términos de propiedades de absorción y / o resistencia mecánica y conductividad en un proceso de negro de horno no debe considerarse como una modificación menor sobre la técnica anterior, que se pueda lograr mediante experimentación de rutina, y por tanto, el nivel inventivo de la nueva reivindicación 1 debe reconocerse.

Dado que las características de la red de estructura cristalina de carbono en la nueva reivindicación 11, así como los compuestos que comprenden estas redes en la nueva reivindicación 14, son el resultado directo del proceso de las nuevas reivindicaciones 1 a 10, las mismas consideraciones con respecto a D1 y D2 (argumentado anteriormente) y las propiedades del material de negro de humo allí descrito, se aplican mutatis mutandis y, por lo tanto, estas reivindicaciones también deben considerarse inventivas a la luz del estado

de la técnica citado. En aras de la exhaustividad, también nos gustaría presentar lo siguiente con respecto el nivel inventivo de la nueva reivindicación 13.

El Examinador cree que la red de estructura de carbono cristalino de la reivindicación 11 estaría "sugerida" por los documentos D1 o D2 del estado de la técnica (y por lo tanto no sería inventiva), porque no habría evidencia del efecto técnico logrado por el producto reivindicado. No estamos de acuerdo por los siguientes motivos:

Las redes de estructura cristalina de carbono de la reivindicación 11 se proporcionan por el proceso de la invención. El solicitante estaría indebidamente limitado al tener que definir la estructura del producto como fabricado por el proceso más allá de la definición de la nueva reivindicación 11. Es imposible y poco práctico caracterizar las redes en características estructurales, o para el caso, utilizando características funcionales. Teniendo esto en cuenta, el solicitante discrepa respetuosamente en que las redes de la reivindicación 11 (obtenidas mediante el proceso de cualquiera de las reivindicaciones 1 a 10) no serían distintas de las de D2.

La reivindicación 11 describe una red de estructura cristalina de carbono, en la que dichas estructuras de carbono están interconectadas químicamente a través de una multitud de uniones, incluidas las uniones en Y y en H. D2 describe redes de nanoestructuras de carbono obtenidas usando deposición química en fase de vapor (CVD), en contraste con el proceso de negro de horno de la presente invención. El proceso de negro de horno, según la invención, garantiza tiempos de reacción muy cortos, es decir, entre 10 ms y 1000 ms, como resultado del uso de una alta velocidad de gas y del diseño específico del reactor en comparación con otros procesos, como la deposición química en fase de vapor (CVD), aplicado en D2. El tiempo de reacción determina el tamaño de partícula, respectivamente a las dimensiones del nódulo. Cuanto más corto sea el tiempo de reacción, más pequeñas serán las partículas.

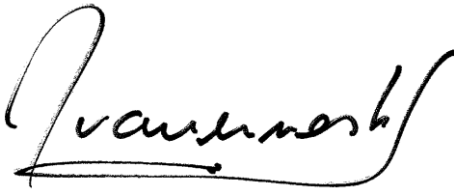
En un proceso de negro de horno se pueden lograr tamaños de partículas más pequeños de las nanoestructuras cristalinas de carbono, como lo demuestran los datos de la solicitud de patente en comparación con los de D2. En D2, la FIG. 3a muestra una imagen TEM de una red de nanotubos de carbono, que indica la escala de 1 μm , en la que las estructuras más gruesas y más largas son grupos de nanotubos más pequeños ([0020]); La FIG. 4 indica que los nanotubos están interconectados químicamente, donde los puntos negros son catalizadores de nanopartículas que se usaron para hacer crecer los tubos ([0022]); La Fig. 8 muestra redes de nanotubos de carbono cultivadas usando (a) hierro y (b) nanopartículas de catalizador de plata ([0025]), lo que indica una escala de 2 y 20 μm , respectivamente. Como se argumentó anteriormente, no hay enseñanza (ni siquiera una pista o sugerencia) en D1 que pueda guiar al experto en la alteración del proceso en D2 para lograr estos valores. Las redes del proceso de la invención muestran inherentemente un mayor volumen de cristal (mayor grado de cristalinidad) y un tamaño de agregado más

pequeño que las redes producidas por CVD en D2. Por lo tanto, sostenemos que la reivindicación 11 es inventiva sobre D2, ya sea de forma aislada o combinada con D1.

En conclusión, todas las reivindicaciones presentadas son claras e implican un nivel inventivo sobre D1 y D2.

En vista de todo lo anterior, ruego a usted estudiar nuevamente la solicitud con base en las modificaciones realizadas y proceder de conformidad.

Cordialmente,



Juan Carlos Cuesta Quintero.

C.C. 79.339.809 de Bogotá

T.P. 43.273 del C.S. de la J.

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NC2021/0009160 - NC Modificación a las reivindicaciones - Solicitado en Patente
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Carbon spheres

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ABSTRACT

The discovery of fullerenes has opened up new studies in shaped carbon materials. In particular the discovery that carbon atoms in fullerenes showed curved sp^2 bonding also led to the discovery of single walled carbon nanotubes and a re-investigation of carbon fibers and tubes. The area of shaped carbon materials has since been dominated by studies of carbon nanotubes. The discovery has, however, also impacted on the well known spherical carbons exemplified by carbon blacks. Over the last two decades this has led to a resurgence of interest in solid carbon spheres as well as core-shell spheres and hollow carbon spheres. In this review, developments in the synthesis, doping and functionalization of spherical carbon materials (but not fullerenes) are highlighted. The chemical and physical properties as well as the uses of the spheres are also described.

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1. Introduction

The discovery of fullerenes in the mid-1980s [1] has led to an upsurge in interest in the structures and shapes of carbon containing materials, in particular when the carbons are in the ‘nano’ regime [2,3]. In the past two decades many differently shaped carbon materials (SCMs) have been synthesized and characterized and their properties in a range of different environments studied.

These shaped materials include tubes and fibers [4,5], onions [6–11], spheres [12–16], horns [17], calabashes [18], flasks [19], etc. In particular, carbon nanotubes (CNTs) have been extensively studied and this area has provided a strong focus for much work in the study of SCMs. The other type of structure that has a long history of study and has again become a recent focus of attention is the spherically shaped carbon material. A spherical shape is the shape adopted by materials during synthesis (growth, nucleation) [20] and is determined by considerations of energy minimization. Spherically shaped carbon materials have been known for decades and their properties have been exploited in many arenas (tyres, batteries, printer inks, etc. [21,22]). Much of the early work has related to the synthesis of spheres in an oxidizing environment (e.g. in the formation of carbon blacks) and industries have been built on this approach to making carbon spheres [23].

Spherically shaped carbon materials have been given many names. These include carbon balls, carbon nanospheres, carbon microbeads, carbon blacks, onions, mesoporous microbeads, etc. While the properties/sizes/morphology of the spheres can certainly vary there appears to be no consistent nomenclature for naming these shaped materials; consequently in this review we will use the generic term carbon spheres (CSs) to cover all carbons that have a spherical or near spherical shape. This will not include the fullerene family of carbons.

The spherical shape is not peculiar to carbon; indeed numerous studies of spherical silica have indicated the wide range of synthetic strategies and approaches that can be used to make spherical materials [20]. A key target when making spherical materials is to ensure that they are monodisperse and that the size (diameter) and the chemical properties of the external rim can be controlled.

Many CSs have been shown to be made of layers of carbon that typically form broken concentric layers emanating from the core. CSs are attracted to each other by van der Waals forces and this leads to agglomerated collections of CSs. When CSs have diameters

of less than 1000 nm they also tend to accrete, i.e. bond together to form necklace or bead like structures. Thus, although CSs are normally discussed as though they are discrete, they often form connected solid extended chains (Fig. 1). These chains are formed early in the synthesis process and are not necessarily due to post-synthesis treatments. Mechanisms that have been proposed to explain their formation are described in this review. Spheres can also be built up from carbon layers that are perpendicular to the sphere rim [24,25].

The study of CSs can be categorized in four different ways. Firstly, spheres can be described as solid, core-shell or hollow [20]. Secondly, they can be classified according to their ‘nanometric texture’, i.e. in terms of whether the spheres are made of concentric, radial or random layers (Fig. 2) [24].

Thirdly, it has also been proposed that spheres can be categorized in terms of their size, in particular their diameter [26]. In this method three categories are recognized (i) well graphitized spheres (2–20 nm), (ii) less graphitized spheres

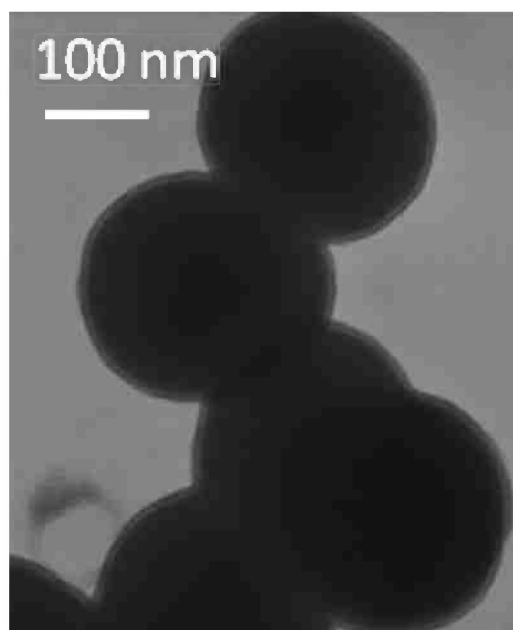


Fig. 1. A transmission electron microscope image of CSs that have aggregated to form a necklace.

Random orientation Concentric orientation Radial orientation



Fig. 2. Cartoon indicating radial, concentric and random carbon layer orientations in carbon spheres.

(50–1000 nm) and carbon beads (>1000 nm). Fourthly, it is possible to classify spheres in terms of strategies used in their synthesis. It appears that the procedures used to make spherical carbon materials such as chemical vapor deposition (CVD), arc-discharge, laser ablation, autoclave processes, etc. can produce quite different materials.

1.1. Sphere morphology

A wide variety of CSs have been synthesized and a few comments on the morphology of the spheres are appropriate.

1.1.1. Diameters

The sizes of CSs are known to range from a few nanometers (as found in onions) to many microns (as produced by polymerization reactions). In most instances in a synthesis procedure a wide range of diameters are generated and it is becoming more common to reflect this in reports in terms of bar graphs or by a statement about the sphere diameters and their standard deviation.

1.1.2. Surface areas

The surface areas of CSs vary from very low ($<2 \text{ m}^2 \text{ g}^{-1}$) to very high values ($>1200 \text{ m}^2 \text{ g}^{-1}$). These values can be tailored by the synthesis procedures with hard spheres being associated with low surface area carbons.

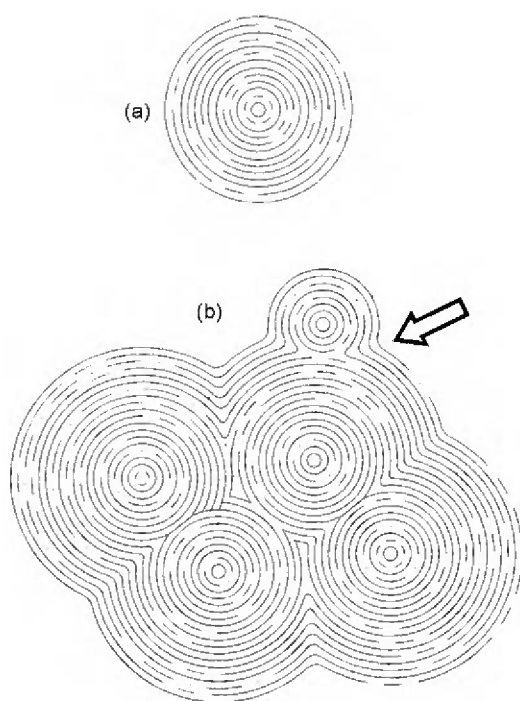


Fig. 3. Schematic representation of carbon black. (a) Carbon onion like structure; (b) aggregate of carbon-onion like structures (arrow indicates 'neck' between carbon-onions) [27].

1.1.3. Accretion

The smaller CSs, typically made by CVD procedures, generally are found in necklace form, i.e. the spheres are linked (accreted) together typically in a 2D strand that can extend over tens of spheres (Fig. 1). It appears that the sphere linkages appear early in the synthesis process and involve the graphite layers encapsulating spheres in the necklace. The spheres are thus chemically linked together. Larger spheres normally form as discrete carbon structures that can interact with other spheres through van der Waals bonding.

Fig. 3 shows the effect of heating discrete carbon spheres (a) to form amalgamated structures via sphere coalescence (b) that can take place at high temperatures. Indeed, it has been shown that when carbon balls (CBs) are used as an electrode in an arc-discharge reaction that the spheres accrete at high temperature to eventually give multi-walled CNTs [27]. A model involving defects and heptagon/pentagon structures was used to explain the transformation. Theoretical and experimental studies on spherical objects (oil droplets covered with silica/CTAB) that form accreted structures have recently been reported. These studies suggest that carbon necklaces could be produced with specific geometries and sizes (Fig. 3) [28].

1.1.4. Arrangement of carbon layers

As mentioned above spheres can be formed with their carbon chains/layers/flakes perpendicular or parallel to the carbon core (Fig. 2). The arrangement of the layers has a major influence on the chemical and physical properties of the CSs.

A diagram showing the carbon flakes arranged parallel to the carbon core is shown in Fig. 4 [29]. The flakes typically have sizes in the range of 2–10 nm. The size of the flakes can be determined by TEM or XRD studies. Pyrolysis of the CSs generates a more graphitic structure in which the flakes grow in size.

1.1.5. Hollow and filled spheres

Hollow spheres can be made by a number of generic approaches, the most popular being a templating process. In the template procedure a spherical material (metal complex, micelle, silica, etc.) is covered by a carbon containing material that is

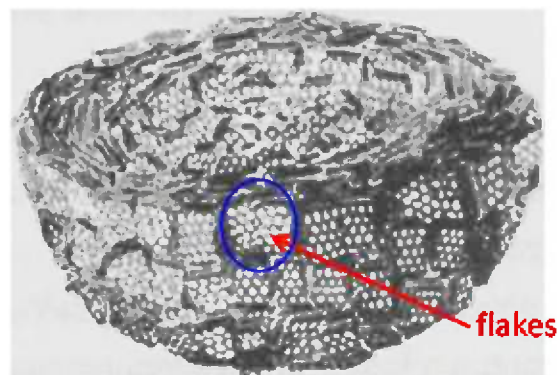


Fig. 4. Model showing cutaway of a single carbon black particle with concentric layers. Parallel orientation of ordered layer groupings and diminishing graphitic order near particle center [29].

Table 1

Carbon spheres: Synthesis and size details.

Catalyst; carbon source	Synthesis conditions	Carbon sphere size	Reference
<i>Arc-discharge</i>			
Polyethylene terephthalate	Carbon balls were heated to 1100 °C; arc-discharge	100 nm	[50]
Carbon rod containing Fe–Ni; acetylene	A current of 70–90 Å was passed through two electrodes in an acetylene medium at a pressure of 0.05–0.06 MPa	50–100 nm. The material showed that the cell electrode has a high reversible capacity	[53]
Ni; coal	40–50 V and a current of 50–70 Å were used; under helium at pressure of 500–700 Torr	10–20 µm. Exist in different forms such as balls, net-like structures and plate like materials	[54]
Fe electrode; ethanol	An ultrasonic homogenizer was used at 600 W and 20 kHz to irradiate 300 ml of liquid ethanol. The voltage between the anode and iron tip-cathode was kept at 55 V using a regulated DC power supply, and the current of the power unit was set at 3.0 A	100–200 nm	[55]
<i>Laser ablation</i>			
Fe cake; CH ₄	An iron cake was molten under argon at a 40 kW frequency. Afterwards CH ₄ gas at 5 kPa was introduced	5–50 nm	[56]
Co, Ni; carbon aerosol	1700–2400 °C	50–100 nm	[57]
MgO–Ni supported on Si; CH ₄	700–800 °C, 1600 Pa CH ₄ , radio frequency 220 W	100–800 nm	[58]
Anthracene	700–1000 °C, CO ₂ laser power 30 W	CSs were produced depending on the collection point on the target; 100–400 nm and 1–2 µm	[59]
Iron; CH ₄	900–1100 °C	1.2–35 µm	[60]
<i>Shock-compression</i>			
Fullerene	A shock-compression up to 57 GPa was used	300 nm	[61]
Pyrolytic graphite	2995 °C for 1 h	8–70 nm	[63]
<i>Non-catalytic chemical vapor deposition</i>			
Toluene	1100 °C	60 nm–1 µm	[67]
Toluene/acetylene	1000 °C for 20 min	200 nm	[68]
Styrene, toluene, benzene, hexane, cyclohexane and ethane	900 and 1200 °C were employed	50 nm–1 µm	[69]
Asphaltene	950 °C	300–400 nm	[70]
Corn starch	Oxidized corn starch was carbonized at 2600 °C	5–25 µm	[71]
Tetrahydrofuran			[72]
<i>Catalytic chemical vapor deposition</i>			
Zn–Se; toluene	1100 °C for 3 h	40–120 nm	[73]
Melamine-formaldehyde resin	1000 °C under nitrogen, and silica was removed by HF	~1.2 µm. The spheres had a very high surface area (1460 m ² g ^{−1}) and pore size 31 nm	[74]
Si; benzene and acetonitrile	900 or 1000 °C	Single, double shelled and nitrogen doped spheres were synthesized ranging from 460 to 1600 nm	[76]
Kaolin supported Fe, Co, Ni; acetylene	650 °C	400–2000 nm	[77]
Kaolin supported Fe, Co, Ni, Cu; acetylene	Same procedure used above	400–2000 nm	[78]
Ni; acetylene	700 °C	50 nm. A mechanism for formation of nanopearls was proposed. Material showed high field emission	[79]
Ni/Al ₂ O ₃ ; CH ₄	600 °C	5–90 nm	[80]
NiO/Al; CH ₄ /N ₂	600 °C	5–50 nm	[81]
Tungsten; CH ₄	1650 °C	5–7.5 µm	[82]
Co/MgO; CH ₄	600 °C	50–200 nm. The effect of different metal oxides was demonstrated	[83]
Fe or Ni particles; kerosene	1000 °C	80–100 nm	[85]
Ferrocene; camphor	1000 °C	Carbon nanobeads about 250–850 nm covered with graphitic shell of 80–100 nm	[86]
Transition and/or rare earth metal oxides; CH ₄	1100 °C	~210 nm. Mechanism for formation of CSs is proposed	[89]
Mo powders; CCl ₄	600–900 °C	Temperature affects the size and hollowness of CSs	[90]
Mesitylene	700 °C for 3 h	2.5 ± 0.05 µm. A mechanism for CS formation was proposed	[93,94]
Au tube; polyethylene, various acids	650 °C, 30 MPa	2–6 µm	[95]
Au tube; paraformaldehyde and water	850 °C at 100 MPa	No sphere formation	[96]
Sugar	190 °C for 5 h	1–5 µm. These spherules were used in lithium storage batteries as support for the lithium	[97]
Polyethylene terephthalate	700 °C for 3 h	2–10 µm. These ultra hard spheres with low surface area (2.1 m ² g ^{−1}) were paramagnetic	[40]

