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Colloidal Carbon Spheres and Their Core/Shell Structures with Noble-Metal Nanoparticles**

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Colloidal micro- and nanospheres have been of continuous research interest, since their intrinsic properties can be finely tuned by changing parameters such as diameter, chemical composition, bulk structure, and crystallinity. Up to now, they have found a broad range of applications in fields such as drug delivery, biodiagnostics, combinatorial synthesis, and photonic band-gap crystals (PBG).[1–3] The success of these applications strongly depends on the availability of colloidal spheres with tightly controlled size and surface properties.[1,2] However, until now, only amorphous silica and some colloidal polymer spheres can be routinely prepared with satisfactorily narrow size distributions.[4] As-prepared colloidal nano- and microspheres usually have relatively inert surfaces, which make surface modification almost unavoidable before use as supports or templates.[3,5]

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Coating the spheres with noble-metal nanoparticles (NMNPs), oxide nanoparticles, or semiconductor quantum dots could endow the spheres with specific catalytic, magnetic, electronic, optical, or optoelectronic properties and greatly widen their utility in fields such as electronics, magnetism, optics, and catalysis.[3,5–13] For instance, the immobilization of transition-metal nanoparticles (TMNPs) on these spheres could allow them to retain high catalytic or biocatalytic activity on recycling, enhance their pH and temperature stability, and enable easy separation from reaction media for reuse.[10,11] In previous reports, immobilization was achieved by two main methods: "layer-by-layer" coating with organic ligands or polyelectrolytes as "glue",[5–8] and "in situ" formation by dispersion copolymerization of styrene and a polyamine in the presence of metal salts.[11] These methods clearly suffer through elaborate surface compositions, manipulation of complex experimental parameters, and/or time-consuming steps for immobilization. We have developed a convenient and controllable hydrothermal synthetic route to hollow ZnSe microspheres.[14] Herein we report an approach to monodisperse colloidal carbon spheres in the size range 150–1500 nm which inherit the reactivity and hydrophilicity of the starting material.

To investigate the chemical reactivity of as-prepared carbon spheres, noble-metal (Ag, Au, Pd, Pt) nanoparticles were loaded onto or encapsulated in carbon spheres to form hybrid structures. A layered structure integrating differently sized noble-metal nanoparticles was obtained when a combination of both synthetic strategies was utilized.

The carbon spheres were prepared from glucose under hydrothermal conditions at 160–180 °C, which is higher than the normal glycosidation temperature and leads to aromatization and carbonization.[15–17] The narrow size distributions of the final products were demonstrated by TEM and SEM observation. Figure 1a and b show typical TEM and SEM images of such colloidal carbon nanospheres with diameters of 200 and 1500 nm, respectively. Some spheres in Figure 1a formed hexagonal contacts with one other, and this suggests potential use in construction of photonic crystals or other nanodevices.

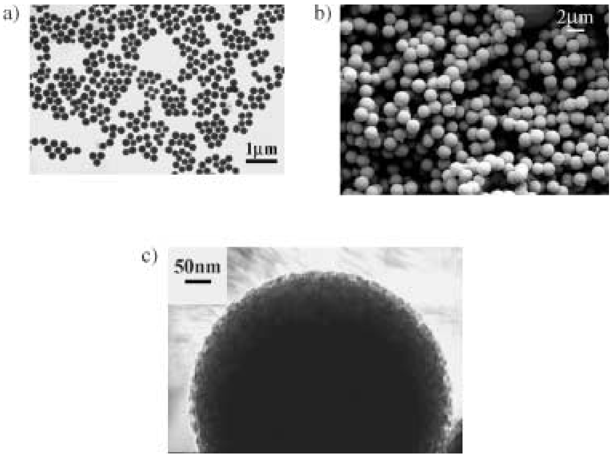

Figure 1. a) SEM image of 200-nm carbon spheres prepared at 0.5 M, 160 °C, 3.5 h, b) TEM image of 1500-nm carbon spheres prepared at 1 M, 180 °C, 10 h, c) Magnified TEM image of an individual carbon sphere.

The diameters of the carbon spheres were influenced by reaction time, temperature, and concentration of starting material, of which the first-named was dominant. At constant concentration and temperature (e.g., 0.5 M, 160 °C), as the time increased from 2 to 4, 6, 8, and 10 h, the diameter grew from 200 to 500, 800, 1100, and 1500 nm.

