Seeded Synthesis of Monodisperse Core–Shell and Hollow Carbon Spheres

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The production of high-quality, monodisperse, non-agglomerated carbon spheres above 500 nm by colloidal means remains challenging. In this work, a detailed study of the parameters affecting the heterogeneous growth of carbon by hydrothermal carbonization has been performed. Polystyrene (PS) micrometer spheres were used as seeds allowing to control the production of high-quality polystyrene-in-carbon hybrid spheres up to 900 nm with a relative standard deviation below 5%. Furthermore, the removal of the polymeric seeds by pyrolysis yields hollow carbon spheres keeping the narrow size distribution constant. These results may open new paths for the rational design of highly porous and well-defined tailored carbon materials for applications in key areas such as energy and photonics.

Monodisperse colloidal spheres either acting as a template or as a direct material are demanded in numerous applications such as sensors, batteries, supercapacitors, fuel cells, colloidal catalysis, sorption, drug delivery, or photonic crystals, among others. Control over shape, size, surface functionality, porosity, and colloidal stability are essential properties for their successful integration in a wide range of applications. Depending on the functionality intended different materials are best suited. Recently, carbon spheres (CSs) of sizes ranging from nano- to micro-scale have drawn attention not only for their versatile properties, including high thermal stability and controlled reactivity by proper surface functionalization, but also for the sustainable synthesis, which can be carried out with the use of renewable carbon precursors. Numerous methods have been developed for the fabrication of CSs including chemical vapor deposition (CVD), pyrolysis of organic compounds, arc-discharge, nanocasting processes, and hydrothermal carbonization (HTC), which is based on the polymerization of carbon sources (e.g., monosaccharides and polysaccharides) initiated by the formation of C—O—C bonds. These methods have been gathered in recent reviews. Lately, HTC has been gaining ground because of the mild synthesis conditions required, giving high-purity products and its potential usage to produce hybrid materials including multifunctional core–shell, hollow-shell, or hard structure spheres. Due to their facile removal, silica or polymeric spheres (mainly PS) have been used as hard templates to fabricate hollow CSs. The formation mechanism of carbon nanospheres by homogeneous nucleation and growth reaction, studied by Fourier Transform Infrared (FTIR) and X-ray Photoelectron Spectroscopy (XPS) has been previously proposed. Since the first hard CSs fabricated via HTC, several modifications of the synthetic approach have been developed to produce a broad palette of multifunctional hybrid spheres, which can accommodate metals in the core or produce metal oxide hollow spheres in post-thermal treatments. CSs can develop hierarchical porosity or be organized into 3D structures.

In general, the use of hollow CSs have special interest for energy production. Likewise, assisting in the fabrication of photonic crystals CSs may play as building blocks not only because they can be assembled into a 3D structure with high packing efficiency, but also because they can be removed under orthogonal conditions.

Despite recent progress in the synthesis of colloidal CSs by heterogeneous nucleation and growth, the resultant CSs show relatively broad (above 5%) size distribution for spheres above 500 nm or yield irregular, non-spherical shapes. Thus, to fabricate high-quality monodisperse CSs ranging from 400 to 900 nm (the range of interest for optical applications) with very narrow size distribution (<5%) is still a great challenge.