Table 1 (Continued)

Catalyst; carbon source	Synthesis conditions	Carbon sphere size	Reference
Glucose, polystyrene and P123	180 °C for 12 h	1.5 μm , wall size 150 nm. Spheres were measured to have very high surface area $1249 \text{ m}^2 \text{ g}^{-1}$. Pd-CSs were used for ethanol oxidation reaction	[98]
Si particles; sucrose	850 °C for 5 h	Diameter of 340 nm and surface area $788 \text{ m}^2 \text{ g}^{-1}$	[99]
Methylcellulose	400 °C for 6 h	1–5 μm	[100]
SiC powders; various organic acids	600–850 °C for 40–80 h (pressure = 100–200 MPa)	The CS size was not given	[101]
CaC ₂ and oxalic acid	65 °C	80–100 nm	[102]
Ferrocene; C ₂ Cl ₄	550 °C for 16 h at 8 MPa in an autoclave	30–580 nm	[105]
Ferrocene; ammonium chloride	2 MPa argon, 700 °C	Hollow spheres of diameter 1 μm and 75 nm shell thickness were prepared. Mechanism for the formation of spheres was reported	[106]
Ferrocene; NH ₄ Cl	0.1–4.3 MPa and temperatures 450–700 °C for 0.5 h	1–10 μm	[107]
Ferrocene; CaC ₂ , chloroform	350 °C for 3 h	50–250 nm and inter-layer distance of 0.34–0.4 nm. BET surface area of $48 \text{ m}^2 \text{ g}^{-1}$	[108]
FeCl ₃ ; CaC ₂ and CCl ₄	350 °C for 3 h in a sealed autoclave	0.3–1.8 μm and shell thickness of 30–80 nm	[109]
Ferrocene; 1,2-dichlorobenzene	180 °C for 24 h	Temperature and ferrocene to 1,2-dichlorobenzene ratio influenced the sphere synthesis	[110]
Ferrocene; C ₆ Cl ₆	500 °C for 4 h	The spheres had surface area of $594 \text{ m}^2 \text{ g}^{-1}$ and pore size distribution of 5 nm. The hydrogen storage capacity up to 242 mAh/g achieved	[111]
Sodium; hexachlorobenzene	160 °C for 10 h	Small ball like particles with diameter of 50–100 nm were obtained	[112]
Sodium; hexachlorobenzene	400 °C for 10 h	50–500 nm	[113]
NaN ₃ ; poly(tetrafluoroethylene)	550 °C	50–150 nm. Formation mechanism reported	[114]
Co/Ni; NaNH ₂ , CCl ₄	190–230 °C for 24 h	400–600 nm with shell thickness 50 nm	[115]
Ni foil; acetone	550 °C for 12 h	4–5 μm	[116,117]
Mg powder, Na ₂ CO ₃ ; CCl ₄ - benzene	450 °C for 10 h	150–600 nm	[118]
Hg ₂ Cl ₂ ; CS ₂	750 °C for 12 h	Multi-shelled CSs with diameter 1 μm and shell thickness 30 nm were obtained	[119]
Ni; cyclohexane	550 °C for 8 h	The average shell spacing was 0.34 nm and the shell thickness 3–4 nm	[120]
Glucose and 1-butyl-3-methylimidazolium tetrafluoroborate	160 °C for 20 h	CSs with diameter 1 μm	[121]
Ferrocene; anthracene	800 °C for 12 h	Effect of Fe/C ratio and temperature were studied. Increase in Fe/C ratio leads to increase in yield	[122]
Mg; glycerin	650 °C for 12 h	Carbon onions with diameter 60–90 nm and shell-shell spacing of 4.5 nm were produced	[17]
Li; supercritical CO ₂	650 °C, 1000 atm 10 h	Graphitic atomic planes separated by 0.34 nm with 450 nm diameter	[125]
Li, K; supercritical CO ₂	550 °C, 10 h	Effect of binary metal on synthesis of solid carbon nanospheres	[126]
Ca, supercritical CO ₂	550 °C in 24 h	1–2 μm	[128]
Mg; poly-tetrafluoroethylene, supercritical CO ₂	650 °C for 6 h	~1 mm; mechanism proposed	[129]
(101) Ca(OH) ₂ ; supercritical water	550 °C for 12 h	140–200 nm	[130]
Novolac-type phenolic resin, supercritical water	800 °C for 30 min under a nitrogen flow	4 nm, with surface area $919 \text{ m}^2 \text{ g}^{-1}$ and mesoporosity about 17%	[131]
Pitches	350 and 450 °C	5–8 μm with very high surface areas $> 2600 \text{ m}^2 \text{ g}^{-1}$	[132–139]
Isotropic naphthalene pitches	380–430 °C for 1–12 h	1–10 μm	[140]
1,8-Dibutyl-1,3,5,7-octatetrayne	800 °C under an inert atmosphere	2–316 μm	[141]
Naphthalene-derived isotropic pitch	600 and 900 °C	100–300 nm	[142–144]
Water-in-oil emulsion of ammonia	80 °C for 1 h	2–30 μm	[145,146]
Silica spheres; furfuryl alcohol	900 °C	Spheres diameter $< 1 \mu\text{m}$ with surface areas of $> 1000 \text{ m}^2 \text{ g}^{-1}$	[147]
Poly(divinylbenzene)	500 °C for 3 h	3–5 μm	[148]
NaOH; resorcinol-formaldehyde/cetyltrimethylammonium	1000 °C for 4 h	370–820 nm with high surface area $1777 \text{ m}^2 \text{ g}^{-1}$	[149]
Iron doped polypyrrole nanoparticles	850 °C for 5 h	30–60 nm with surface area $\sim 361 \text{ m}^2 \text{ g}^{-1}$	[150,151]
Polystyrene	600 °C for 3 h	350 nm	[152]
Vinylidene chloride and acrylonitrile	600 °C for 2 h	125–150 μm with surface area of $692 \text{ m}^2 \text{ g}^{-1}$	[153]
Aluminium incorporated silica; phenol-resin or poly(divinylbenzene)	850 °C for 7 h	Diameter and shell thickness of spheres 220 nm and 55 nm, respectively	[154]
Melamine and formaldehyde	800 °C for 2 h	1500–2000 nm. The surface area of the mesoporous CSs was found to be $1330 \text{ m}^2 \text{ g}^{-1}$	[155]
Si ₃ N ₄ ; poly(phenylcarbene)	1000 °C for 2 h	0.5–2 μm	[156]
Phenol-formaldehyde resin		450–500 nm	[157]
NH ₄ Cl; potato starch	600 °C for 1 h		[167]
AgNO ₃ ; pollen grains	600 °C for 6 h in air and nitrogen	Effect of concentration and treatment time on the size of silver nanoparticles	[168]

Table 1 (Continued)

Catalyst; carbon source	Synthesis conditions	Carbon sphere size	Reference
Glucose	180 °C for 20 h	2 μm . CSs were used as bioactive injectable filler for bone tissue regeneration	[169]
Glucose with sodium dodecyl surface	900 °C for 2 h in nitrogen	300 nm to 1 μm . Pt nanoparticles were supported on the spheres and the catalyst was used for electrochemical oxidation of methanol	[170]
Au on SiO_2 ; CCl_4	800 °C	Shell appears to be 1–2 nm	[171]
Acetylene, BF_3/MeOH		350–700 nm. Material showed good electron conductivity	[178,179]
Silica spheres; benzene, acetonitrile	1000 °C	CSs with an external diameter of around 810 nm and a shell thickness of about 60 nm	[76]
Melamine/formaldehyde	1000 °C for 5 h	400 nm	[183]
Iron doped polypyrrole	800 °C	50 nm; nitrogen content was about 4–5%	[184]
Mg, NiCl_2 ; $\text{C}_3\text{N}_3\text{Cl}_3$	400 °C for 2 h	250 nm	[185]

permitted to self-assemble and following C–C bond formation on the surface of the sphere a filled core–shell structure is synthesized. The interior of the sphere can have materials that have properties that may be exploited. For example, if the core is made of a magnetic material then magnetic fields can be used to manipulate the CSs [30,31].

Alternatively the core can be removed, usually thermally, to generate a hollow sphere. The template is hence sacrificed in the synthesis. Polyelectrolyte capsules and related materials also allow for synthesis of hollow spheres, but in this method growth within the cavity rather than in the shell to give parachute like morphologies takes place [32].

The synthesis of hollow inorganic spheres by control of temperature was recently reported. The procedure allowed for the synthesis of double-shelled and in principle multi-shelled spheres of vanadium oxide [33]. The methodology was proposed to yield the structures by chemical reaction control, and the materials produced were proposed to have high thermal stability. This methodology has implications for making stacked multi-walled CS structures.

Further details on the procedures used for making hollow and filled spheres are mentioned elsewhere in the review.

1.2. The review

During the past three decades the availability and ready access to characterization techniques at the nanometric scale (in particular scanning probe microscopy and electron microscopy techniques) have allowed a more detailed investigation of well known and novel materials. This is also true of carbon materials including CSs. A review of the area of CSs, with particular emphasis on data collected in the last two decades, is thus timely.

In this review of CSs we have opted to categorize spheres in terms of the strategies used in their synthesis. However, the discussion and the table accompanying the review permit an analysis of the information in terms of all the other categories mentioned above.

The literature in this area is vast as carbon materials have been made by humans for thousands of years. It appears that CSs were formed billions of years ago as reflected by recent discoveries of their presence in meteorites [34]. Early documentation reveals that carbons (as soot) were first used by humans for wall paintings. The study of candle flames and the soot produced by the burning of candles has been actively studied since some early reports in the mid-1850s by Faraday [35]. Knowledge of the production and composition of soot is important in preserving historical and cultural artifacts that are contained in churches and chapels [36]. These soot particles are known to mainly be in the form of spheres. In more recent times the products from candle soot have been collected, acid treated, separated and the spherical components

(<2 nm) shown to have fluorescent properties determined by their rim chemistry [37].

An enormous literature on the industrial and commercial production of CSs is available. The various spheres produced differ in their composition and surface functionality that arises from combustion of the carbon source used to produce the solid carbons. These materials are known by many names, determined in part by their synthetic source. For example; acetylene black is made from acetylene [38] and they are produced and sold commercially by many suppliers (e.g. Cabot, Printex, Degussa, Tokai Carbon Co. Ltd.). The commercial materials are extensively used in printing pigments, paints, coatings, rubber products and so on. More recent interest has been stimulated by their use in Li batteries [39] and their potential mechanical properties [40].

Most of the early work, published before the 1980s, focused on the synthesis and characterization of the carbon blacks (CBs) and related spherical carbons and especially their applications in industry. The production processes used to make the carbon blacks are to be found in the patent literature. Thus, literature dating back to 1928 reveals that early studies were focused on the theories and predictions of the reinforcing properties of CBs in rubbers as well as the physical properties of CBs (adsorption, surface area and pore size measurements) [41–46].

The discovery of fullerene in 1985 re-invigorated interest in spherical carbons. Indeed the finding had an impact on carbon black science, in terms of the similar electron affinity characteristics of solid spherical colloids and fullerenes and hence the radical acceptor properties of the two types of spherical carbons [47].

In this review, the main focus will be on describing the synthesis of CSs and their applications. There has been an explosion of publications in this field; consequently the review cannot be exhaustive. It is hoped that the most significant publications have been covered. The focus is not on studies reported prior to 1990. CSs discussed will cover the major types: solid spheres, hollow spheres, core–shell spheres with diameters ranging from the nano to the mesoscale.

The review will not cover fullerenes and their chemistry. This work can be found in numerous textbooks and reviews [48,49].

Many pertinent reports on spherical carbons that are discussed in this review are summarized in Table 1.

2. Synthesis

The last few decades have witnessed an exponential growth in the field of carbon nanotube studies worldwide and this has led (often accidentally) to the synthesis of many other SCMs including carbon spheres (CSs). The synthesis of these SCMs and in particular CSs can broadly be divided into two types, associated with the reaction temperature used to make the spheres. The first procedure

is based on the high temperature decomposition of carbon containing materials in an inert atmosphere (chemical vapor deposition, arc-discharge and laser ablation processes). The second procedure consists of the low-temperature pyrolysis and catalytic decomposition of organic compounds by the heat treatment of polymers or other materials, often in an autoclave. The influence of the carbon source, oxygen, catalysts, additives, flow rates, pressure, reactor design, all play a role in influencing the properties of the synthesized CSs (surface area, chemistry, size, density, etc.) formed in all the procedures. It has been suggested that the 'new' CSs 'must be distinguished from carbon blacks in terms of 'microstructures and approaching schemes' [50] and are not the same as carbon blacks (CBs) [51]. However, many of the novel high temperature routes described in recent years to produce CSs appear to lead to products with many similar properties to CBs, suggesting that there may indeed be numerous similarities between CBs and many of the new spherical carbon materials reported in the literature.

CSs have also been synthesized in matrices by procedures that do not presently lead to their extraction and use. For example, the synthesis of spherical carbons deposited in metals such as iron, have been detected. However, their role outside of this environment has as yet not been explored.

In constructing a SCM from carbon precursors a key issue relates to competition between π - π stacking of graphite layers to give layered materials versus the reduction in surface energy associated with a spherical shape.

2.1. Arc-discharge

The arc-discharge process was the original procedure used to make synthesized CNTs in useful quantities [52]. In this process, a discharge causes the negative carbon electrode to sublime at high temperatures while the carbon reconfigured as it cooled and collected on the cathode or in the reactor. In the process many SCMs are produced, including CSs.

He et al. have described a process for the synthesis of carbon nanoballs using acetylene and coke powder as carbon source in the DC arc-discharge apparatus shown in Fig. 5 [53]. A carbon rod (containing Fe and Ni) was used as the anode in the arc system while a high purity graphite rod ($\varnothing$ 30 mm $\times$ 20 mm) was used as the cathode. A current of 70–90 A was passed through the two electrodes in an acetylene medium at a pressure of 0.05–0.06 MPa while the voltage between the two electrodes was in the range of 30–35 V. The spheres that formed varied in size between 50 and 100 nm.

Qiu et al. [54] reported the successful synthesis of carbon materials (balls, net-like and plate-like forms) from coal derived

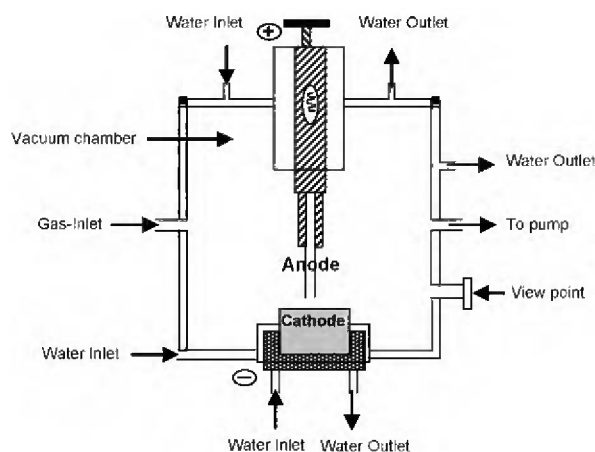


Fig. 5. Schematic of the DC arc-discharge equipment used by He et al. [53].

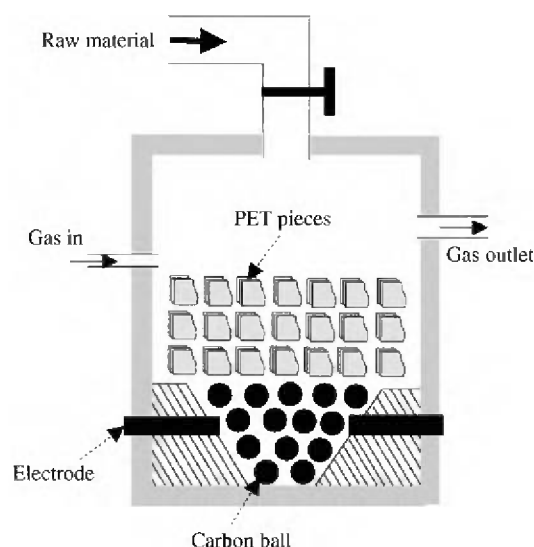


Fig. 6. Preparation of carbon spheres by arc-discharge [50].

carbon rods by a conventional arc-discharge method. A semi-char rod was obtained by heating coal at 450 °C under 20 MPa pressure for 1 h in the presence of nickel particles as catalyst, followed by carbonization. The char-rods were used as the anode in the arcing system while a high purity graphite rod (16 mm in diameter) was used as the cathode (40–50 V; 50–70 A) in a helium atmosphere (500–700 Torr). The soot-like deposits on the bottom, the inside upper cover and the walls of the reactor were collected separately. Carbon balls with diameters of 10–20 μ m were found in the soot collected from the walls of the reactor.

A non-classical arc-discharge procedure using polymers as carbon source has also been used to make spheres. Polyethylene terephthalate (PET) resin (from recycled bottles) was used for the production of CSs at a pyrolysis temperature of 1100 °C, using an arc-discharge process [50]. The reactor employed is shown in Fig. 6. Approximately 200 carbon balls with a diameter of 3 cm, were placed at the bottom of a furnace in the vicinity of two electrodes. The carbon balls were heated in a flow of argon until the resistance of the carbon balls reached their highest level. Pieces (3 cm $\times$ 3 cm) of PET bottles were then introduced into the furnace. The carbon balls were heated to 1100 °C in argon. After achieving the reaction temperature, the resistance of the carbon balls was increased and arc-discharge occurred among the carbon balls. At the same time the PET pyrolyzed and was converted to a solid product. The resultant products that precipitated at the gas outlet were collected after arc-discharge (2 h). The resultant 'carbon balls and nanospheres' were characterized by XRD, SEM, TEM and Raman spectroscopic techniques. The approximate diameter of the spheres was observed to be ca. 100 nm.

Hollow and filled CSs were synthesized by use of a DC arc-discharge method. The plasma (55 V, 3 A) was generated between Fe electrodes in ethanol (Fig. 7). The method required ultrasonic irradiation of the solution. A wide size range (5–1000 nm) of so-called carbon nanocapsules, i.e. spheres filled with iron carbides, were produced. Magnetic separation reduced the particle size spread to 100–200 nm [55]. In summary, the arc-discharge procedure can be used to synthesize CSs but yields tend to be low and so to date studies using this technique have been limited.

2.2. Laser ablation and plasma processes

Carbon tubes and spheres have been synthesized by thermal plasma processes. This method is based on the use of a thermal

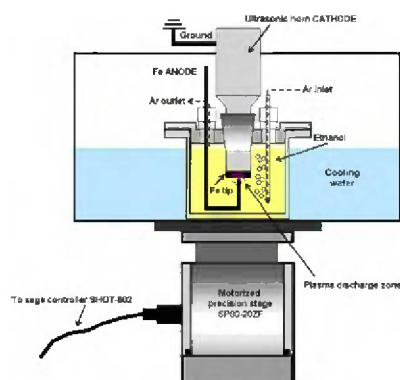


Fig. 7. Diagram of arc-discharge apparatus [55].

plasma which vaporizes the carbonaceous precursor in the presence of a metal catalyst. In the laser ablation process, a pulsed laser vaporizes a graphite target in a high temperature reactor while an inert gas is bled into the chamber. The carbon nanoparticles develop on the cooler surfaces of the reactor, as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanoparticles.