Various chemical reactions of glucose can take place under hydrothermal conditions and result in a complex mixture of organic compounds,[14,15] and this makes it difficult to determine the exact chemical reaction in the sealed vessel. According to our experimental results, the growth of carbon spheres seems to conform to the LaMer model,[18] shown schematically in Figure 2. No carbon spheres formed when a 0.5 M glucose solution was hydrothermally treated below 140 °C or for less than 1 h. However, the orange or red color and increased viscosity of the resulting solutions indicate that some aromatic compounds and oligosaccharides are formed,[15] in what has been denoted the "polymerization" step. When the solution reached a critical supersaturation (e.g., 0.5 M, 160 °C, 3 h), a short single burst of nucleation resulted. This carbonization step may arise from cross-linking induced by intermolecular dehydration of linear or branchlike oligosaccharides, or other macromolecules formed in prior

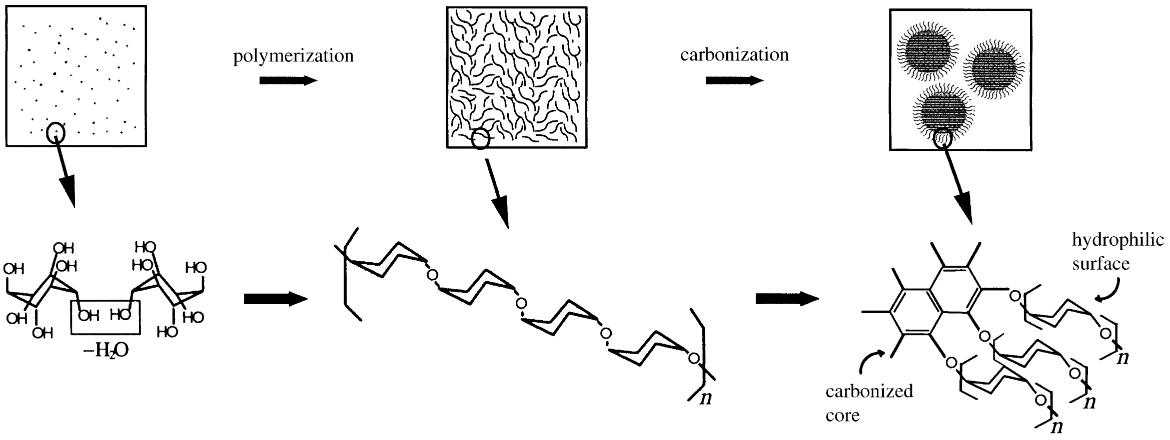

Figure 2. Schematic growth model for carbon spheres (in the final step, the carbonized core and the hydrophilic surface formed by dehydration are schematically represented by aromatic rings and polysaccharides, respectively).

step. The resulting nuclei then grew uniformly and isotropically by diffusion of solutes toward the particle surfaces until the final size was attained. The diameters of these nanospheres could thus be tuned in the range from 150 nm (the initial core size, and the smallest size we attained) to 1500 nm by controlling the growth parameters. The TEM image of an individual sphere (Figure 1c) showed some nanosized pores distributed uniformly on the surface, which could caused by removal of residual organic compounds, such as oligosaccharides from the surface by washing with water and alcohol. These pores could not only increase the surface area, but also aid penetration of reactive species. In comparison to the synthesis of polymer or silica spheres, two features become apparent: 1) our approach is an absolutely "green" method. The monodisperse colloidal nanospheres were obtained in aqueous glucose solutions, and no toxic reagents were used. 2) The synthetic procedure involves none of the organic solvents, initiators, or surfactants which are commonly used for preparation of polymer micro- or nanospheres. This ensures that the as-prepared nanoparticles are nontoxic enabling their used in biochemistry or biodiagnostics.

Dehydration and aromatization are usually regarded as a process of decreasing the number of functional groups.[15] The FTIR spectrum (Figure 3a) was used to identify the functional groups present after hydrothermal treatment. The bands at $\tilde{\nu} = 1710$ and $1620\ \mathrm{cm^{-1}}$, attributed to C=O and C=C vibrations, respectively, support the concept of aromatization of glucose during hydrothermal treatment. The bands in the range $\tilde{\nu} = 1000$–$1300\ \mathrm{cm^{-1}}$, which include the C−OH stretching and OH bending vibrations, imply the existence of large numbers of residual hydroxy groups. Partially dehydrated residues in which reductive OH or CHO groups are covalently bonded to the carbon frameworks improve the hydrophilicity and stability of the microspheres in aqueous systems, and greatly widen their range of applications in biochemistry, diagnostics, and drug delivery, and as templates for hybrid core/shell structures or hollow/porous materials. For instance, they could be covalently bonded to biomacromolecules and used as a hydrophilic drug-delivery system,[19] or react with metal ions to form metal nanoparticles, which could be used as probes for detection of molecules by surface-enhanced raman scattering (SERS).