Here, we present the synthesis of monodisperse CSs via HTC assisted by PS latex as seeds, which can be transformed into hollow CS by a simple thermal treatment. We take advantage of the PS features related to good colloidal stability and sphericity to better control the final morphology. The use of PS spheres as template has recently been reported to produce high-quality hollow carbon spheres with sizes below 150 nm or larger ones in multistep synthetic approaches. Our goal is, however, to achieve CSs ranging from 500 to 900 nm with size distribution below 5% by simple means. Our approach is based on a heterogeneous growth over PS seeds to produce PS@C hybrid spheres due to the adsorption of HTC glucose decomposition products over the PS surface without applying tedious synthetic
procedures. Special emphasis is given to optimize the experimental conditions in order to obtain high-quality spheres gaining control over parameters well described by the heterogeneous nucleation and growth principles. \[ 30 \] Furthermore, the versatile PS@C hybrid spheres can also be used as templates to fabricate monodisperse, high-quality hollow CSs by pyrolysis. The resultant spheres show 10% shrinkage in diameter and preserve the initial size distribution. Furthermore, although pyrolysis is known to yield agglomerated products, \[ 31 \] the hollow CSs reported here are non-agglomerated. Other methods previously reported to avoid aggregation include multi-step methodologies such as the growth of intermediate SiO\(_2\) layers, \[ 29 \] the use of additional surfactants, \[ 18 \] or even hypercrosslinking strategies. \[ 32,33 \] To the best of the authors’ knowledge, spherical, non-agglomerated PS@C spheres and hollow CSs have never been reported with such control over size range and distribution by means of such simple, green, and straightforward methodology. Thus, broad interest is envisioned for both hybrid and hollow systems in the development of electrode materials in fuel cells, batteries, supercapacitors, supports in catalysis, or building blocks for the assembly of hierarchically complex structures such as opal-like ones working as photonic crystals in the IR.

Scanning electron microscopy (SEM) images in Figure 1 show representative examples of PS\(_{490}\)@C hybrid spheres grown at different temperatures (160, 170, and 180 °C) and for three different glucose concentrations, namely, 0.35, 0.42, and 0.56 M after 8 h of reaction. Further information with data obtained for PS\(_{260}\), PS\(_{330}\), and PS\(_{549}\) including PS@C hybrid sizes, size distribution, shell thickness information, temperature, and employed glucose concentrations (including different values than those reported in Figure 1) can be found in Table S1 (Supporting Information). As can be seen in Figure 1, the HTC reaction of glucose in the presence of PS seeds at temperatures above 160 °C generates PS@C with diameters ranging from 550 to 1340 nm. Besides, the HTC treatment does not alter the spherical morphology of the initial PS seeds. The diameter of the PS@C spheres changes by modifying the operational conditions, according to the well-established factors affecting heterogeneous nucleation and growth. Images provided in Figure 1 illustrate the fact that certain reaction conditions lead to secondary populations of spheres. While selective precipitation methods can be employed to separate these populations the goal of this work is the direct production of non-agglomerated, high-quality PS@C hybrid spheres in a wide size range of sizes, with very low polydispersity and avoiding the presence of secondary populations. To do so, several parameters have to be optimized including glucose concentration, temperature, and reaction time for different PS seed sizes. The concomitant relationship between temperature and glucose

![Figure 1. SEM images of PS\(_{490}\)@C hybrid spheres obtained at different HTC temperatures (160–180 °C) and glucose concentration after 8 h of reaction. Size of the main population of spheres ± standard deviation (in nm) and relative standard deviation (RSD) are also included. Scale bar, 1 µm.](image-url)
concentration for a given reaction time (8 h in all cases) subject to the restriction of formation of PS@C spheres without secondary nucleation imposes limits on the ranges of glucose concentration and reaction temperature. In this particular case, these limits are 0.42 \text{ M} and 170 °C. Higher concentration or higher temperature ends up in the appearance of a second population of small CSs as shown in Figure 1f–i. The upper temperature is limited to 180 °C where for different PS seeds, non-spherical and agglomerated products are observed (not shown).

These results are in good agreement with previous reports about CSs formation,[5,34] in the presence or absence of templates. Additionally, it is remarkable that the resulting PS@C hybrid spheres are not agglomerated in all cases. We believe this is the result of the use of glucose (which provides this advantage over other polysaccharides),[33] and the combination of the experimental conditions here reported, including the absence of additives or surfactants.[29] Table S1 (Supporting Information) shows the final sizes of PS@C hybrid spheres, covering a range from 279 up to 1500 nm (± 6%) including those samples in which a second population of spheres is present.