Ma et al. [56] reported the synthesis of carbon coated iron nanoparticles using a laser-induction heating evaporation technique. An iron cake was placed in a graphite crucible in an evacuated chamber (<10 Pa) and the system was flushed with argon before increasing the pressure to 2 kPa with argon. A high frequency induction power of 40 kW was then applied to melt the iron cake. Simultaneously, a continuous wave CO_2 laser (power of 4–4.5 kW) was used to irradiate and vaporize the molten iron. CH_4 gas was introduced into the reactor (total pressure 5 kPa, 1 h) and core-shell iron-carbon nanospheres were produced with diameters ranging from 5 to 50 nm (Fig. 8).

By use of a thermal plasma method Okuno et al. successfully synthesized nano-bells in the form of a nano-neckless [57]. In this report, carbon black coated with 3% Ni and 3% Co was used as catalyst and as carbon source. A carbon aerosol generated from the above was injected into a plasma produced from a plasma gas (mixture of helium and nitrogen). The thermal plasma vaporized the carbon source and the quenched samples were collected. The temperature required for the nano-neckless synthesis was 1700–2400 °C. The diameter of the nano-neckless' was in the range of 50–100 nm. These materials are proposed to form in a similar manner to that observed in the synthesis of CNTs.

Yang et al. synthesized amorphous hollow carbon spheres (HCSs) using radio frequency plasma enhanced CVD from methane/ H_2 in the presence of MgO and Ni nanoparticles supported on silica. A radio frequency power of 220 W was used (reactor temperature: 700–800 °C). The diameters of the CSs produced ranged from 100 to 800 nm. The hollow nature of the sphere was produced by use of a tungsten tip (Fig. 9). A mechanism entailing the role of the various reactants in the HCS synthesis was proposed [58].

The choice of the electrode used in a laser-induced methodology also impacts on the carbon products obtained. Bystrejewski et al. [59] made solid CSs using a compressed anthracene/graphite target that was heated by a 30 W CO_2 laser. The reaction temperature was estimated to be between 700 and 1000 °C, a temperature at which the anthracene would be decomposed. Two sizes of CSs were produced depending on the collection point on the target. These ranged between 100 and 400 nm and 1 and 2 μm ; it was suggested that the size differences related to the 'concentration of available species' at the target surface.

A microwave plasma assisted CVD process was used to make CSs comprising of radial nanoflakes at 900–1100 °C. The materials were grown on iron substrates (5 kW plasma) from CH_4 . The process to produce the spheres (1.2–35 μm) entailed a liquid carbon source on a molten steel surface [60].

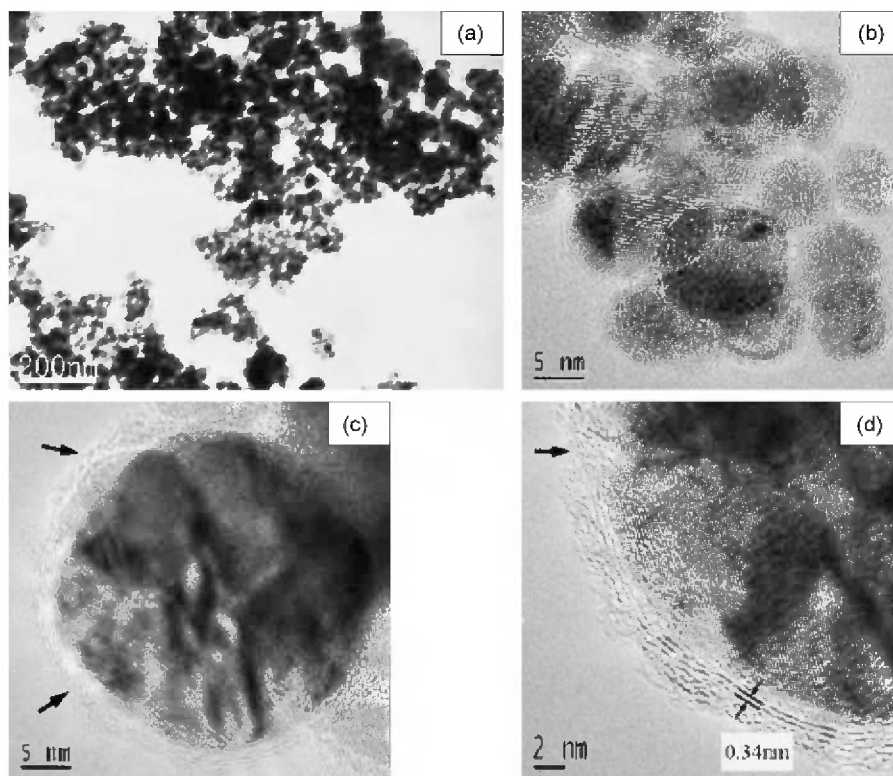


Fig. 8. TEM and HRTEM images of as-prepared Fe-C nanoparticles and their corresponding EDX spectrum. (a) TEM overview; (b) HRTEM overview; (c) enlarged HRTEM image of an Fe-C nanoparticle; (d) enlarged HRTEM image of part of the nanoparticle in (c) [56].

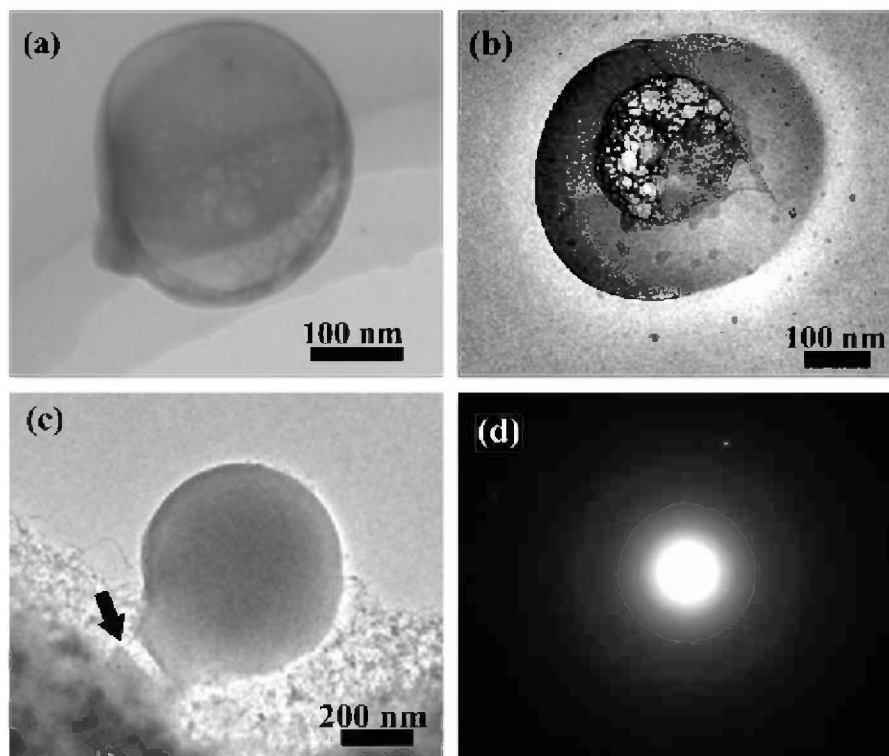


Fig. 9. TEM images from (a) an as-deposited hollow carbon sphere (HCS) and (b)–(c) the roots of HCSs damaged by a sharp tungsten tip. (d) A SAED pattern for a single HCS [58].

2.3. Shock compression techniques

The use of a high pressure (57 GPa) shock compression technique using a fullerene as a carbon source has been reported to make CSs. The spheres were hollow with an estimated size of about 300 nm. Remarkably, a high degree of graphitization was noted ($L_a = 290$ nm). The spheres were proposed to be made via graphitization from liquid phase spherical carbon bubbles [61]. A planar shock wave technique has also been reported to produce spherical carbons from a pyrolytic graphite cube [62].

2.4. Chemical vapor deposition

The chemical vapor deposition (CVD) method is the process in which a volatile carbon source is converted into a solid non-volatile carbon product. When the process entails the use of a catalyst the process is known as a catalytic chemical vapor deposition (CCVD) method.

The CVD process is a versatile process and many variants of the method have been used to make SCMs. These processes differ in the means by which the chemical reactions are initiated (the activation process), the type of reactor used and the process conditions. Generally the CVD process uses two generic approaches.

- (a) *Variation of operating pressure.* Four different regimes can be identified: (i) atmospheric pressure CVD (APCVD), (ii) low-pressure CVD (LPCVD); the lower pressure tends to reduce unwanted gas phase reactions, (iii) ultrahigh vacuum CVD (UHV CVD) and (iv) a high pressure process performed in an autoclave.
- (b) *Variation of the physical characteristics of the vapor.* (i) Gas phase CVD; in this process a gas is added directly to a reactor, (ii) sublimation CVD; a solid is converted directly into a gas for use in the CVD process, (iii) direct liquid injection CVD; a CVD process in which the precursors are in liquid form (liquid or

solid dissolved in a solvent). Liquid solutions are injected into a vaporization chamber. Then the precursor vapors are transported to the substrate as in a classical CVD process. This technique is suitable for use of liquid or solid precursors. (iv) Aerosol assisted CVD; a CVD process in which the precursors are transported to the substrate by means of a liquid/gas aerosol. This technique is suitable for use with non-volatile precursors.

In the above procedures, the direct pyrolysis of a carbon source is generally carried out in a quartz tube placed in an electronically controlled furnace. The reaction is typically carried out at atmospheric pressure. If a catalyst is used it can be added as a 'floating' catalyst [63,64] or a supported catalyst can be placed in the quartz reactor. The carbon source is then introduced into the reactor, usually in the presence of an inert gas, generally nitrogen or argon. This mode of synthesis has often been used in CVD processes to make CNTs [65,66].

Two types of reactor configurations, based on the orientation of the furnace, are possible; the horizontal and vertical configurations (Fig. 10).

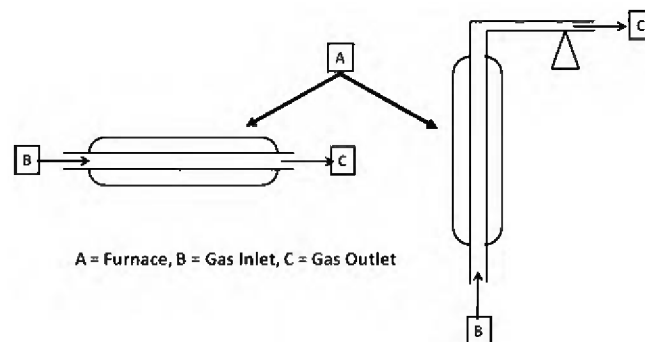


Fig. 10. Horizontal and vertical CVD systems.

2.4.1. Non-catalytic chemical vapor deposition

In this approach a carbon source is decomposed at high temperature in a furnace to yield SCMs and in particular CSs. This is the approach used to make industrially important CSs such as carbon black. The procedure to make CBs entails the use of oxygen to generate high surface area spheres. Many recent reports on CS synthesis have focused on the generation of low surface area CSs that are produced in the absence of oxygen. A variety of parameters control the size, shape and yield of CSs such as temperature, flow of carbon source, deposition time, etc. Also of importance is the time the CSs spend in the reactor. In a vertical reactor the reaction times will be short (<1 min) and consequently secondary reactions involving annealing of the spheres and sphere growth are limited. In contrast, use of a horizontal reactor results in the spheres being kept at high temperatures for longer time periods (typically 15–60 min). The effect is that the outer shell becomes more crystalline with time.

Qian et al. [67] reported that CSs can be produced from toluene at 1100°C using an experimental setup consisting of two furnaces. The temperature of the first furnace was kept at 200°C where toluene, injected into the furnace by a syringe pump, was vaporized. The vapors were carried to the second reactor by nitrogen and/or argon and/or hydrogen gas. The average diameter of CSs produced ranged between 60 nm and $1\text{ }\mu\text{m}$. The effect of carrier gas, carrier gas mixtures and flow rate was studied in detail. When the toluene was decomposed over an AAO (anodic alumina oxide) template the size of the CSs formed close to the template was smaller, implicating the template in the synthesis process. Similarly, Aili et al. have reported the synthesis of CSs at 1000°C from acetylene/toluene as carbon source [68]. After cooling, carbon microspheres were collected (diameter 200 nm) and subjected to various heat treatments to enhance the graphitization process. The surface areas were typically found to be $10\text{ m}^2\text{ g}^{-1}$. CSs have also been produced from pentane using a single reactor system at

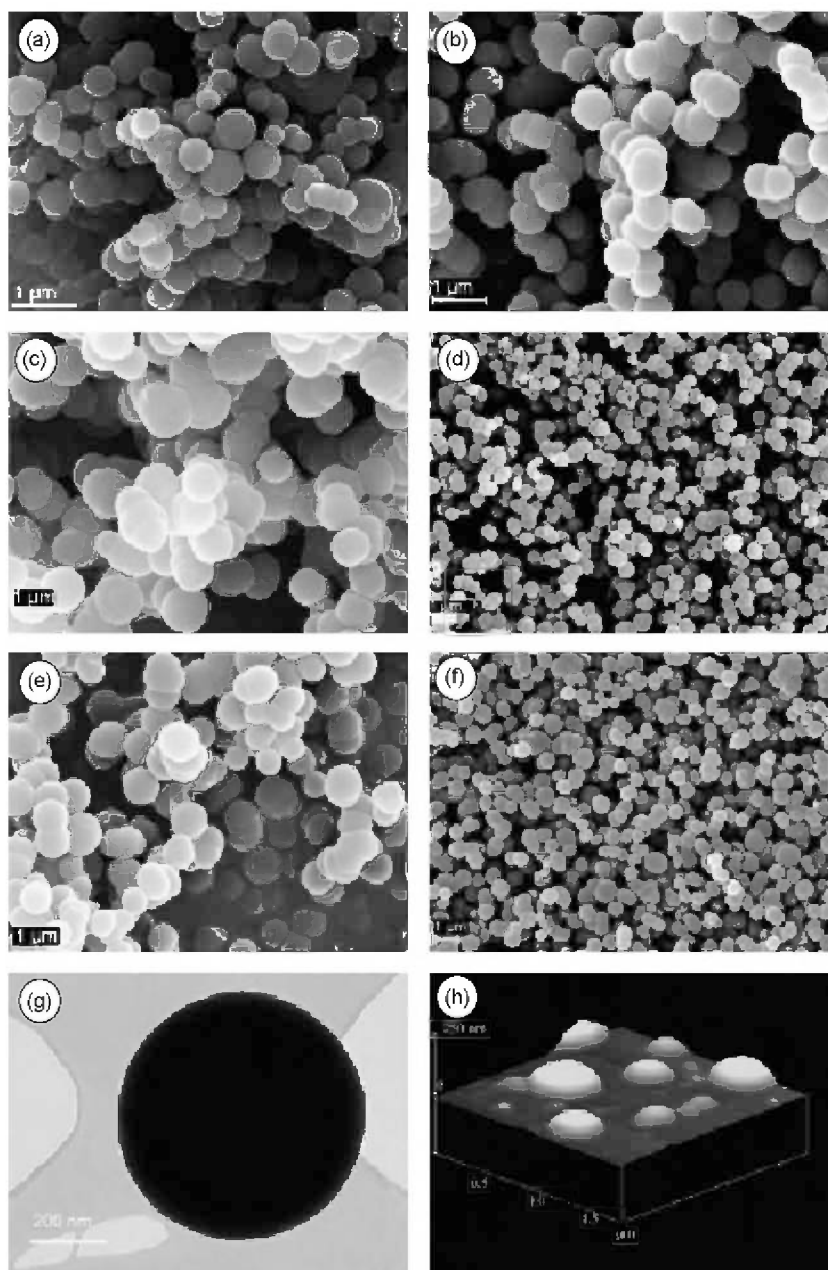


Fig. 11. SEM images recorded for the pyrolysis of: (a) styrene, (b) toluene, (c) benzene, (d) hexane, (e) cyclohexane, (f) ethylene, (g) typical TEM and (h) typical AFM images [69].

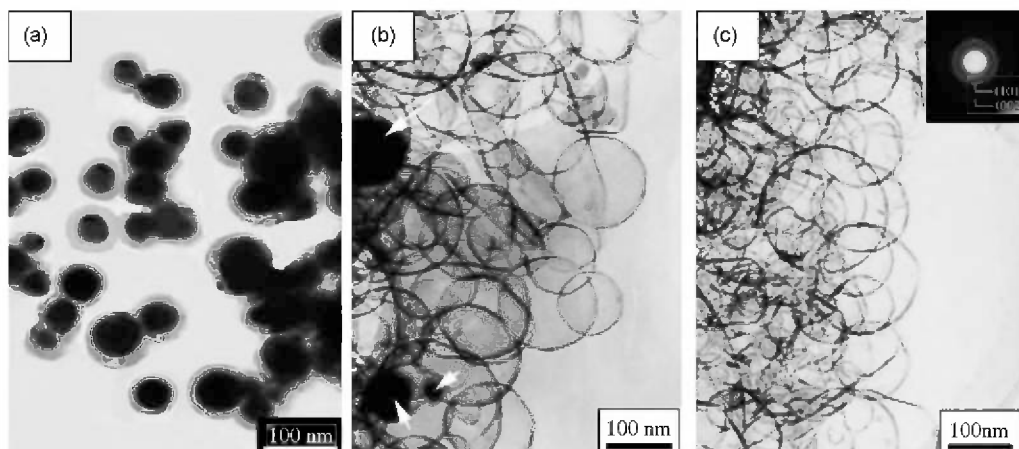


Fig. 12. (a) A typical TEM image of the carbon-encapsulated ZnSe nanoparticles. (b) The TEM image of the hollow carbon nanospheres obtained at 1200 °C for 30 min (some unconverted carbon-encapsulated ZnSe nanoparticles are shown with arrows). (c) The TEM image of the hollow carbon nanospheres obtained at 1200 °C for 60 min (insert is the corresponding SAED pattern of the products) [73].

$T > 800$ °C. The study indicated that a catalyst was not required for CS synthesis, as mentioned by other authors [69].

Large scale production of CSs, with diameters ranging from 50 nm to 1 μm was achieved with different substrates such as styrene, toluene, benzene, hexane, cyclohexane and ethane [69]. A double furnace apparatus was used for the pyrolysis of the liquid hydrocarbons; the liquid hydrocarbon was introduced into the first furnace at 250 °C. The feedstock vapor was carried through the reactor by argon to the higher temperature (900–1200 °C) pyrolysis furnace. In this study, the effect of feed rate, temperature and time on the diameters of the CSs was established. Key findings include: $T > 800$ °C is required for CS formation; the carbon source has some effect on the CS morphology (Fig. 11); the feed time determines the CS size; accretion occurs during pyrolysis and long reaction times lead to more crystalline CSs.

Heavy hydrocarbons have also been used to make CSs. Asphaltene, a carbon rich residual byproduct of petroleum formation processes, was used for the synthesis of CSs. The asphaltene vaporized outside the furnace and the vapors were carried with argon gas to the carbonization zone in the furnace where the temperature was around 950 °C. The average diameter of the spheres ranged from 300 to 400 nm [70].