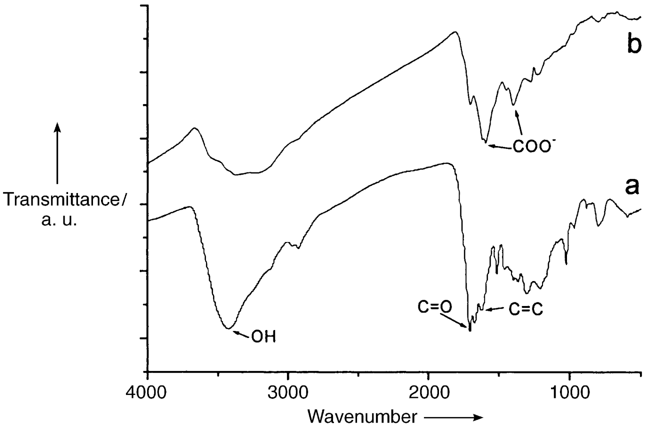

Figure 3. FTIR spectra of carbon spheres: a) sample unloaded with noble metal, and b) sample loaded with silver nanoparticles.

To demonstrate the reactivity of as-prepared carbon microspheres, silver and palladium nanoparticles were loaded onto their surfaces by room-temperature surface reduction or by the reflux method. Figure 4a shows silver-loaded carbon spheres prepared at room temperature by ultrasonication in 1M $AgNO_3$ solution. Thanks to the moderate synthesis conditions, the silver nanoparticles decorating the carbon nanospheres were usually no larger than 15 nm (Figure 4b). Energy dispersive X-ray analysis (EDXA) of the spherical core/shell structure revealed the elemental constitution of the noble-metal-loaded spheres (Figure 4c): two major peaks, corresponding to carbon and silver, and one weak peak (≈0.8 keV) indicating the presence of oxygen. The effectiveness of the reflux method was demonstrated by loading palladium nanoparticles onto the surfaces of carbon spheres, which occurs at a far lower concentration (0.1→0.02M). After 20 min under reflux, the carbon spheres were covered by a uniform shell of 10–20-nm palladium nanoparticles (Figure 4d,e).

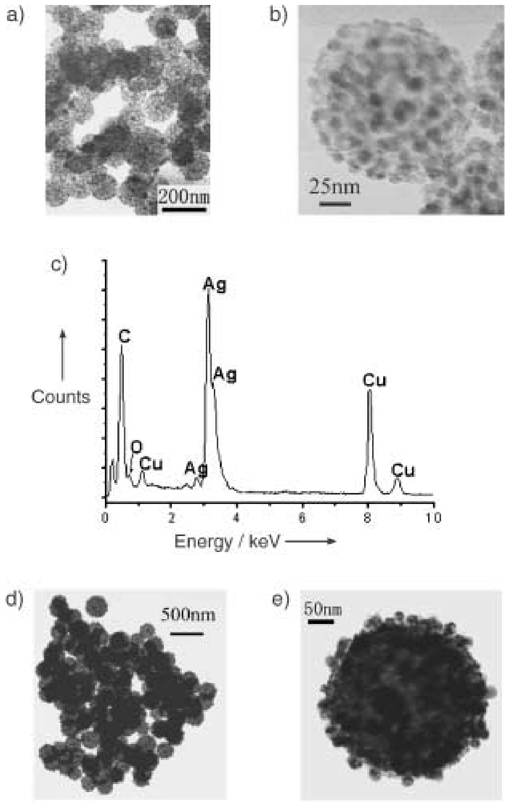

Figure 4. a, b) Carbon spheres loaded with silver nanoparticles at room temperature. c) EDXA spectrum of silver-loaded carbon spheres. d, e) Carbon spheres loaded with palladium nanoparticles by the reflux method.

The surface redox reactions decreased the number of reducing organic functional groups, as revealed by the FTIR spectrum (Figure 3 trace b). The O−H stretching band centered at 3500 cm^{-1} was weakened. Two major peaks centered at 1590 and 1390 cm^{-1} could be attributed to asymmetric and symmetric stretching vibrations of COO$^-$ groups,[20] respectively, and this suggested that the final products of oxidation were carboxylates.