In order to describe the size increase through glucose carbonization, rather than providing a diameter ratio it is convenient to define a volume ratio \( \gamma = \frac{V_f}{V_i} \) because it directly measures the carbon produced. Furthermore, since the synthesis of carbon occurs on the surface of the spheres present in the autoclave, which depends on the amount of seeds and their size, it is convenient to normalize that figure to the total surface available \( S \). We define: \( \gamma' = \frac{\gamma}{S} \). Figure 2 shows the \( \gamma' \) ratio as a function of glucose concentration for several PS sizes at two temperatures (160 °C, black symbols and 170 °C, gray symbols) after 8 h of reaction time. Only data from reactions that yielded no secondary populations are shown. Normalization to the total available area for each PS seed (determined by sphere size and amount) ensures a clear correlation for the carbon growth over equal areas. Overall, a clear trend is observed indicating that the increase in particle volume indeed responds to the glucose concentration. For PS\textsubscript{260} seeds, the absolute final to initial volume ratio \( \gamma \) ranges from 1.5 up to 12 times for glucose concentration ranging from 0.2 to 1.1 \text{ M} at 170 °C. This glucose concentration range can also be used for slightly larger seeds (PS\textsubscript{330}) without the formation of new nuclei and yielding similar volume increases at 160 °C. However, such a range must be reduced when larger seeds are used if secondary nucleation is to be prevented. For larger seeds, the available surface area decreases as the size squared leading to an effective supersaturation. For these cases, the possible glucose concentration is limited to 0.83 \text{ M} or a second population of CSs is produced.

The growth rate with glucose concentration at higher temperature (170 °C) is higher and the range of glucose concentration for single population production is narrower as compared to lower temperature. The former effect is because temperature favors the hydrothermal reaction and the latter because the homogeneous synthesis is boosted by the scarcity of available surface. Thus, for samples with the lowest specific surface available (i.e., PS\textsubscript{549}), only low temperature and low supersaturation conditions yield a monodisperse product. In all cases, a linear tendency can be inferred. According to the literature and to our own results under similar concentrations, 180 °C is the common temperature employed for homogeneous nucleation and growth following the La Mer model, in which monodisperse particles are obtained by the separation of nucleation and growth from a supersaturated solution.[36] As is well known, temperature should be decreased in a heterogeneous growth in order to avoid the formation of secondary nuclei. This is in good agreement with the above reported results, in which temperatures in the range between 160 and 170 °C yield PS@C spheres without a second population under the conditions reported here (at the same glucose and PS seed concentrations). However, as evidenced in Figure 2, higher temperatures provide faster growth (above twice in volume and an order of magnitude in size) which may be advantageous. In order to optimize 180 °C as synthesis temperature different reaction reactions have been explored.

Figure 3 shows the maximum glucose concentration preventing secondary populations for various conditions. These concentrations are plotted for 170 (left bars), 175 (middle bars), and 180 °C (right bars) and two reaction times, 6 (back, dashed bar) and 8 h (front, solid bar). One can readily see that higher temperature or longer reaction time lead to secondary spheres populations. For the glucose concentrations and PS seed sizes studied here, control over the reaction time is key when higher temperatures are employed.

The interdependence between glucose concentration and time is evidenced in
the SEM images, where PS$_{490}$@C hybrid spheres are grown at a fixed glucose concentration of 0.56 M for 5 (Figure 3b), 6 (Figure 3c), and 8 h (Figure 3d), respectively. While 8 and 6 h of reaction yield PS$_{490}$@C hybrid spheres with clear secondary nucleation, reducing the reaction time to 5 h ends up in a very homogenous and monodisperse product. Data including reaction times for additional glucose concentrations are summarized in Table S1 (Supporting Information), which also includes information about the tunability of the shell thickness. Optimizing temperature, glucose concentration, time, and seed size, the shell carbon thickness in hybrid PS@C spheres (showing no second population) can be varied between 0.1 and 1.2 times the radius of the PS seed (see the Supporting Information).