Most studies entail the use of a carbon source that only contains carbon and hydrogen. However, the presence of other elements such as oxygen can lead to good quality CSs. Reports have appeared confirming that corn starch [71] and tetrahydrofuran [72] can produce CSs with diameters of 5–25 μm , respectively.

2.4.2. Catalytic chemical vapor deposition

This procedure represents a variation of the above non-catalytic CVD CS synthesis strategy. Many experiments using catalysts have been performed to make CNTs but in the process CSs were synthesized. This usually occurs at high temperature when a crossover from CNT to CS formation occurs. Indeed, it appears that when the metal catalyst plays little role in CNT synthesis, CSs are formed. This suggests that the metal does not play a primary role in the synthesis of solid CSs; rather it plays the role of modifying the type of carbon radicals that are formed in the gas phase and that lead to carbon deposition to form the solid CSs. The metal (or non-metal) catalyst material could also act as a template providing the nucleation sites for hollow sphere formation. Clarification is, however, still needed to resolve this issue. Various reports that have appeared in the literature on the use of catalysts in CS synthesis, starting with templating procedures, are described below.

ZnSe nanoparticles were used as a template, to exploit the synthesis of hollow carbon nanospheres. Synthesis of carbon encapsulated ZnSe nanoparticles was performed under a constant flow of argon at 5×10^{-2} Torr. Toluene, the carbon source, was injected into a horizontal furnace, containing ZnSe, at a temperature of 1100 °C for 3 h. Further, encapsulated ZnSe was removed by heating the sample at 1200 °C for 60 min. Removal of the ZnSe template gave hollow CSs with diameters of 40–120 nm (Fig. 12) [73].

A templating method was used to make nitrogen doped CSs (NCSs) [74]. Mesoporous CSs were prepared by a polymerization-induced colloid aggregation method by using a melamine-formaldehyde resin as carbon precursor and fumed silica as a hard template. In a typical procedure, melamine and formaldehyde were added into deionized water at 85 °C. The resulting precursor solution, after cooling to 40 °C, was poured into a silica colloid solution and the pH of the mixture was adjusted to 4.5 by HCl. The mixture was kept at 40 °C for 3 h. After filtration, washing and drying the composite was firstly cured at 180 °C for 24 h in air, followed by carbonization at 1000 °C to obtain a carbon/silica composite. Finally, the silica was leached out from the material using hydrofluoric acid to obtain a mesoporous carbon material. The average diameter of the spheres was ~ 1.2 μm and the sphere had a very high surface area ($1460 \text{ m}^2 \text{ g}^{-1}$) with a uniform shell thickness of 31 nm.

A CVD method was used to make smooth single shell, deformed single shell, double shell and nitrogen doped shell carbons using silica spheres [75] as templates and benzene as a carbon source. Before actual pyrolysis, pre-synthesized silica spheres were heated to 900 or 1000 °C under a nitrogen atmosphere. Benzene vapors were passed over the silica spheres (4 h) placed in the center of a quartz tube in the furnace, with the help of nitrogen carrier gas. After reaction the silica spheres were dissolved away using a HF solution to generate hollow CSs. The hollow CSs were dispersed in ethanol and a silica layer was grown on the surface of the CSs. A carbon coating on the silica-carbon-hollow sphere was then produced by passing benzene over the spheres. The silica was removed by HF to give double-shelled hollow CSs (Fig. 13). Using the same method, nitrogen doped spheres were also synthesized using vapors of acetonitrile. The microscopic features and shell thickness depend on the silica sphere diameter, temperature and reaction time [76].

Miao et al. [77,78] reported the synthesis of a large quantity of CSs using Kaolin supported transition metal salts (Fe, Co, Ni, etc.) as catalysts. Aqueous solutions of transition metal salts (Co, Ni, Fe) were coated on a Kaolin catalyst surface or ceramic plate in the

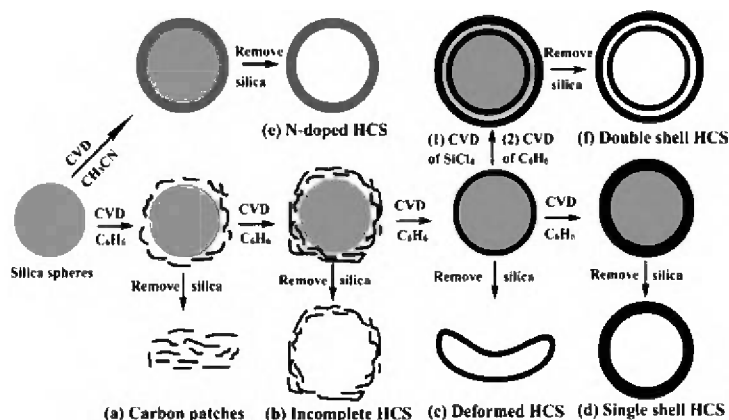


Fig. 13. Schematic illustration of the fabrication steps for various carbon spheres (HCSs): (a) discrete carbon patches acting as the building blocks of HCSs, (b) incomplete HCSs because of insufficient CVD time, (c) deformed HCSs prepared using large silica spheres as templates with a short CVD time, (d) intact single shell HCSs prepared with a long CVD time or a high CVD temperature, (e) N-doped HCSs prepared using acetonitrile as a carbon source, (f) double shelled HCSs prepared using a three-step CVD method: first, CVD of carbon on the surface of silica spheres; second, CVD of silicon tetrachloride on the surface of the carbon–silica spheres; third, CVD of carbon on the surface of the silica–carbon–silica spheres [76].

form of a thin plate and dried at 60 °C. The thin layer of catalyst was placed in the ceramic boat *facing down* in the center of a quartz tube. The carbon source used in this study was acetylene and the reaction temperature was 650 °C. The synthesized spheres were observed to have average diameters of 600–800 nm with a typical inter-layer distance of 0.33–0.35 nm. Reaction parameters such as temperature, time and flow rate were varied. In separate experiments it was shown that spheres that were collected close to the inlet position in the reactor were larger (1.8 μm) than those collected close to the outlet position (600 nm).

A CVD synthesis method in which acetylene (as carbon source) and nitrogen were passed over nickel metal clusters (700 °C) gave monodisperse CSs. The spheres were linked in a long continuous string to form a foam-like macroscopic structure. The diameter of the solid CSs was 150 nm [79]. Not unexpectedly CNTs were formed at lower temperatures (600 °C).

Modification of a Ni catalyst (Ni/Al₂O₃) using a sol–gel procedure and use of CH₄ as carbon source gave hollow carbon nanospheres (5–90 nm) at 600 °C. The Ni is believed to act as catalyst/template for the growth of the CSs as some particles contained Ni [80]. In an earlier paper a similar study gave hollow carbon materials that were referred to as carbon onions (5–50 nm) [81].

A hot filament CVD procedure has been used to synthesize CSs. Indeed a hot filament process has been developed using a W filament to generate CSs from in situ generated WC microspheres [82]. The process involves heating the W to 1650 °C and decomposing CH₄ over the catalyst to give the CSs with diameters of 5–7.5 μm (up to 25 μm using long reaction times) (Fig. 14).

Zhong et al. [83] reported the preparation of carbon nanomaterials (nanotubes and spheres) by the decomposition of methane in the presence of a cobalt encapsulated catalyst. The supports used for the catalyst synthesis were alumina, lanthana, ceria and magnesia. The nickel metal supported on magnesium oxide was prepared from cobalt nitrate and was used for carbon nanotube synthesis [84]. The catalyst was activated at 700 °C prior to use. The reaction was carried out at 600 °C for 1 h. After reaction, the mixture was subjected to treatment with concentrated sulfuric acid to dissolve away the metallic catalyst. The diameters of the nanotubes and balls were observed to be between 10 and 40 and 50 and 200 nm, respectively. A mechanism in which the carbon nanoballs were grown after nucleation of carbon on the surface of the catalyst was proposed. It was found that the use of Al₂O₃, CeO₂ and La₂O₃ as the Co catalyst support or using CO as reactant gas resulted in the formation of MWCNTs. The product distribution

(nanotubes and balls) solely depended on the reaction conditions used.

Pradhan and Sharon [85] synthesized carbon nanotubes and beads from kerosene as carbon source in the presence of nickel and iron catalysts. In a typical procedure two furnaces were connected

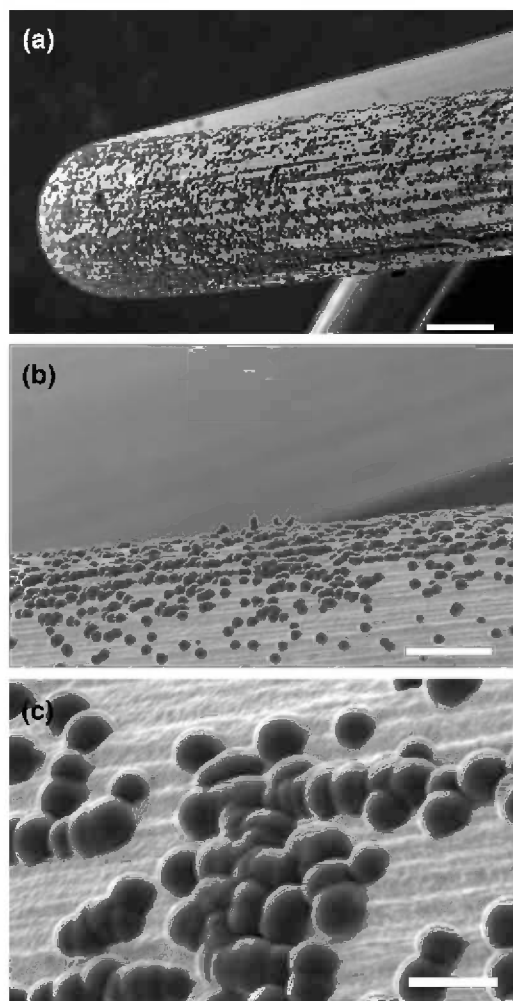


Fig. 14. SEM images from a W filament sample showing carbon microspheres. Scale bar in (a) is 200 μm in (b) is 100 μm and (c) is 20 μm. The diameters are in the range ~10 to ~20 μm [82].

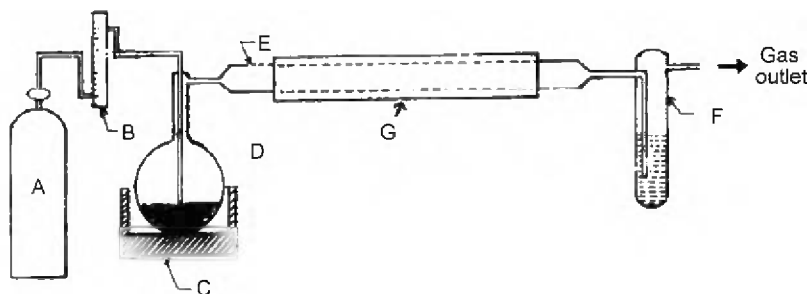


Fig. 15. Pyrolysis unit to produce carbon nanobeads. A is the gas cylinder, B the flow meter, C the heating mantle, D the flask containing a camphor and ferrocene mixture, E the quartz tube inside the furnace, F the water bubbler and G is the furnace [86].

in series. The carbon source was placed in the first furnace (held at 200 °C) and a quartz boat containing the catalyst was placed in the second furnace. The temperature in the second furnace was 1000–1100 °C. The kerosene vapor was carried to the second furnace in nitrogen gas. The average diameter of the spherical nanobeads formed was between 600 and 900 nm.

Iron complexes have been suggested to be promising candidates for the synthesis of various SCMs, including CSs, under mild experimental conditions. Various organometallic complexes, in particular containing iron, have been tested as catalysts for the synthesis of CSs.

Sharon et al. used camphor as carbon source and ferrocene as catalyst in a two stage reactor to produce CSs (Fig. 15). The long reaction times (up to 4 h) resulted in the formation of core-shell carbon structures (500–850 nm) as well as small (264 nm) and large size (441 nm) spheres [86]. The pyrolysis was carried out at 1000 °C for 4 h. The core-shell carbon nanobeads of about 250–280 nm in size were covered with an 80–100 nm thick fibrous amorphous carbon layer.

The use of mixed valence oxide catalysts (MVOCC) have also been reported for use in the synthesis of CSs in the hope that such a system would lead to easier separation of the encapsulated catalyst after carbonization [87]. The low cost process was used for the synthesis of high purity CSs and CNTs [88]. Wang and Kang synthesized various carbon microspheres using a catalyst containing transition and/or rare earth metal oxides with mixed valencies (MVOCC method). They prepared CSs from CH₄ as carbon source at 1100 °C [15,89]. Most importantly they analyzed the flake arrangements that made up the spheres ($d = 210$ nm) and proposed a mechanism for the CS synthesis. Use of MnO₂ in the MVOCC method (CH₄/900–1050 °C) gave spheres and hollow or filled spherical structures called calabashes, presumably formed by a mechanism similar to that used to explain the synthesis of other hollow spheres [18].

Reaction of CCl₄ with Mo powders in a furnace at 600–900 °C gave carbon containing spheres (1–5 μm) at low temperature and smaller solid spheres (200–300 nm) at high temperature. MoC_x species were implicated as templates [90].

2.5. Autoclave methodologies

The synthesis of carbon nanomaterials under mild temperature condition is a challenge. A procedure that has been adopted to overcome this limitation has been to use high pressures. In this approach reactants are placed in various types of metal autoclaves and then heated to various (typically low) temperatures. Assumptions are made that the autoclave material does not affect the reaction. This is an assumption that must be used with care. There are many examples in the catalysis literature where reactors have indeed impacted on reactions of carbon; sometimes with disastrous effects [91,92].

During the reaction there is a pressure build up (autogeneous pressure) and this pressure will impact on the reaction product. It

is also possible to use gaseous carbon sources in the reaction. Pressure can also be applied in the reaction by the use of an inert gas.

The reaction of carbon reagents to give CSs has been shown to occur in both the presence and absence of a catalyst under high pressure (and temperature). In many instances a reducing agent has been added to the carbon/metal mixture and by choice of halogenated carbon sources a wide range of fluffy, hard, solid, hollow and metal filled CS structures have been made.

2.5.1. Non-catalytic methods

The most facile high *P*/high *T* method is to perform the reaction in the absence of a catalyst. Indeed Pol et al. have decomposed a range of common organic reagents, many having aromatic character, in a Swagelok reactor (autoclave) at 700 °C for 3 h under argon [93,94]. When mesitylene was used as carbon source, a perfect spherical morphology of non-graphitic carbon was observed in 77% yield with an average diameter of 2.5 μm. A continuous 'sausage-like' structure was formed by sudden cooling of the reaction vessel (Fig. 16). A comparison with similar data obtained under flow conditions (1 bar) revealed that smaller diameter CSs were produced in the later method. The morphology of the product was determined by the carbon source with, for example, pentane and diphenylmethane giving egg shaped materials.

Earlier studies have been carried out on various carbon materials in an autoclave at high pressure. Thus, reaction of various acids and PET/PE (polyethylene) at 650 °C at 30 MPa (gold tube inside an autoclave) gave a range of CSs with different sizes. A study of the reactant C/H ratio, as well as the use of mixtures of reactants with polyethylene or PVC indicated that this ratio was important in generating the carbon spherules (2–6 μm) [95].

In a similar manner paraformaldehyde and water were heated in a gold tube in an autoclave at 850 °C at 100 MPa; no spheres were observed but cones were detected [96]. The use of ethylene glycol under similar conditions did give carbon black.

The polymer polyethylene terephthalate (PET) has also been used as a source for CS synthesis. PET was converted into hard spheres (2–10 μm) by reaction in a small stainless steel reactor at 700 °C for 3 h. These ultra hard spheres with low surface area (2.1 m² g⁻¹) were paramagnetic [40].

Sugar (in water) has been used as a carbon source to make CSs in an autoclave. The process required reaction at 190 °C for 5 h. Further graphitization occurred in a furnace (argon flow/1000 °C). A mechanism was proposed for CS formation similar to the emulsion polymerization mechanism for CS formation (see Section 4). The sphere size (1–5 μm) could be controlled by the sugar solution concentration (Fig. 17) [97].

The reaction of a solution of glucose, polystyrene and P123 (as template) in an autoclave at 180 °C for 12 h gave a carbon deposit that after treatment in a microwave generated hollow CSs (1.5 μm; wall size 150 nm). The removal of the PS and P123 gave high porosity, high surface area (1249 m² g⁻¹) spheres [98].

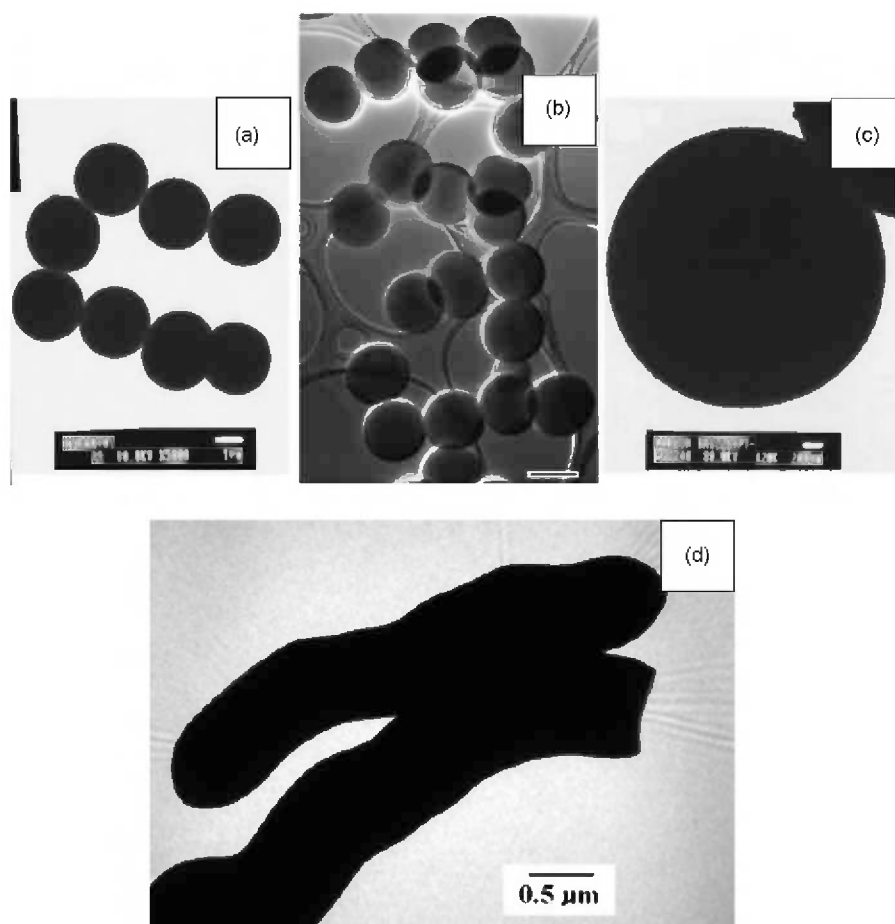


Fig. 16. Transmission electron micrographs of (a) mono-dispersed CSs synthesized in air, (b) mono-dispersed CSs synthesized in Ar, (c) single carbon spherule at high resolution, and (d) 'sausage-like' carbon bodies [93].