A surprising feature of these carbon spheres is their ability to encapsulate nanoparticles in their cores with retention of the surface functional groups. Nanoparticles of gold and silver could be encapsulated in carbon by in situ hydrothermal reduction of noble-metal ions with glucose, or by using silver nanoparticles as nuclei for subsequent formation of carbon spheres. The latter is a more general method that can be used for the encapsulation of various colloidal nanoparticles, such as metals, oxides, and chalcogenides. Figure 5a shows micrographs of gold-cored carbon spheres prepared by the former method. Carbon spheres containing one or two metal nanoparticle cores were obtained. The samples for TEM observation were tilted by ±25° to check whether the nanoparticles were always encapsulated at the centers of the carbon spheres rather than attached to the surface. Figure 5b shows carbon spheres containing silver nanoparticles prepared by the latter method. Silver nanoparticles with different morphologies were encapsulated in the carbon spheres (Figure 5c). The diameter of the noble-metal nanoparticles could be manipulated in the range of 8–50 nm. This procedure protects the silver nanoparticles with carbon and retains the surface functional groups for loading other functional groups, enzymes, antigens, or other nanoparticles.

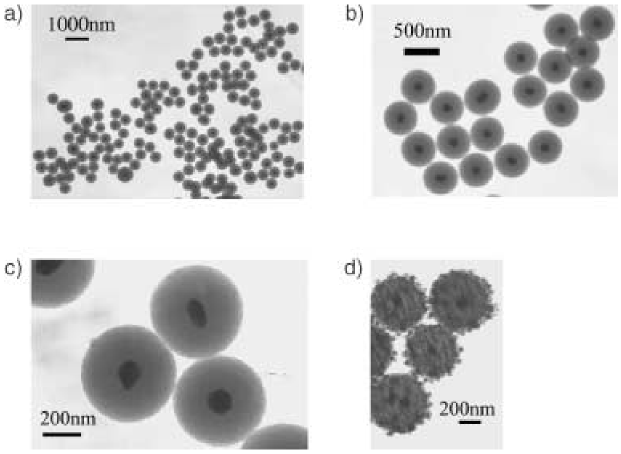

Figure 5. NMNP-encapsulated carbon spheres prepared in different ways: a) Au-cored carbon spheres from hydrothermal reduction and encapsulation method, b,c) silver-cored carbon spheres from encapsulation of silver nanoparticle seeds, and d) layered structure with an silver core, a platinum shell, and a carbon interlayer, formed by seed-based encapsulation followed by the reflux method.

The ability of the retained functional groups to load nanoparticles was demonstrated by reductive loading of platinum nanoparticles onto silver-cored carbon spheres. A layered structure consisting of an Ag core about 60 nm in size, a platinum shell composed of 10–20-nm platinum nanoparticles, and a carbon interlayer was prepared in this way (Figure 5d). The layered structure should be of interest to physicists and material scientists, since the optical (including Raman and IR), electronic, and catalytic properties of NMNPs are size-dependent,[21,22] and this kind of structure integrates differently sized NMNPs in a single system. In fact, the silver and other metal nanoparticles generated by our method could be replaced by each other, and this opens an avenue to tailoring the structures and hence the properties of these hybrid structures, as well as exploring the distinct properties of noble metal nanoparticles. Furthermore, the silver-loaded carbon nanoparticles could be transformed into hollow structures by ion-exchange and thus form more complex structures.[23]

The stability of colloids was affected by the decoration and encapsulation of noble-metal nanoparticles on/in the carbon spheres. Colloidal suspensions of spheres with diameters of 200 and 500 nm were stable for one month and 10 days, respectively. While for the noble-metal-loaded spheres (e.g., the sample shown in Figure 5c), the time decreased to 3–5 days. However, when the mixtures were shaken or ultrasonicated for 5 s, a homogeneous suspension was formed at once.