We believe that the control over monodispersity avoiding secondary nucleation exerted by reaction time is related to the evolution of functional groups on the surface of the CSs as the reaction proceeds. As has been reported,[12,29] the evolution of the carbonization reaction implies an increase in the formation of double carbon bonds. We suggest that the increase in double carbon bonds as glucose carbonization proceeds (producing harder spheres) might promote the second population observed at high temperature. Although out of the scope of this work, the secondary spheres growing off the parent spheres observed in several SEM inspections (not shown), attest to an effect previously observed in other systems.[37]

As mentioned before, hollow CSs can be obtained by further calcination of PS@C hybrids spheres in an air atmosphere. Figure 4 shows transmission electron microscopy (TEM) images at different magnifications of the hollow spheres obtained from initial PS$_{260}$@C hybrid spheres. TEM images evidence the quality and monodispersity of the samples after the thermal procedure. A shrinkage of about 10% in diameter, 25% in volume can be detected (TEM of spheres prior to pyrolysis shown in Figure 4b Inset). Figure 4c shows the thermogravimetric analysis of PS$_{260}@$C hybrid spheres from RT to 600 °C. Here, a weight loss is apparent from 300 °C. The inflection point (highlighted by a deep minimum in the first derivative of the weight loss curve) indicates the largest rate of change at 437 °C. This mass loss can be assigned to the PS decomposition. At 600 °C 50% of the material still remains. At this temperature, the mass loss might be due to different carbonization process into carbon network.

The porosities of both the PS@hybrid system and hollow CS have been evaluated by N$_2$ adsorption measurements (see Figure S1, Supporting Information). These measurements show that CSs present type-I isotherms, indicative of the microporous structure and a marked N$_2$ adsorption below $P/P_0 = 0.04$. The PS@C hybrid spheres have a low porosity, the Brunauer–Emmett–Teller (BET) surface area being less than 10 m$^2$ g$^{-1}$ which roughly corresponds to the geometric area of the spheres. In contrast, hollow CSs increase their surface area to 540 m$^2$ g$^{-1}$ after pyrolysis at 500 °C or to 860 m$^2$ g$^{-1}$ at 800 °C with specific pore volumes of 0.2 and 0.32 cm$^3$ g$^{-1}$, respectively. The surface area increase at those temperatures is due to elimination of volatile compounds by
carbonization leading to highly microporous carbon-based shell framework. Additionally, the homogenous porosity on carbon shell is confirmed by pore diameter distribution (see Figure S2, Supporting Information). Pyrolysis at 500 °C creates pores with sizes distributed around 1.2 nm with an incipient additional population centered around 1.6 nm for 800 °C which we believed is related with other degasification reactions.

FTIR spectra show that oxygen groups are present on the spheres surface (see Figure S3, Supporting Information). The –OH (ν = 3400 cm⁻¹) and C=O (ν = 1704 cm⁻¹) vibrations decrease when the pyrolysis temperature is increased, which suggests a hydrophobic surface after PS removal.

Summarizing, in this work a systematic study of factors affecting the synthesis of carbon spheres by heterogeneous nucleation and growth is reported. Fine control over temperature, time, glucose concentration, and size of the initial seed (polystyrene beads), allows the synthesis of excellent hybrid polystyrene-carbon spheres in terms of size distribution (bellow 5%), and shape with no-aggregation in a size range between 500 and 900 nm. The hybrid polystyrene-carbon spheres can be easily transformed by pyrolysis in hollow carbon spheres with preserved monodispersity. This approach provides a synthetic route not only because it yields highly monodisperse spheres, in contrast with traditional HTC glucose products, but also because it offers a control method to synthesize functional hollow carbon spheres with potential in energy applications.

Experimental Section

Chemicals: Polystyrene latex aqueous dispersions (10% vol) were purchased form Fisher or microParticles GmbH. PS sphere sizes employed were 260, 330, 490, and 549 nm, which are referred to as PS

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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