Sucrose solutions and silica particles (impregnated with AlCl_3) were placed in an autoclave and heated to $200\text{ }^\circ\text{C}/10\text{ h}$ followed by heating in a furnace at $850\text{ }^\circ\text{C}/5\text{ h}$; HF etching of the product gave hollow spheres (340 nm , surface area $788\text{ m}^2\text{ g}^{-1}$) [99].

A methylcellulose sol was prepared by addition of methylcellulose to distilled water at room temperature [100]. The hydrothermal treatment of the sol with concentrations of $1.0\text{ wt\%}$ was carried out in a stainless steel autoclave at $400\text{ }^\circ\text{C}$ for 6 h . After cooling to room temperature, the solid product was separated from the oil containing liquid product by filtration and washed with dilute hydrochloric acid and pure alcohol. Finally, the black product was dried in a vacuum for 3 h . The authors reported the aggregated carbon nanospheres that were produced had diameters of $1\text{--}5\text{ }\mu\text{m}$ and very smooth surfaces.

SiC powders and various organic acids (malonic acid, glycolic acid, citric acid, sucrose, formic acid, acetic acid, ascorbic

acid, succinic acid and malic acid) were encapsulated in gold tubes in Roy–Tuttle reactor vessels and heated for $40\text{--}80\text{ h}$ at $600\text{--}850\text{ }^\circ\text{C}$ ($P = 100\text{--}200\text{ MPa}$). The carbon products formed were typically accreted, spherical in shape (nano and micro-sized), and had surfaces that were irregular and had 'stretched pore spaces'. Quartz crystals were also observed. The role of C/O/H containing fluids in the synthesis process was discussed. No catalyst or diamond seeds were needed to make the spheres [101].

Xie et al. reported the synthesis of high quality CSs at a temperature as low as $65\text{ }^\circ\text{C}$. In this procedure, CaC_2 and oxalic acid was heated in an autoclave to produce high quality and uniform size ($80\text{--}100\text{ nm}$) spheres [102].

Shaped carbon particles have been synthesized in the absence of a catalyst using olive oil as carbon source under an autogenic pressure at $700\text{ }^\circ\text{C}$ for 3 h [103,104]. The polar and equatorial

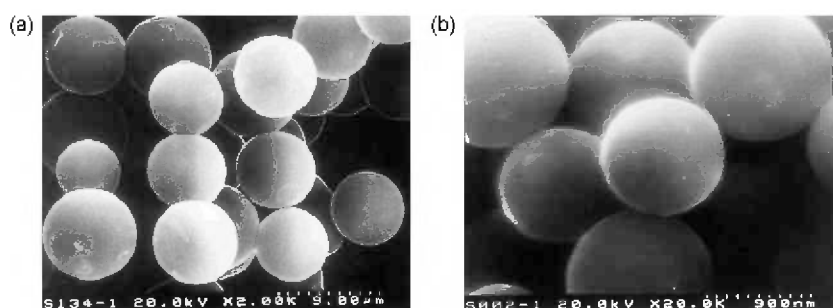


Fig. 17. SEM image of monodispersed HCS. Spherules with two sizes are demonstrated here, (a) $5\text{ }\mu\text{m}$ and (b) $1\text{ }\mu\text{m}$ [97].

diameters of the prolate spheroid shaped carbon were in the range of 1.5 and 3 μm .

2.5.2. Catalytic and reducing procedures

Both catalysts and reducing agents can be used to convert carbon containing materials to CSs and a general procedure to make CSs in an autoclave has been developed. For example, the use of a chlorinated carbon source and a metal reducing agent placed in an autoclave, and heated under an inert gas can yield CSs. The solvent does not have to be chlorinated and in principle any reducing agent could be used to convert the carbon gas or liquid into a solid SCM. In many instances the autoclave used is a metal reactor and the role of the reactor material may play a catalytic role in the reaction.

Qian et al. [105] reported a novel procedure for the synthesis of both hollow and filled CSs by the catalytic pyrolysis of C_2Cl_4 using ferrocene as catalyst. In a typical procedure a mixture of ferrocene and the carbon source was heated to 550 $^\circ\text{C}$ under approximately 8 MPa for 16 h. The size of the spheres obtained from the method was measured to be in the range of 30–580 nm.

Jia and co-workers used a similar synthesis procedure to make hollow CSs using ferrocene (carbon source) and ammonium chloride as starting materials. The mixture of ferrocene and ammonium chloride was heated to 700 $^\circ\text{C}$ in an argon atmosphere up to 2.8 MPa pressure for 30 min. The product was collected after cooling to room temperature and revealed the formation of an iron amine complex in the form of droplets which in turn served as template to form the CSs (1–10 μm) [106,107].

Yin et al. [108] synthesized CSs at 350 $^\circ\text{C}$ in a stainless steel autoclave. The autoclave was charged with calcium carbide,

chloroform (as carbon source) and ferrocene as catalyst and heated for 3 h. The ‘fluffy’ CSs had a BET surface area of 48 $\text{m}^2 \text{g}^{-1}$ and ranged in size between 50 and 250 nm. In a related reaction iron chloride was also used as a catalyst to make hollow carbon microspheres. Fluffy hollow CSs with a diameter of 0.3–1.8 μm and shell thickness of 30–80 nm were successfully synthesized via a FeCl_3 catalyzed solvo-thermal reaction in a sealed autoclave at 350 $^\circ\text{C}$ for 3 h, using CaC_2 and CCl_4 as carbon source and reactant [109].

Reaction of ferrocene and 1,2-dichlorobenzene (180 $^\circ\text{C}$ /24 h) in a Teflon-lined autoclave gave carbon ‘hollow trees’ as well as some CSs. As the temperature was increased, or the ferrocene/1,2-dichlorobenzene was increased the CS formation increased [110].

Neckless-like hollow CSs were successfully synthesized from hexachlorocyclopentadiene and ferrocene. A quartz tube (20 mL capacity) containing the reactants was heated to 500 $^\circ\text{C}$ for 4 h in a stainless steel autoclave under an argon atmosphere. Neckless-like hollow CSs were formed with diameters of 50–100 nm and lengths of several micrometers. BET surface area measurements revealed that the CSs led a high surface area of 594 $\text{m}^2 \text{g}^{-1}$ and average pore size of at 5 nm [111].

Hexachlorobenzene as carbon source, and sodium as catalyst, were mixed and placed in an autoclave at 160 $^\circ\text{C}$ for 10 h [112]. It is believed that the NaCl generated during the reaction acted as a template for the synthesis of core-shell CSs. The NaCl core could be removed from the CSs by annealing above 1400 $^\circ\text{C}$. These hollow CSs were characterized by XRD, SEM and TEM. TEM studies (Fig. 18) revealed significant changes in morphology from solid spheres to hollow spheres.

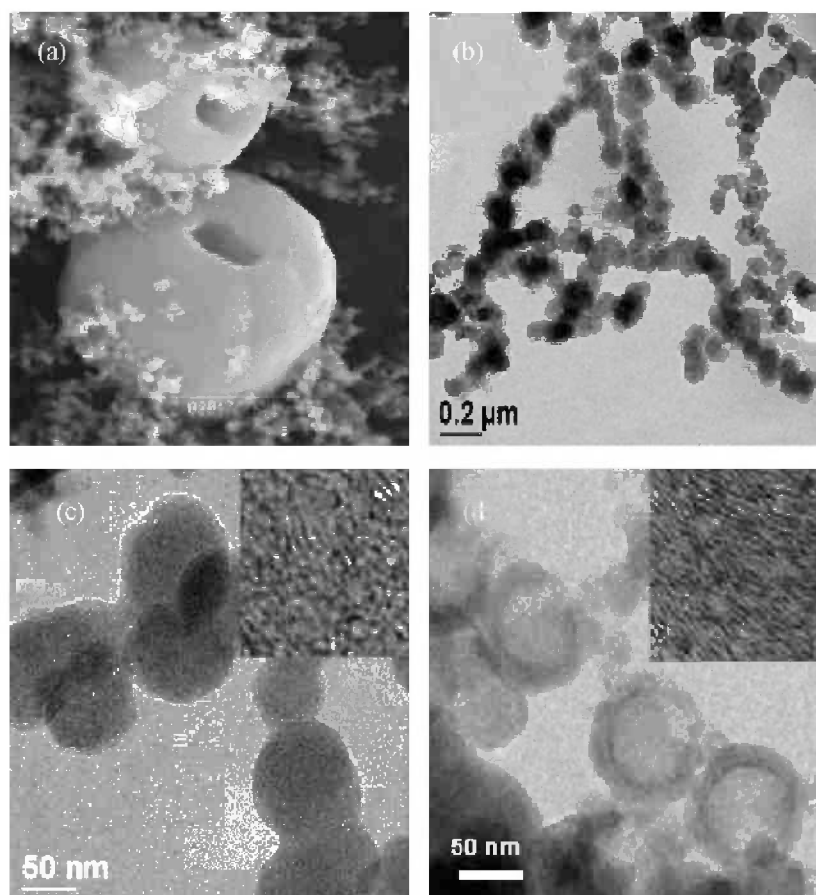


Fig. 18. SEM and TEM pictures of the products. (a) SEM picture of the sample before washing. (b and c) TEM pictures of the sample after washing. (d) TEM image of the sample after washing and annealing at over 1400 $^\circ\text{C}$. Insets of (c and d) show the detailed carbon structure by HRTEM [112].

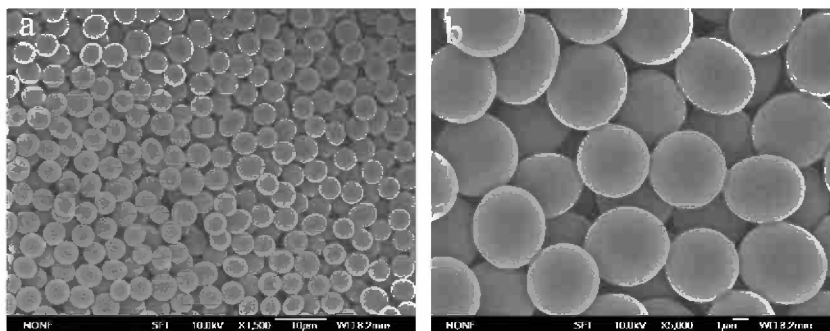


Fig. 19. (a) The panoramic FE-SEM image of carbon microspheres grown on the surface of Ni foil; (b) an enlarged FE-SEM image, illustrating the CSs has uniform size and sphericity [116].

Hollow CSs (150–500 nm) were produced when hexachlorobenzene as carbon source, and sodium as reductant, were mixed and placed in an autoclave at 400 °C for 10 h [113]. Hollow CSs (50–150 nm) were made from the polymer poly(tetrafluoroethylene) (PTFE) by heating the polymer with NaN_3 at 550 °C [114].

Xie et al. synthesized hollow CSs and vessels from CCl_4 in the presence of NaNH_2 . The reaction was catalyzed by a Co/Ni alloy (1:1 molar ratio Co:Ni) at 190 °C [115]. The autoclave was heated to 230 °C and was then maintained at 190 °C for 24 h. The average diameter of the hollow spheres was 400–600 nm and the thickness of the shell was ca. 50 nm. The yield obtained for the spheres by this procedure was 10%.

Zhang and co-workers [116,117] successfully synthesized uniform carbon microspheres by a substrate assisted route by carbonization of acetone at 550 °C for 12 h. In a typical procedure, a Ni foil was sonicated and placed in a titanium alloy autoclave containing acetone. Carbonization of acetone at 550 °C led to the synthesis of microspheres. The product formed was analyzed using FE-SEM (Fig. 19). The average diameter of the CSs was observed to be 4–5 µm. Use of Cu or Zn foils led to ellipsoidal product morphologies. In the absence of the foil only irregular carbon particles were obtained.

Qian et al. used Mg powder, Na_2CO_3 as catalyst, and CCl_4 as carbon source to make hollow spheres. The reaction was performed at 450 °C for 10 h in benzene as solvent at autogenous pressure. The CSs with diameter of 150–600 nm have been synthesized by a medial-reduction route [118]. Multi-shell spheres were also synthesized by using Hg_2Cl_2 as disproportionation reagent and CS_2 as carbon source at 750 °C for 12 h in a stainless steel autoclave under argon. The product obtained was heated with HNO_3 at 120 °C for 10 h to give purified multi-shell carbon microspheres [119].

Coral-like accreted hollow carbon microspheres were synthesized using nickel as catalyst and cyclohexane as carbon source. An autoclave filled with nickel powder and cyclohexane was heated at 550 °C for 8 h. The reactor was then suddenly cooled to room temperature. The CSs produced were then subjected to an oxidative treatment with nitric acid. The shell was found to be composed of 11 well-aligned carbon sheets with an average fringe spacing of 0.34 nm and thickness of 3–4 nm [120].

An ionic liquid has been used in the synthesis of hollow carbon microspheres. In a typical procedure, a reaction mixture consisting of glucose and 1-butyl-3-methylimidazolium tetrafluoroborate (ionic liquid) was placed in a Teflon-lined stainless steel autoclave. The autoclave was maintained at 160 °C for about 20 h, and then cooled to room temperature. A black precipitate was collected by filtration and washed with distilled water and absolute ethanol. Finally, the products were dried at 50 °C [121]. Hollow carbon microspheres with a average size of 1 µm and spherical shape were prepared and their electrochemical capacitance character-

istics studied. The selected area diffraction pattern confirmed the morphology of the CSs.

Recently [122] CSs were synthesized from varying mixtures of ferrocene and anthracene, sealed in evacuated quartz tubes placed in a furnace. The temperature of the tube was raised to 500 °C to achieve decomposition of the reactants and the temperature was then raised to 800–1000 °C. The CS/CNT ratio increased as the temperature increased. The CS/CNT ratio was also influenced by the Fe/C ratio.

The reaction of glycerin with Mg in a stainless steel reactor (650 °C/12 h) generated a black powder that was shown to comprise of 80% carbon onions (60–90 nm). The highly amorphous spheres had a shell-shell spacing of 4.5 nm. The results were contrasted with similar experiments using a Mg/alcohol mixture in which CNTs and carbon cones were synthesized [17].

2.6. Supercritical fluids

A variant of the autoclave methodology entails the use of supercritical fluids. A supercritical fluid is any substance found at a temperature and pressure above its thermodynamic critical point. A supercritical fluid can diffuse through solids like a gas, and dissolve materials like a liquid. Supercritical fluids can be regarded as “hybrid solvents” with properties between those of gases and liquids, i.e. a solvent with a low viscosity, high diffusion rates and no surface tension. Additionally, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties to be “tuned”. Carbon dioxide and water are the most commonly used supercritical fluids. Supercritical carbon dioxide has been used as solvent and carbon source for the synthesis of carbon nanoparticles [123,124].

CSs, nanotubes, graphite and amorphous carbon were formed in supercritical carbon dioxide (650 °C, 1000 bar pressure, 10 h) in the presence of metallic lithium [125]. The in situ prepared Li droplets reduced CO_2 to carbon and acted as template for the growth of the spheres. The CSs obtained by this method were observed to be 450 nm in diameter. In a similar way, various temperatures were used to determine the effect of temperature on the physical properties of the spheres. Qian et al. [126] synthesized CSs (ca. 300 nm) by varying the synthesis temperature in the range 260–550 °C in the presence of a binary metal mixture of lithium and potassium. A key finding was that the Li/K alloy generated core-multi-shell structures not observed when the individual reducing agents were used [127]. Similarly, metallic calcium led to the synthesis of 1–2 µm diameter spheres at 550 °C in 24 h. The spheres were characterized by Raman spectroscopy, XRD and SEM [128].

The magnesium catalyzed reaction of polytetrafluoroethylene gave CSs in supercritical carbon dioxide as solvent. In a typical reaction, magnesium, polytetrafluoroethylene and dry CO_2 were

sealed in an autoclave and the autoclave was heated to 650 °C for 6 h to give the spheres [129].

Supercritical water has also been utilized to make CSs. Amorphous carbon nanospheres with diameters of 140–200 nm were synthesized by treating polytetrafluoroethylene at 550 °C with $\text{Ca}(\text{OH})_2$ as defluorinating reagent in supercritical water for 12 h [130]. Similarly, CSs were synthesized by heating phenolic-resin spheres to 800 °C for 30 min under a nitrogen flow [131].

2.7. Mesoporous microbeads

Another spherical form of carbon/graphite called mesoporous carbon microbeads (MCMBs) has been known since the 1960s [25]. MCMBs are different from carbon blacks because they are synthesized mainly from ‘pitches’ which include coal-tar and petroleum derived pitches [132,133], typically heat treated at temperatures between 350 and 450 °C. The MCMBs generally have low surface areas of about 4 m² g⁻¹ and are sold commercially in particle sizes ranging from 5 to 8 μm (e.g. Osaka Gas Co. and Shanshan Co. Ltd) [134–137]. However, it has been shown that MCMBs can be activated to obtain MCMBs with very high surface areas >2600 m² g⁻¹ [138,139]. MCMBs have recently been synthesized using other forms of pitches such as isotropic naphthalene pitches [140] as well as by the pyrolysis of organic polymers [141].

Naphthalene-derived isotropic pitch was used for the synthesis of CSs. Firstly, isotropic pitch was dissolved in quinoline, and then this solution was added into an aqueous solution of nitric acid under stirring to give droplets. The quinoline was extracted to avoid adhesion of the pitch particles. The dried pitch particles were oxidatively stabilized in air at 280 °C for 30 min before carbonization between 600 and 900 °C. The diameter of the spheres ranged from 100 to 300 nm [142–144].

A water-in-oil emulsion, that used an amphiphilic carbonaceous material (ACM) and urea, allowed for the synthesis of hollow carbon microbeads [145]. In a typical synthesis procedure a mixture of ACM in ammonia solution was added into heated oil to form a water-in-oil emulsion (80 °C/1 h). The solution was then heat treated. The carbon beads were studied using TEM and were found to have diameters in the range of 2–15 μm with a wall thickness of 1 μm. The effect of heat treatment and urea concentration was investigated. The density of the hollow carbon microbeads decreased with increasing concentration of urea and with decrease in the heat-treatment temperature. In similar fashion the synthesis of carbonaceous gel beads using alkaline aqueous solution and olive oil at 90 °C gave CSs with sizes from 2 to 30 μm [146].

2.8. Carbonization routes

Heat treatment of carbons will lead to a structural ordering but not necessarily carbon graphitization. This is determined by the microstructure of the starting carbon material.

In a carbonization process SCMs are initially made in a solution process and then carbonized at high temperature to generate graphitic structures. The requirement is that the carbon that is graphitized has a high vapor pressure so that decomposition and not melting/sublimation occur in the high temperature reactor. Polymeric materials made of carbon are ideal reactants for making CSs. Polymers have received a great deal of attention for the synthesis of carbon nanoparticles in the last decades. Polymers can have a unique π -conjugated system and high carbon content. Pyrolysis of polymeric materials leads to the formation of nanotubes, nanospheres, etc.