A SERS analysis of unloaded carbon spheres showed no clear peaks (Figure 6 trace a) owing to their poor crystallinity in the as-formed state. In contrast, silver-loaded spheres showed two strong peaks at 1585 cm^{-1} and 1390 cm^{-1} (Figure 6 trace b), which were attributed to in-plane vibrations of crystalline graphite and disordered amorphous carbon, respectively.[24] The greatly increased signal-to-noise ratio suggested promising applications of this kind of noble-metal-loaded carbon spheres in developing convenient and sensitive methods for trace analysis and studying adsorption behavior, etc.[25] Since spherical objects are easily packed and assembled into arrays,[1,9] and biomacromolecules such as proteins can be adsorbed on NMNPs,[9] our method provides new basic units for the construction of nanodevices for use in biochemical detection. Furthermore, since carbon is far more stable than polymers with respect to high-temperature stability and resistance to acids, bases, and solvents, these hybrid structures should have clear advantages over NMNP-decorated polymer spheres in fields such as catalysis or detection.

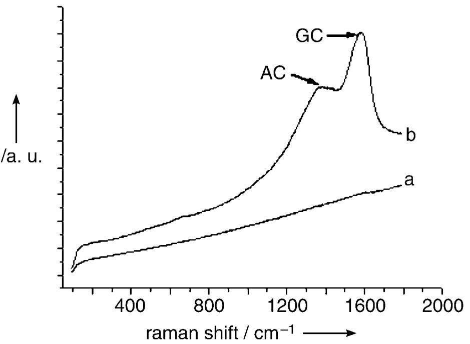

Figure 6. Raman spectra of carbon spheres: a) unloaded with noble metal, and b) loaded with Ag nanoparticles. GC: graphitic carbon, AC: amorphous carbon.

In summary, monodisperse colloidal carbon microspheres were prepared from aqueous glucose solutions by hydrothermal synthesis, and encapsulated nanoparticles were also obtained by this procedure. The synthesis is convenient, and the as-formed colloidal spheres inherit functional groups from the starting material and have reactive surfaces, which facilitate loading with NMNPs and make it possible to integrate differently sized NMNPs in layered structures. Furthermore, the synthetic strategy can be transferred to other systems such as oxides, chalcogenides, and nitrides for the formation of hybrid, hollow, or porous structures. Thus, the synthesis of these carbon spheres opens an avenue to tailoring the structure, composition, and morphology for use in fields such as drug delivery, porous ceramics, adsorbents, and catalysis.

Experimental Section

Carbon nanospheres: Glucose (4–8 g, analytical purity, Beijing Chemical Reagent Factory) was dissolved in water (40 mL) to form a clear solution, which was placed in a 40-mL teflon-sealed autoclave and maintained at 160–180 °C for 4–20 h. The black or puce products were isolated by centrifugation, cleaned by three cycles of centrifugation/washing/redispersion in water and in alcohol, and oven-dried at 80 °C for more than 4 h.

Loading silver nanoparticles onto carbon spheres: Newly prepared nanocarbon spheres were dispersed in water with the aid of ultrasonication to give a 0.5 wt % suspension. 1 mL of this suspension was added to 1 M $AgNO_3$ (10 mL) solution drop by drop with vigorous stirring. The mixture was supersonicated for 10 min, aged for 1 h, and subjected to four centrifugation/water wash/redispersion cycles to remove silver ions. The resulting powder was centrifuged, redispersed in alcohol, and deposited on a copper grid for TEM observation.

Reflux method: 5 mL $\approx$0.2 wt % of an aqueous suspension of carbon spheres was heated under reflux for 5 min and then 0.1 M $PdCl_2$ was added drop by drop under vigorous stirring until the final Pd ion concentration reached 0.02 M. The suspension was refluxed for 20 min before sampling and rinsing.

Encapsulation of Au and Ag nanoparticles: A solution of $HAuCl_4$ (1 mL, 0.02 M) or freshly prepared silver colloid[26] (1 mL, ca. $10^{13}\,mL^{-1}$) was added to a glucose solution (40 mL, 0.5 M) with stirring to form clear solutions. The subsequent procedures were the same as described above for the synthesis of carbon spheres.

Synthesis of layered structures: A suspension (5 mL) of carbon spheres (ca. 50 nm) encapsulating Ag nanoparticles was heated under reflux for 5 min, and then 0.02 M K_2PtCl_6 solution was added until the Pt concentration reached 0.005 M. The suspension was heated under reflux for a further 20 min before sampling and rinsing.

Characterization: All the samples were characterized by TEM (Hitachi H800, acceleration voltage 200 kV), SEM (Leo 1530), Raman spectroscopy (Renishaw RM1000 Raman spectrometer, excitation wavelength 514 nm), and FTIR spectroscopy (Perkin-Elmer Spectrum GX).

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