It is also possible to carbonize the carbon containing reactant in the presence of a template and this can generate hollow CSs. This

process can take place in an autoclave (see Section 2.5) but generally is performed at atmospheric pressure under an inert gas.

The synthesis of mesoporous silicas by conventional routes, using different length surfactants led to materials with varying mesopore diameters. The silica spheres were then treated with furfuryl alcohol (the carbon source), again by standard procedures, and after heat treatment up to 900 °C monodisperse carbon/silica core-shell structures were obtained. Treatment with HF removed the silica to leave the HCSs. The interesting feature was the observation that the spheres had a radial arrangement of pore channels, derived from the silica mesopores. The sphere and pore size were influenced by the surfactant used to make the silicas [147].

Poly(divinylbenzene) colloidal particles were used as a carbon source for the synthesis of carbon particles the were obtained by evaporation, condensation and an aerosol reaction technique. Further, these colloidal particles were subjected to carbonization at 500 °C under an inert atmosphere of nitrogen for 3 h. The average sphere diameter was 3–5 μm [148].

A resorcinol-formaldehyde/cetyltrimethylammonium polymer in the presence of cetyltrimethylammonium bromide as core agent and 1,3,5-trimethylbenzene and *tert*-butanol as co-surfactant was used to synthesize nanowires and nanospheres using a NaOH catalyst. The polymer was prepared by heating the reagent mixture at 90 °C for 24 h. After heating, the product was washed with water and ethanol. Further acid treatment was done with hydrochloric acid. Finally, the product was heated at 1000 °C for 4 h under nitrogen. The concentration of *tert*-butanol played a crucial role in the synthesis of nanowires and nanospheres. The size of the nanospheres formed was found to be 260–650 nm [149].

Jang et al. reported the synthesis of magnetic carbon nanoparticles using iron doped polypyrrole nanoparticles. Iron doped polypyrrole nanoparticles were prepared by addition of dodecyltrimethyl ammonium bromide (as surfactant) to a mixture of decyl alcohol and water. To the above solution a pyrrole and iron chloride solution was added drop wise. After chemical oxidation and polymerization of the pyrrole monomer at 3 °C for 2 h, the resulting product was washed with water and ethanol to remove the surfactant and other reagents and give the CS product. Jang and co-workers has similarly synthesized carbon nanocapsules using polypyrrole. Fabrication of magnetic carbon nanoparticles was done by carbonization of iron doped nanoparticles in a quartz tube at 850 °C for 5 h under a nitrogen atmosphere. The average diameter and surface area of the particles were 30–60 nm and 361 m² g⁻¹, respectively [150,151].

Platinum supported on hollow CSs were synthesized by pyrolysis of polystyrene. In a typical procedure, polystyrene spheres were added to a solution of cetyltrimethyl ammonium bromide, sucrose and a platinum salt in sulfuric acid. The mixture was stirred for 12 h to obtain a bright yellow solid of platinum/sucrose adsorbed on polystyrene. After washing, the solid product was subjected to pyrolysis at 600 °C for 3 h under a nitrogen atmosphere [152].

Nitrogen doped carbon microspheres were made through carbonization of a copolymer of vinylidene chloride and acrylonitrile. The copolymer microspheres were synthesized by a suspension polymerization technique. The mixture of vinylidene, acrylonitrile and azobisisobutylvaleronitrile (used as initiator) was added to a saturated Na₂SO₄ solution containing bentonite (used as synthesis template) under vigorous stirring for 10 h at 45 °C. The resulting copolymeric spheres were washed with hot water and acetone to remove the bentonite. The carbonization was performed in a quartz tube (170 °C for 12 h and 300 °C for 1 h) and the product finally carbonized at 600 °C (2 h) [153].

Yu et al. [154] demonstrated the synthesis of hollow core mesoporous shells using aluminium incorporated silica spheres as

template and a phenol–resin or poly(divinylbenzene) as carbon source. The aluminium incorporated silica spheres were treated with either phenol–resin or poly(divinylbenzene) at 130 and 170 °C, respectively, to form a polymer/silica composite. This polymer/silica composite was then carbonized at 850 °C for 7 h under nitrogen to produce hollow core mesoporous shells.

Melamine and formaldehyde were mixed with a silica colloidal solution at a pH of 4.5 (40 °C for 3 h) under static conditions. This led to a melamine–formaldehyde/silica composite. Initially, the composite was heated to 180 °C for 24 h in air and then carbonized at 800 °C for 2 h to give a carbon/silica composite. The average sphere diameter was about 1500–2000 nm. After treatment with hydrofluoric acid, silica was etched out to give hollow CSs [155]. The surface area of the mesoporous CSs was found to be 1330 m² g^{−1}.

Yang et al. [156] successfully prepared CSs from poly(phenylcarbene) as carbon source. The poly(phenylcarbene) was dissolved in THF and spin coated onto the surface of polished Si₃N₄ to give a polymer film. The THF was evaporated at 100 °C and then the film was carbonized at 1000 °C for 2 h under argon atmosphere. The diameter of the spheres was in the range of 0.5–2 μm.

A phenol–formaldehyde resin was synthesized in either the gas phase or the liquid phase using silica spheres with diameter in the range of 450–500 nm. The average diameters of the spheres synthesized using the gas phase synthesis procedure was 500 nm with shell thickness of about 10 nm. On the other hand the shell thickness was 40–50 nm when the liquid phase synthesis procedure was used (Fig. 20) [157].

Biomaterials such as fruit shell, stones, pollen grains, bacteria and viruses have also been used as sources of carbon that can be carburized at high temperatures [158–166]. Biomaterials have advantages in that they are abundant, have a low cost and a high carbon content. Disadvantages are that they have a large size and irregular shapes.

Potato starch was used as carbon source for the synthesis of CSs [167]. The potato starch prior to a heat treatment was treated with NH₄Cl for 1 h. The impregnated starch was dried at 40 °C for 5 h

and then carbonized at 600 °C for 1 h under a nitrogen flow. The carbonized starch was further heated at 2600 °C to give graphitized CSs.

Oleracea [168], synthesized a silver/carbon nano-composite using pollen grains as a carbon source. In a typical experimental procedure to prepare silver/carbon composites, pollen grains were ultrasonically dispersed in a AgNO₃ aqueous solution of a known concentration and the solution was kept in the dark under magnetic stirring. After a desired period of time, the pollen grains were filtered off and washed several times with deionized water. The AgNO₃-treated pollen grains were then dried in a vacuum at room temperature, followed by calcination at 300 °C in air for 6 h and then at 600 °C under a nitrogen atmosphere for another 6 h. After naturally cooling to room temperature, a black carbonized product was obtained.

A hydrothermal synthesis procedure was used to prepare carbon microspheres from glucose as carbon source [169]. The aqueous solution of glucose (1 mol) was heated for 20 h at 180 °C. A dark product was separated by centrifugation and dried at 60 °C for 12 h. The apatite-forming ability of the CSs was evaluated by soaking them in a simulated body fluid. The effect of soaking showed numerous apatite clusters with cotton morphology were formed on the surface of the CSs (Fig. 21).

Glucose and sodium dodecylsulfate were heated at 170 °C for 10 h. The hollow carbonaceous composites obtained through the hydrothermal synthesis process were then further heated at 900 °C and this led to the formation of 300 nm to 1 μm diameter hollow carbonaceous composites possessing spherical and hemispherical shapes. These microspheres were used as a support for the anchoring of platinum nanoparticles [170].

2.9. Odds and ends

A variation of the reduction method in which a halogenated carbon has been reduced to give a spherical graphitized carbon has been reported. In this reaction, small gold particles (1 nm), were covered with silica (sol gel process). The Au@SiO₂ particles were

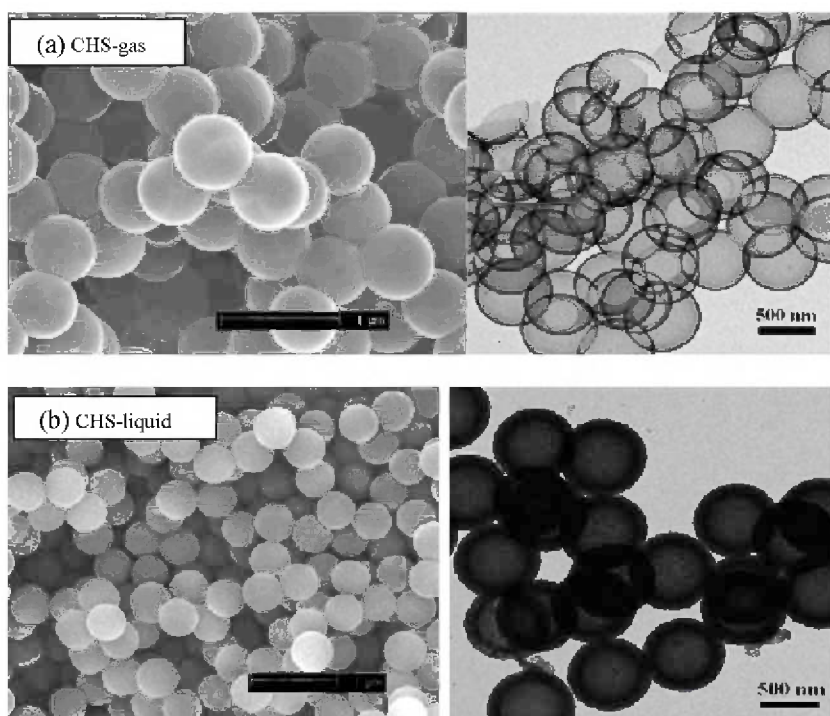


Fig. 20. SEM and TEM images of CHSs formed in gas (a) or liquid (b) phase [157].

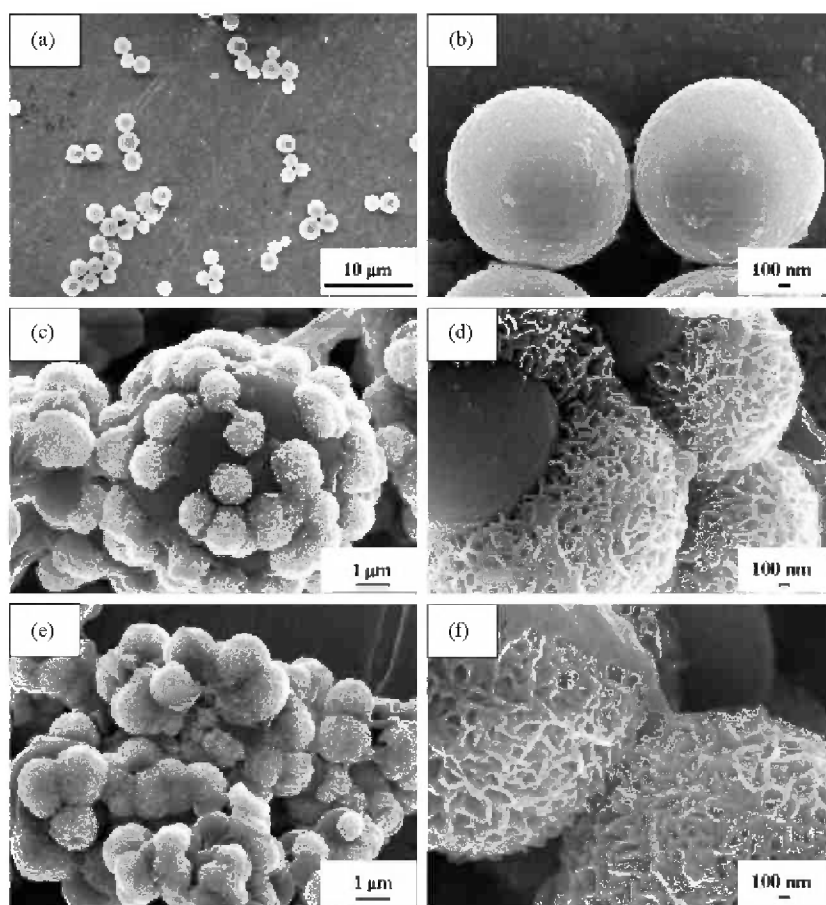


Fig. 21. SEM microstructures of carbon microspheres before and after soaking in simulated body fluid (SBF) for 5 and 10 days. (a and b) Before soaking; (c and d) after soaking for 5 days; (e and f) after soaking for 10 days [169].

dispersed in CCl_4 . A slow (catalytic) reaction occurred in which the Au was removed from the core and was replaced by carbon anions, i.e. C@SiO_2 core-shell spheres were synthesized [171].

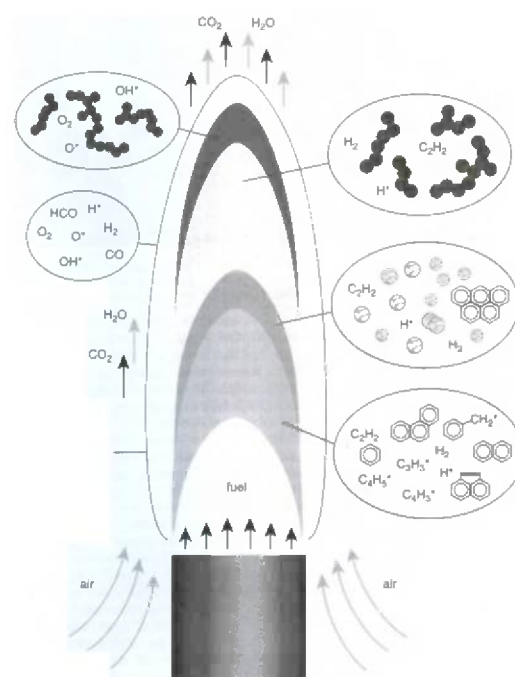
3. Mechanisms of formation

Numerous mechanisms have been proposed for the synthesis of CSs; mechanisms that appear to depend on the reaction conditions, carbon source, catalyst, etc. In this review the proposed mechanisms for CS synthesis will be discussed according to whether a catalyst/template is present or absent.

Soot particles are typically spherical in shape and the mechanism of their growth has been extensively studied. The key features are conversion of a carbon source typically into C and H radicals (and O containing radicals if O is present), and finally reaction to give the CSs (Fig. 22). It is expected that most gas phase CS syntheses, independent of the carbon source, will occur in a similar fashion [35].

The growth mechanism of carbon produced by gas phase non-catalytic routes was studied by Lahaye et al. [172,173]. In describing the mechanism for the formation and post-oxidation of particulate carbons (carbon black and soot formed in the gas phase), five factors were considered to be crucial: carbon black precursors and their formation; carbon black particle inception; the agglomeration of nuclei into particles and of particles into aggregates; surface growth, and post-oxidation of the carbon black.

It was confirmed that in all pyrolytic systems as well as in flames, three possible routes to carbon particles can be proposed,



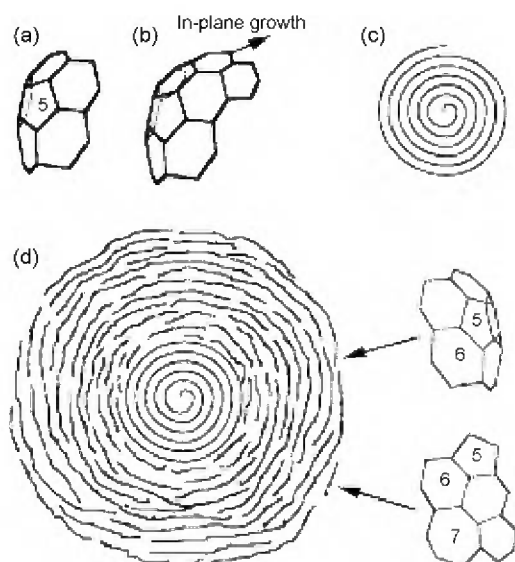


Fig. 23. (a) Nucleation of a pentagon, (b) growth of a quasi-icosahedral shell, (c) formation of a spiral shell carbon particle proposed by Kroto and McKay, and (d) growth of a large size carbon sphere [51].

namely (a) via polyacetylenes, (b) via polyaromatic hydrocarbons (PAHs) and (c) via the formation of a carbon vapor resulting from the dehydrogenation of initial hydrocarbon molecules. PAHs were proposed to be the precursors to carbon nuclei. While attempts have been made to study carbon particle inception, it has been found that PAHs grow during dehydrogenation and progressively develop the properties that characterize carbon black with time. It is believed that in a flame, there is no true particle nucleation.

The manner in which nucleation of carbon atoms/radicals give the larger spheres is not known in detail. One proposal is that the sphere is nucleated from a pentagonal ring followed by a spiral shell growth (Fig. 23) [51]. This type of mechanism was proposed by Kroto and McKay [174] to explain the formation of large fullerenes.

The surface of a CS appears to have an unbroken carbon layer when the CS is very small (carbon onion). In this instance curvature of the carbon layers is noted. However, CSs produced by most of the methods described in the review have diameters >10 nm and these CSs do not have unbroken carbon layers but rather have a surface made of carbon graphitic flakes and these are believed to contain many dangling bonds at their edges [15]. These flakes are arranged perpendicular to the CS core and produce concentric layers of carbon domains. Thus it can be said that the spheres are composed of curling graphitic flakes with random twisting, and these flakes are not closed shells. Ideally, to form a graphitic carbon sphere, the atomic structure of each flake and the graphitic lattice must be modulated to accommodate the curvature of the sphere. This requires the presence of pentagonal and heptagonal rings so that the curvature of the carbon sphere can be achieved (Fig. 24).

Kang and Wang [14] has attempted to analyze the flakes in terms of heptagon, pentagon and hexagon ring structures (Fig. 25). This analysis allows for sphere curvature without formation of a continuous carbon layer as found in CNTs.

Levesque et al. [79] reported a mechanism based on the above ideas for the catalytic chemical vapor deposition of acetylene gas. The acetylene was decomposed into atomic carbon and hydrogen by a nickel nano-catalyst. This gave wavy 2D flakes obtained by the combination of pentagonal and heptagonal structures together with the planar hexagonal structure of graphene in order to accommodate the curvature of the carbon sphere. Aggregation of concentric layers gave rise to the solid carbon nanospheres. As the

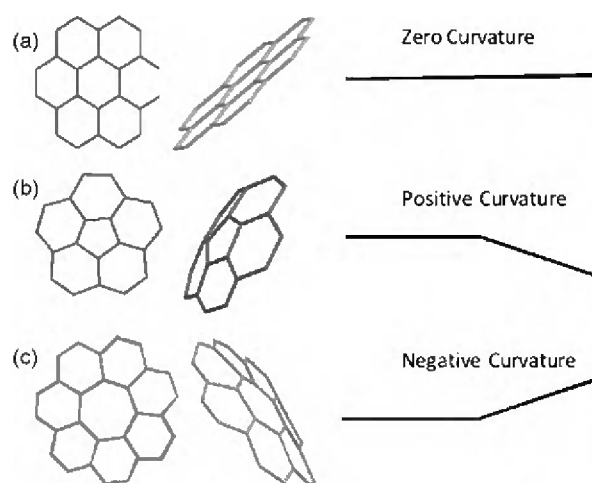


Fig. 24. Schematic representation of graphitic flakes. (a) Hexagonal, (b) pentagonal, and (c) heptagonal. Pentagonal and heptagonal carbon rings introduce changes in the curvature of the graphitic flakes [15].

flakes are in the range of 4 nm, the superposition of these flakes, concentric layer by concentric layer, statistically created the 3D nanocrystallites.

The growth of the sphere, i.e. the addition of added carbon layers to the CS is due to deposition of carbon from the gas phase. This growth is influenced by the carbon source and the reaction conditions (T, P, flow rate, time in the reactor). At the typically high temperatures used to make the CSs the carbon source will decompose into fragments (neutral and charged) and radicals. These will provide the building blocks for the flakes. Gas phase analysis of the effluent gas after CS formation in a flow reactor has revealed the synthesis of large carbon fragments (e.g. PAHs) and these could also generate the flakes. Studies in which the carbon source is varied during the sphere growth could be revealing.

The other types of CS that can be formed involve carbon layers that are perpendicular to the sphere core. Mechanistic descriptions of the formation of these radial CSs (Fig. 2), have not been studied in detail.

The role of catalysts in gas phase CS synthesis is less obvious. Many authors have shown that a catalyst assists with the CS synthesis (see above). In some instances a metal particle is found at the center of a carbon layer (core-shell structure) and this can be removed to give a hollow CS. In this instance it is clear that the

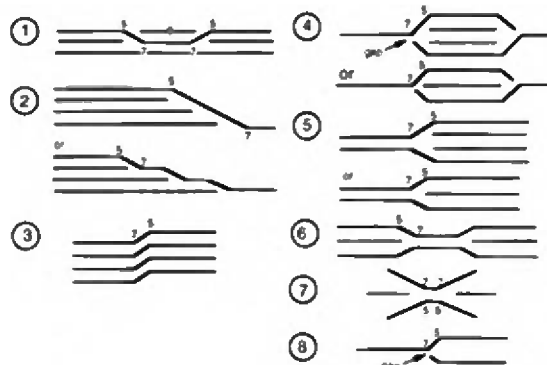


Fig. 25. Two-dimensional structural models of graphitic flakes produced by the combination of pentagonal (5), hexagonal (6), and heptagonal (7) carbon rings. The pentagons are paired with heptagons. In these models, the inner graphitic layers are assumed to be located beneath the models. It must be pointed out that the 3D curving of the graphitic surface is symbolically represented by a 2D line in order to be compared to the experimental images provided by HRTEM [14].

metal acts as a template and catalyst for the synthesis. However, in many instances the CSs formed in the presence of a catalyst are solid. In these cases it seems more likely that the catalyst plays the role of aiding the decomposition of the carbon source rather than in assisting with the polymerization reaction. It appears that in many examples reported, that as the temperature of the reaction is increased, the product changes from a tubular (metal as template and catalyst) to a spherical shape (metal no longer acting as catalyst), consistent with the above suggestion.

Both hollow and core-shell CSs can be explained from a common mechanism, as it is assumed that the hollow core is formed by leaching of the core after the CS has formed. In the above cases a metal particle acts as both a template and catalyst to form the CSs. In the initial step carbon will deposit on the metal particle. This carbon will cover the metal particle and finally growth of carbon layers will lead to the final structure. The mechanism may have similarities to the growth mechanisms used to explain carbon fiber and CNT growth. Thus, the initial carbon deposit may have originated from gas phase fragments. This carbon could then dissolve in the metal and re-precipitate as graphitic carbon or the carbon could merely diffuse over the metal surface to form C–C bonds and a carbon layer. Once this layer has formed the metal will not be accessible to further carbon deposits and the mechanism will then be similar to that described for non-catalytic growth of CSs.

Some further mechanistic details for specific examples are described below.

Qiu et al. [54] have synthesized CSs using an arc-discharge method (nickel catalyst/coal electrode) and speculated that at high temperature, graphitic crystallites or nanocrystals form from the carbon source. The nickel acts as a catalyst. In the arc-discharge process it is proposed that large numbers of electrons are produced, which adhere to the surface of active nanocrystallites and this improved the fluidity of the crystallites. In this process nickel particles play an important role in binding the smaller crystallite particles to form bigger crystallites in the gas phase.

Mechanisms for the growth of carbon onions have been summarized in a review [11]. Many of the proposals made for the growth of onions are similar to those proposed for growth of larger CSs. Thus in the CVD process a metal catalyst is suggested to act as a template for carbon deposition and graphitization. A key issue relates to whether, (i) carbon layer formation occurs by crystallization of an outer carbon layer followed by growth of layers below this layer and the metal core or (ii) via a process of deposition (followed by graphitization) from the gas phase. A CVD mechanism based on ferrocene/heavy oil reactants, entailing carbon growth away from the template/catalyst and supporting mechanism (ii) is shown in Fig. 26.

A general mechanism for the synthesis of CSs using organometallic compounds has been proposed (Fig. 27) [104]. In this process ferrocene was decomposed at 400 °C to form iron and carbon. The iron atoms assembled together to form large particles at 2 MPa and 400 °C. These large iron particles reacted with ammonium chloride (in the vapor phase), to form microsized spherical droplets of iron amine complexes. These complexes have a high sticking coefficient which enhanced the adsorption of the carbon feedstock. In this way the iron amine complex acted as a plating agent. The carbon obtained after decomposition of ferrocene formed a coating on the spherical droplets of the iron amine complex. Finally the iron droplets seeped out from the defects and pores of the carbon shell leaving behind the hollow CSs.

Various mechanisms have been proposed to generate CSs from the pyrolysis of polymeric compounds. Jang and Yoon [150] proposed a mechanism for the synthesis of magnetic carbon nanoparticles from micelles using dodecyltrimethylammonium

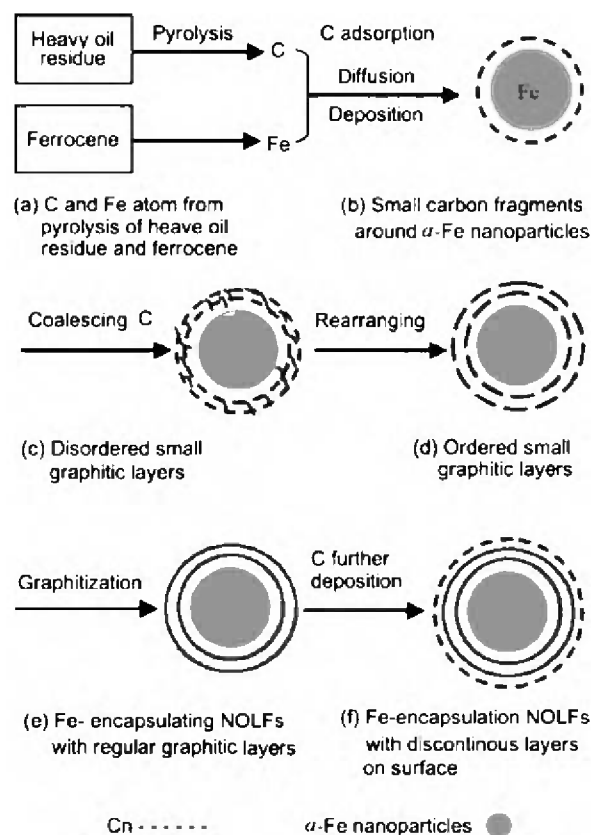


Fig. 26. Growth model of Fe-encapsulating NOLFs from heavy oil residue [11].

bromide and decylalcohol as co-surfactant (Fig. 28). After formation of the micelles, a polymeric carbon source was added to form the iron based species, which was oxidized to form iron doped nanoparticles. These nano-particles, after carbonization, formed magnetic carbon nanoparticles.

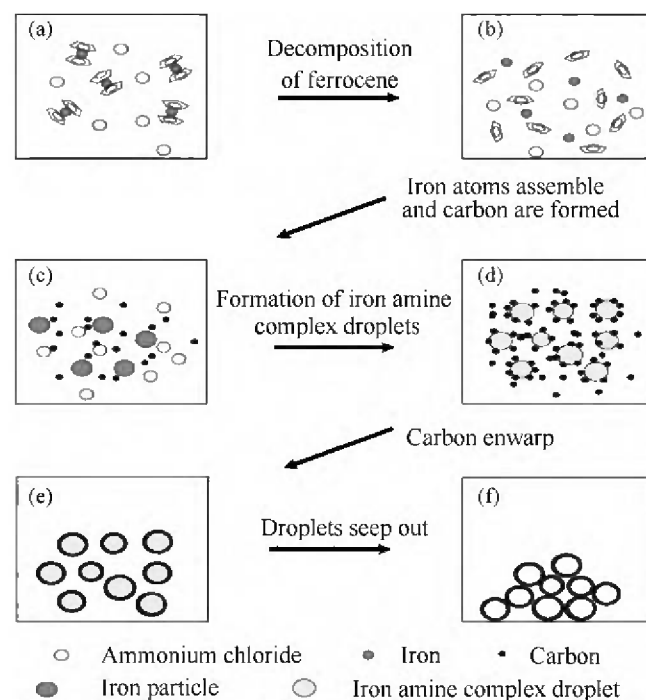


Fig. 27. Schematic illustration of the formation mechanism of HCSs from ferrocene and NH_4Cl [106].

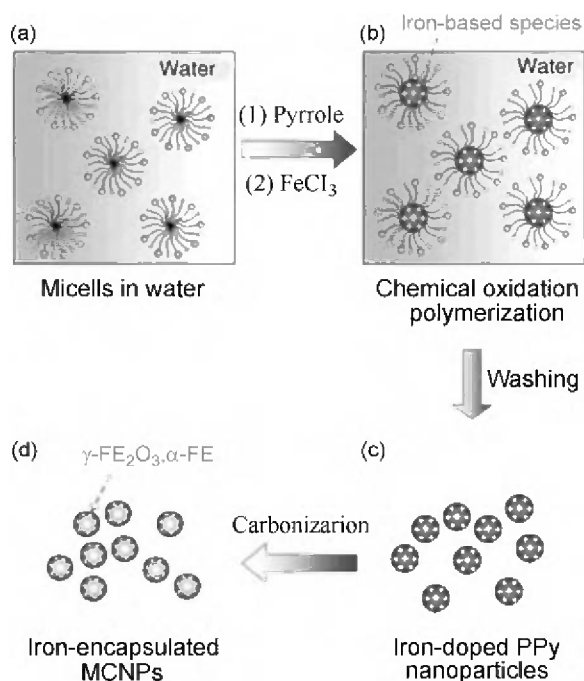


Fig. 28. Fabrication of PPy nanoparticles (a–c) and MCNPs (c and d) with uniform diameters [150].

4. Chemistry of CSs

Allotropes of carbon are associated with both carbon hybridization and curvature. Spherical carbons should contain curved sp² carbon atoms. The presence or absence of curved sp² carbon as well as the functional groups associated with the carbon surfaces will have a bearing on the chemistry associated with CSs. However, it appears that 'there is no compelling evidence for the dominant, or even substantial, presence of curved sp² nanostructure in soot or carbon black' [175]. Thus the chemistry of CSs still needs to be evaluated in terms of the role of curved sp² carbons.

A wide range of carbon sources has been used to make CSs that vary from methane to glucose and includes PAHs, carbon oligomers and polymers. Typically the carbon source is polymerized at high temperature and in the process smaller molecules such as H₂O, CO and CO₂ are eliminated. In a typical CVD process, spheres are synthesized with the carbon layers horizontal with respect to the core. The sphere surface is non-ideal and consists of graphite flakes that contain functional groups (COOH, OH, etc.). These groups can be converted into other organic groups by conventional organic chemistry procedures. Functional groups can also be added to the CSs by acid or base treatment. Alternatively the chemistry of the sphere can be modified by doping procedures that permit addition of elements such as N and B into the sphere structure. The doping or functionalization modifies the wettability of the sphere surface.

It is this ability to not only tailor the physical properties but also the chemical properties that allows CSs (and all shaped carbons) to be used in a wide range of applications.

4.1. Doped spheres

Spheres can be doped by two procedures; by generating spheres using carbon sources that contain the doping element or by post-synthesis addition of doping elements to already made spheres. The most common element that has been used to dope carbon is nitrogen [176,177] and limited studies have been reported on doping using other elements such as boron and sulfur.

Mondal et al. [178,179] reported the synthesis of boron doped CSs using acetylene and B sources at 800 °C under a flow of an inert gas. For example, boron doping of spheres using acetylene as C source and BF₃/MeOH solutions as B source gave low B-doping levels detected by laser ablation ICP-MS. The conductivity of the B doped CSs was lower than that of the undoped CSs.

NH₃ is commonly used to produce N doped carbon blacks [180,181]. Other gaseous reagents such as CH₃CN, have also been used [182]. Alternatively, solid N containing sources can be used. Thus treatment of Ketjen Black EC3001 with polymeric resins made from formaldehyde and melamine, urea, thiourea or selenourea under N₂ at 400–1000 °C gave N doped CBs (2.2–8.4%N).

Carbon microspheres were synthesized by polymerization of vinylidene chloride and acrylonitrile in the presence of bentonite as template. After template removal, graphitization at 600 °C gave monodisperse (125–150 μm) high surface area (692 m² g^{−1}) N doped CSs. These materials with N surface composition ranging from 3 to 8% were used to support Ni particles. The XPS studies revealed that at high temperatures the N content decreased [153].

Reaction of Stober silica spheres at 900 °C or 1000 °C with benzene vapor containing 5 wt% acetonitrile gave composite carbon/silica spheres. Removal of the silica spheres using HF gave hollow N doped spheres. The diameter of the silica sphere determined the diameters of the product, e.g. 730 nm silica sphere templates, gave CSs with an external diameter of around 810 nm and a shell thickness of about 60 nm [76].

The polymerization of melamine/formaldehyde mixtures as a function of temperature gave spheres that grew to 400 nm after pyrolysis at 1000 °C for 5 h. These were studied for their conductance behavior [183]. N doped mesoporous carbons were also produced by polymerizing melamine and formaldehyde in the presence of fumed silica. The spherical particles were then treated with HF to remove the silica and this left a highly porous material (ca. 1.2 μm diameter; 1460 m² g^{−1}) with N content between 7 and 8% that was used to synthesize electrodes for capacitance measurements. The synthesis procedure is similar to that described to make hollow spheres templated from spherical silica particles. Variation of the silica particle size and reaction temperature led to variation in the sphere size [74].

N doped nanoparticles with a spherical like shape (ca. 50 nm) have been produced by thermally decomposing Fe doped polypyrrole particles at 800 °C. These N containing metal nanoparticles (4–5% N) were treated with Pd and used in a range of catalytic reactions [184]. It was shown that the N doped materials resulted in a strong Pd-support interaction that aided various catalytic reactions (Heck, Suzuki, Sonogashira).

Li et al. synthesized nitrogen enriched CSs using Mg powder as catalyst and C₃N₃Cl₃ as carbon and nitrogen source in a stainless steel autoclave at 400 °C for 2 h. Uniform spheres with mean size about 250 nm in diameter were synthesized. In this process nickel particles were encapsulated in the CSs [185].

Post-doping procedures have been used to dope carbon blacks. For example Vulcan XC-72 was treated with S₄P₁₀ (300 °C) or NH₃ (800 °C) to give S containing CB (5.6%S) or N containing CB (0.7%N) materials. The doping content was determined by XANES and the N was shown to be present in both pyrrolic and pyridinic forms while the S was present as S and SO₄^{2−}. The CBs were used as supports for Pt, and TEM studies revealed that the Pt particle sizes were smaller on the doped CBs [186]. This ability of N doped carbons to 'nucleate' metal particles has also been observed for N doped CNTs [187,188].

4.2. Functionalized spheres

The rim of a carbon sphere is made up of carbon flakes. These carbon flakes are comprised predominantly of aromatic structures,

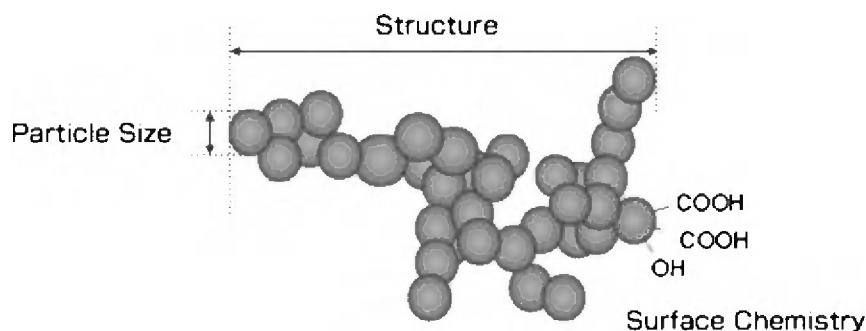


Fig. 29. The structure of carbon black showing some functional groups on the surface of the spherical carbon structure.

made up of condensed benzene ring structures. The sp^2 carbon atoms at the edge of the flakes must contain other atoms to satisfy valence requirements. These will typically be O atoms (such as OH, and COOH) or H atoms. This is reflected by elemental analyses and XPS data which always yield an O content of between 1 and 5% for low surface area CSs. Further, to achieve curvature the carbon flakes must also contain C5 and C7 ring structures. Thus the chemistry of CSs will be different from that of graphite and SWCNTs, which are dominated by reactions at the graphite edges of extended fused rings.

Much of the reported chemistry of CSs relates to early studies on carbon blacks, dominated by acid and base reactions or oxidation reactions [189–191].

The chemistry of carbon blacks has been extensively studied. These materials are characterized by “particle size”, “structure”, and “surface chemistry” (Fig. 29). The acidic surface oxides have been the subject of many studies that have been summarized in several reviews [192–194]. The three main properties listed above have a large effect on the practical properties such as blackness and dispersibility when they are mixed with inks, paints, or resins.

Chemical modification of the surface of carbon blacks has been shown to affect their performance as an elastomer filler that is dependent on the type and amount of functional groups present as well as their surface areas [195–198]. Papirer et al. [199,200] studied carbon black reactivity by submitting carbon blacks to a series of chemical treatments such as oxidation with potassium persulfate, severe air oxidation, halogenation with chlorine or bromine, and grafting of short (ethyl, butyl, pentyl) or long (lauroic) alkyl chains in order to modify their surface properties and to correlate their reactivity with their atomic structure. It was observed that under similar reaction conditions, carbon blacks have different behavior depending on their mode of preparation but they generally perform similarly, after a given modification procedure. Larger particles are chemically more reactive (per unit surface area) leading to higher surface coverage by oxygen, halogen and aliphatic grafting than very fine particles of small dimensions.

The fluorination of carbon blacks was studied by Nansé et al. [201–203]. Analysis of the XPS spectra of fluorinated carbon blacks indicated that F is covalently bonded to C at the sphere surface. In the furnace blacks, a minor amount of F, is trapped in micropores. When the blacks are activated (air oxidation at 450 °C), the amount of fluorine in the carbon blacks increased due to a slight increase in the density of reactive sites relative to the development of porosity. The halogenation of carbon blacks has been reported in other studies [204,205].

Surface modification of carbon blacks by oxidation and the influence of oxidation on the activity of immobilized catalase and iron-phthalocyanines were studied by Sosa et al. [206]. The carbon black was oxidized using different reagents (such as H_2O_2 , HNO_3 , and O_2).

The usefulness of diffuse reflectance spectroscopy (DRIFTS) studies on the formation of surface groups on carbon black by

oxidation was reported by Fanning and Vannke [207]. Several other studies involving the use of IR spectroscopy have reported on the detection of functional groups on carbons [208].

Little systematic chemistry has been performed on the newer CSs (hollow; low surface area) that have been prepared.

CSs were studied for their reactivity towards different organic solvents such as HF, $KMnO_4$, CS_2 , 1-methylnaphthalene and 1,2-dichlorobenzene. The spheroidal structure of CSs only changed when the spheres were treated with 0.5 M $KMnO_4$ solution at 80 °C [209,210].

Fullerene-like sites in spherical carbons are expected to be electron acceptors, by analogy with fullerenes. They should thus act as free radical acceptor sites, which have implications for carbon black-rubber interactions [47]. CSs should be able to act as electron poor dienophiles that should undergo Diels-Alder reactions. Preliminary results on the reaction of CSs with the Prato reagent suggest that this may be the case [211].

Grafting of a polymer onto a carbon surface can be achieved by modifying the characteristics of a surface. This can be achieved by reaction of a monomer with the surface followed by a polymerization reaction (‘grafting from’) or by reaction of a polymer with a surface (‘grafting to’). Numerous reports have appeared describing reactions that form CB/polymer composites [212]. The ‘grafting from’ approach is used extensively in polymer chemistry and one variant of this is the ATRP (atom transfer radical polymerization) reaction. Indeed this approach has been applied to the reaction of commercial CBs with n-butylacrylate after the CBs had been appropriately functionalized.

CSs made from styrene [69] have also been reacted with acid to give acid functionalized CSs which were further reacted with $SOCl_2$, glycol, and N,N-dimethylaminopyridine to give a CS-monomer product that was used to initiate the atom transfer radical polymerization reaction. In the presence of CuBr as catalyst and monomer (methylmethacrylate, styrene, glycerol monomethacrylate), reaction proceeded to give CS-polymer materials. These materials, containing hydrophilic substituents, proved to have enhanced solubility in polar solvents [213].

5. Characterization of physical properties

Many techniques are available to study the morphology and structural properties of carbon materials. Transmission electron microscopy, scanning electron microscopy, X-ray diffraction, infrared spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy are the classic techniques that are widely used for the characterization of SCMs.

5.1. Transmission electron microscopy

Transmission electron microscopy (TEM) is one of the prime techniques used for the evaluation of nanomaterials, and in particular CSs. TEM gives information on the structure, quality,

size, diameter, shell thickness of CSs, and the presence of amorphous materials in a mixture. The major advantage of this technique is the generation of high magnification images and the ability to provide morphological and compositional information on a sample.

HRTEM analysis has been performed on CSs prepared from a range of sources [40]. Cross-sectional studies on samples prepared in autoclaves revealed that the CSs have structures based on the Brooks–Taylor model, i.e. with a radial arrangement of carbon layers. This contrasts with HRTEM images of materials produced by CVD procedures where the carbon layers are horizontal to the sphere surface. It is presumed that this internal structure leads to the high strength associated with CSs.

5.2. Scanning electron microscopy

This technique is widely used for morphological studies and it like TEM, also gives the diameter, shape and chemical composition of CS materials.

5.3. X-ray diffraction (XRD)

XRD is widely utilized to determine the crystallinity, inter-layer spacing, structural strain, and impurities in a CS. This is a non-destructive technique which requires little sample preparation. XRD pattern of CSs show the appearance, in particular, of a graphitic peak at 26.2° in 2θ , the width of which gives information on CS crystallinity [39].

5.4. Raman spectroscopy

Raman spectroscopy is an old technique that has been used for the characterization of carbon [214,215]. Laser Raman spectroscopy has been used to study carbonaceous materials including pyrolytic graphite, carbon black, glassy carbon, coal, “white” carbon and sputtered carbon. This technique gives information on the size, strength and arrangement of chemical bonds but less informative on chemical composition. The most significant peaks for CSs are a peak around 1350 cm^{-1} assigned to residual disorganized graphite (called the D band) and a high frequency peak in the range of $1580\text{--}1600\text{ cm}^{-1}$ attributed to a graphite peak (called the G band). The I_D/I_G ratio (intensity of the D band divided by the intensity of the G band) is often calculated to evaluate the graphitic nature of spheres.

5.5. Fourier transform infra-red spectroscopy

This technique is used to study the chemical composition of carbon materials. CSs show two major sets of bands; one at 1630 cm^{-1} and one in the range of $2850\text{--}2920\text{ cm}^{-1}$ which gives information on the C=C groups and C–H groups present on the surface of CSs, respectively. Functional groups (acidic, hydroxylic, carboxylic, etc.) formed after functionalization of CSs can also be detected by IR spectroscopy.

5.6. Mass spectrometry

Mass spectrometric techniques (e.g. GC–MS and SIMS) have been used in many studies to determine the surface properties of CBs. In particular Palmer et al. [216] observed that benzene extracts of CBs were dominated by the presence of fused-ring hydrocarbons.

5.7. Thermogravimetric analysis (TGA)

TGA is a technique that has been widely used for the characterization of CSs. Pure carbon oxidizes in oxygen at

600°C . A study by Tu et al. [217] presented data on the rate of combustion of CBs in various $\text{N}_2\text{--O}_2$ mixtures under conditions in which both the rate of chemical reaction at the surface and the role of diffusion of oxygen to the surface were factors. A quantitative formulation of combustion rate was presented, predicting effects of temperature, gas velocity, and gas composition in agreement with the experimental measurements. The combustion of single carbon particles in an oxidizing environment was investigated [218]. It was found that during extended periods of a particle lifetime thermal inertia entered significantly into the thermal balance.

5.8. Electron paramagnetic resonance (EPR)

Electron paramagnetic resonance studies have been performed on CSs to locate any unpaired electrons. It was found that the EPR signal of CSs have a peak-to-peak separation of 2.11207 mT and a narrow signal with a mean g -value of 1.99519 . This g -factor is in close agreement with the literature values and consistent with the graphitic nature of the material. The EPR signals correspond to aromatic π -radicals, where the unpaired electron is delocalized over the aromatic rings [94,117].

5.9. X-ray photoelectron spectroscopy (XPS)

XPS studies have been conducted to evaluate the chemical state of carbon in CSs. The XPS spectrum shows a strong C1s peak around 284 eV [69].

5.10. Electron energy loss spectroscopy (EELS)

EELS studies of a pyrolysed carbon powder typically depict a sharp peak at 285 eV , suggesting the graphitic nature of the material [86].

5.11. Cyclic voltammetry (CV)

Lee et al. studied the potential sweep CV of microporous carbon nanospheres heated at different temperatures. The specific capacitance of the material was dependent on the reaction temperature. In this case they observed large specific capacitance values that ranged between 122 and 154 F g^{-1} [143].

5.12. Strength measurement

Classical strength measurements of CSs such as that of tensile strength have been measured using compressive loads. The average compressive stress at failure was $830 \pm 69\text{ MPa}$ while the maximum tensile strength before failure was estimated to be $8.3 \pm 0.69\text{ GPa}$. The spheres studied were similar in structure to Brooks–Taylor mesophase carbons [40]. It is to be noted that CSs appear to form ‘hard’ graphitic surfaces if left to anneal in typical horizontal quartz reactors. Further graphitization by annealing at $T > 2500^\circ\text{C}$ also leads to strong carbons materials.

5.13. Other

Ehrburger-Dolle et al. [219,220] measured the intra-aggregate void size distribution (VSD) and the fractal dimension of rubber grade CBs in water or undecane using thermoporometry.

6. Applications of CSs

Because of their high surface area, thermal stability, unique electronic properties, low density and most importantly their tailored structure, CSs, in particular MCMBs and CBs, have been

used in lithium batteries, as a catalyst support, in drug delivery, for the encapsulation of active transition metals, as lubricants, as injectable scaffolds for tissue regeneration, in heterogeneous catalysis, in dye encapsulation, in removal of contaminants from water, enzyme and protein protection, and for magnetic data storage. Many excellent books and reviews are available that have described the uses of carbon blacks and this older information will not be repeated here [221–225]. Rather, recent examples from the literature, showing new (and well known) uses of CSs are highlighted below.

6.1. Batteries, capacitors and fuel cells

MCMBs have been widely used in batteries and electrochemical cells. For example, commercial MCMBs produced from petroleum residue, after heat treatment up to 3000 °C, were evaluated as electrodes in Li and Na cells. The studies indicated that heat treatment at 750 °C gave the best electrochemical data and this was explained in terms of removal of organic surface groups but not all hydrogen atoms from the carbon [221].

It is well known that when amorphous carbons are heated to high temperatures that they become graphitic. The same applies to CSs. CSs produced in the absence of catalyst [69] on annealing at 2800 °C gave materials that showed increased accretion and a change in morphology from spheres to a polygonal shape. Further, the material showed increased graphitic character. The charge-discharge capacity measurements of these annealed carbons indicated that this material had a better performance than normal spheres in terms of larger reversible capacity and longer plateaus in voltage profiles [53,121,39]. Li ion intercalation into as-synthesized CSs gave materials that showed reversible charge/discharge behavior after the first cycle (220 mAh/g) that improved after annealing (280 mA h g⁻¹).

CSs have been extensively used in electrocatalysis.

Metals, particularly platinum and ruthenium, loaded on CSs have shown very promising results in the direct methanol fuel cell [170,152,226].

Pt supported on CBs is often used in fuel cells but the high porosity of the commercial CBs has resulted in poor access of reactant to Pt particles. To overcome this both hollow CSs [227] and MCMBs [228] have been used to support the active metal. Procedures to form small Pt particles (<1.5 nm for 40% loadings) for use in methanol oxidation in direct methanol fuel cells (DMFC) have recently been described. In one process argon plasma reduction of Pt on commercial CBs was achieved [229]. The low onset potential (ca. 18 V) indicated the excellent oxidation activity of the Pt/CB catalysts.

High surface area hollow CSs (1.5 μm) were made from polystyrene beads, and glucose in an autoclave. After reaction the product was treated in a microwave oven to remove the templates. The CSs were then loaded with Pd and tested for ethanol oxidation in an electrochemical cell and peak current densities higher than that found for Pd/C were obtained. The authors suggested that this was due to the hollow structure that generated a material with an open pore structure [98].

PtRu supported on hollow CSs, prepared by using phenol/paraformaldehyde as carbon source and silica spheres as template, was used to make an electrode in a proton exchange membrane fuel cell [227]. The hydrogen electro-oxidation and fuel cell performance were found to be superior (>60%) to an equivalent RuPt/CB electrode. Ag particles supported on carbon can also be used as electrocatalysts. Recently it was reported that Ag supported on commercial CBs, pre-treated with acid, mixed with Nafion, and supported on a glassy carbon electrode was used to oxidize hydrazine. Cyclic voltammetric studies revealed that the oxidation was mass transfer controlled [230]. It was also shown

that high surface area CSs (prepared from sucrose via an autoclave route) can react readily with Ag in an electrochemical cell to give Ag/CS materials (Ag particle size 10–16 nm); these were not tested for catalytic activity [231].

A recent study of a commercial CB with surface modification by H₂O₂ of a PtRu electrocatalyst for methanol reduction was reported [232]. The surface oxidation was suggested to lead to better performance of the catalyst.

In all the above examples the key issue relates to supporting metal nanoparticles on a spherical carbon support. The achievements of making well separated, but stable metal particles that are accessible to the reactant are key to successful electrochemical activity.

The modification of the chemical properties of the CS will impact on activity. This can be achieved by doping or by functionalization (see Section 3) [233]. Doping of CB by nitrogen (2–8%) was achieved by reaction of the CBs with various urea/formaldehyde mixtures, followed by pyrolysis of the mixture. The catalyst was evaluated in a rotating ring electrode setup for oxygen reduction and generated 3% H₂O₂ under the experimental conditions used.

An evaluation of the effect of CB pre-treatment on oxygen reduction using a Fe/CB catalyst revealed the role of nitrogen on the catalyst activity [180]. The results obtained were related to the metal particle size which was influenced by the presence of N atoms in the CS [186]. Li et al. have successfully demonstrated that nitrogen enriched mesoporous CSs can be used for electrochemical capacitors [155].

Other metals, such as gold have also been used in electrochemical studies using CBs [234].

Low surface CSs produced hydrothermally from sucrose in an autoclave were tested in an electrochemical workstation for electrochemical capacitance activity. The CSs were treated with KOH prior to testing. The electrodes had a high specific capacitance (328 F g⁻¹) under a low sweep rate (5 mV s⁻¹) [235].

6.2. Cathode materials for field emission

Cold electron generation via field emission is a key technology for the development of applications in vacuum microelectronics. Uses in space thrusters, miniaturized XRD and radio-frequency generators and flat panel displays can be envisaged. Generally microfabricated metallic emitters have been used as field emitters. However, replacement by carbon, and in particular CSs, can reduce costs, emission instabilities and non-uniformity resulting from aging-induced surface modification of metallic tips. Indeed carbon has been found to be one of the best field emitters. While CNTs can be used as cold-emitters, the tubular structure confines the field emission to the apex region and thus layered films of CNTs show non-uniform emission. CSs by contrast do not require structural orientation for stable, uniform field emission.

Nickel clustered catalyzed synthesis of carbon nanopearls showed good uniform field emission properties. Binh and co-workers [79] studied the field emission behavior of CSs (prepared from acetylene over Ni; size 150 nm) deposited on a metallic wire or conical tip. The CSs, when produced on a planar surface, present a high density of apex areas with a small radius of curvature. Further, since the CSs are made of small flakes they have many reactive sites to enhance the current. Currents up to 50 μA (current density of 1 A/cm³) were obtained.

6.3. Use as strong material

Carbon is a light element and hence materials made from carbon will be light weight. This feature together with carbons

ability to form polymeric materials containing carbon in the sp^2 hybridised state has led to the use of carbon fibres and tubes in many applications where strength is a requirement. Issues that will be important will be porosity and the presence of defects.

The spherical shape of CSs suggests that they will be found useful for tribological coatings or as lubricant additives. Surprisingly this issue has only recently been addressed. Given the high strength associated with the CSs and the use of carbons where strength is required it may be possible to use CSs in shock wave protection materials [236].

A recent publication has indicated that 'ultrastrong' spherically shaped materials are possible. Pol et al. synthesized CSs from PET in an autoclave at 700 °C. The 2–10 μm solid spheres reportedly 'broke one diamond knife and damaged a second' during microtome measurements. The tensile strength of a CS was measured under a compressive load and showed linear behavior with time until the sphere fractured [40].

Ball-on-disk tribometer tests were performed in both humid and dry air on 150 nm size CSs prepared from acetylene [79]. Data suggest that the larger inter-planar spacing between graphite layers in the CSs, compared to graphite (3.35 versus 3.57 Å), the small flakes (typically < 4 nm in size) and the curvature in the layers leads to materials that are easier to shear. Indeed the tests indicated in particular in a dry atmosphere, that the friction coefficient of the CSs was less than for graphite (0.03 versus 0.2–0.5). It was proposed that this arises from the CSs generating a transfer film, though formation of micron sized agglomerates and 'smashed nanopearls' [237]. Tests were also performed in fretting wear tribological contacts with an ellipsoidal-on-flat contact surface geometry. Tribology studies on carbon onions have shown friction coefficient values of ca. 0.1; the larger onions gave the poorest data [238].

Mesocarbon microbeads (MCMBs), after molding and heat treatment [239], have been used as sealants. In a recent study, variations in temperature and pressure during a seal synthesis procedure generated a carbon that had a compressive strength of 402 MPa. These sealants could be used in modern turbopumps that operate at high speeds and pressures. Similarly, MCMBs have been combined with other carbons (naphthalene pitch, CB) to give materials with a compressive strength of 420 MPa [240].

6.4. Catalyst support materials

CSs can be used like most carbons as a catalyst support [241,242]. Advantages over activated carbons and CNTs relate to: (i) ease of synthesis without use of catalysts, (ii) ability to control the physical properties (size, purity level, porosity) and (iii) high yields of pure materials.

Even though there are a number of advantages in the use of CSs as a catalyst support, there are very few reports available in this area. Kang and Wang reported the reaction of CSs, produced by their MVOCC method, with Pt, CdS and WO_3 . The data suggested that WO_3 reacted with the CS under electron beam irradiation and they proposed that the ability of the surface of the CS to react with the metal complexes could be useful in catalysis [243].

A number of different catalytic reactions have been performed in the presence of metal nanoparticles supported on CSs [244–247]. CSs can be used as a support to load metals in the nano or microscale. Most of the reports relate to the use of metal supported CSs in electrochemical applications.

Nitrogen doped magnetic carbon nanoparticles containing palladium metal showed good catalytic activity for Heck, Suzuki and Sonogashira coupling reactions with very good recyclability of the catalyst [184]. Similarly, Pathak et al. developed a catalytic system for Suzuki, Heck and Stille-type C–C bond formation reactions using palladium coated CSs [248].

Mondal et al. performed catalytic hydrogenation of ethylene over Pd supported on CSs at 60 °C. During this study it was discovered that acid treated CSs showed higher catalytic activity than that of non-acid treated CSs [249]. In more recent studies the utilization of CSs as supports for metals used in oxidation, hydrogenation and C–C bond formation reactions has been achieved. Nitrogen doped CSs as support were utilized for loading a range of metals (Ru, Pd, V, etc.), which were further used to study catalytic activity in hydrogenation, Heck and Suzuki coupling reactions, and oxidation reactions, respectively. The doped CSs gave a uniform distribution of metal nanoparticles due to enhanced anchoring [250,251].

Little work has been performed in which CBs have played a role in the area of photocatalysis. The few studies have related to the study of CB/ TiO_2 composites made in particular by doping CBs into sol-gel derived titania [252–254]. It was reported that the composites out-performed the physical mixtures of the TiO_2 and the commercial CBs in terms of a standard photochemical degradation of a methyl violet dye.

6.5. Composites

Composites made with CSs and another carbon (or other element) sources can be made by either physically mixing or by inducing a chemical reaction between the two components. In particular chemical modification of a CS surface will permit chemical binding to a polymer. Many studies have been reported on the use of CSs (in particular CBs) to make composites. The addition of CSs into a polymer should modify the strength, conductivity or other properties of the polymers. Polymerization of poly-N-vinylcarbazole (PNVC) with commercial CBs generated composites that gave conductivities ($10^{-2} \text{ S cm}^{-1}$) higher than for a polymer without CBs [255]. Recently, carbon nanotube/mesocarbon microbead composites were synthesized by in situ condensation from coal-tar pitch. The study showed that the size of samples is diminished and the microtexture of samples tends to be disordered when more CNTs are added [256]. These composites can be used in artefacts and indeed CB/polymer composites have been used as gas sensing devices [257].

6.6. Other uses

Liu et al. [258] have shown that Pd on CSs can be used for the removal of trace amounts of ethylene in agribusiness environments. Ethylene hastens the ripening and aging process of fruits, vegetables and floral products in a storage environment. These hollow spheres were made by templating/polymerizing phenol or divinylbenzene on silica spheres.

Beside their use as fillers in rubber and other polymeric materials, carbon blacks (CBs) have also been tested for various other applications including the extraction of organic pollutants from water as well as in the modification of electronic properties of insulating materials [259–269].

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