

## Synthesis and Characterization of Core-Shell Selenium/Carbon Colloids and Hollow Carbon Capsules

Jimmy C. Yu,<sup>\*,[a]</sup> Xianluo Hu,<sup>[a]</sup> Quan Li,<sup>[b]</sup> Zhi Zheng,<sup>[b]</sup> and Yeming Xu<sup>[b]</sup>

**Abstract:** A novel Se/C nanocomposite with core-shell structures has been prepared through a facile one-pot microwave-induced hydrothermal process. The new material consists of a trigonal-Se (*t*-Se) core and an amorphous-C (*a*-C) shell. The Se/C composite can be converted to hollow carbon capsules by

thermal treatment. These products were characterized by transmission electron microscopy (TEM), powder

X-ray diffraction (XRD), scanning electron microscopy (SEM), selected area electron diffraction (SAED), energy-dispersive X-ray (EDX) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

**Keywords:** carbon • colloids • core-shell structures • hollow capsules • selenium

### Introduction

In recent years, considerable effort has been made to design, fabricate and manipulate nanostructured systems with functional properties.<sup>[1]</sup> Advances in physical methods have led to a molecular-level understanding of the structure-performance relationships, which are strongly related to size, composition, and structural order of the materials.<sup>[2]</sup> This knowledge, together with effective strategies for nanostructure fabrication, has inspired the design and development of new composites for advanced applications. One extremely attractive example of a nanocomposite material is the core-shell structured particles because of their diverse applications, for example, as building blocks for photonic crystals,<sup>[3]</sup> heterogeneous catalysts<sup>[4]</sup> and multienzyme biocatalysis,<sup>[5]</sup> and in surface-enhanced Raman scattering<sup>[6]</sup> and drug-delivery applications.<sup>[7]</sup> Most studies on the core-shell particles have been focused on composites that are typically composed of solid or liquid cores surrounded by shells of polymers, inorganics, or biomacromolecules. They provide the possibility for enhanced functionality and multifunction-

al properties in contrast with their more-limited single-component counterparts. For instance, Fe<sub>2</sub>O<sub>3</sub>/MgO and Fe<sub>2</sub>O<sub>3</sub>/CaO core-shell nanoparticles have higher efficiency than pure MgO and CaO catalysts for SO<sub>2</sub> adsorption, H<sub>2</sub>S removal, and chlorocarbon destruction.<sup>[8]</sup> Co nanocrystals overcoated with a quantum-dot CdSe shell are shown to retain bifunctional magnetic-optical properties, permitting potential applications, for example, optical “reporters” coupled with magnetic “handles” for use in bioassays.<sup>[9]</sup>

In this work, we report on a facile one-pot synthesis of Se/C composite colloids by taking advantage of microwave heating and hydrothermal effects at a relatively low and controllable temperature. Interestingly, the core-shell particles comprise dandelion-like Se nanorod aggregates as the core and amorphous carbon as the encapsulating shell. Such Se/C nanocomposite colloids are expected to be useful in biotechnology applications, as Se is an essential trace element for humans, and carbon black is biocompatible and non toxic. Also, Se is an important elemental semiconductor, because of its many intriguing photoelectrical properties as well as its applications in semiconductor rectifiers, solar cells, photographic exposure meters, and xerography.<sup>[10]</sup> Carbon exhibits high-temperature and high-pressure stability and resistance to acids, bases, and solvents.<sup>[11]</sup> Combination of the two nanomaterials of Se and C provides a model structure for further understanding the core-shell heterostructures and their properties. The composite colloids produced are also expected to have potential applications in electronics, photonics, catalysis, and sensors.

Carbon-based materials with micro- and nanoscale hollow interiors exhibit promising properties for diverse applica-

[a] Prof. Dr. J. C. Yu, X. Hu  
Department of Chemistry and Environmental Science Programme  
The Chinese University of Hong Kong  
Shatin, New Territories, Hong Kong (P. R. China)  
Fax: (+852)2603-5057  
E-mail: jimyu@cuhk.edu.hk

[b] Prof. Dr. Q. Li, Dr. Z. Zheng, Y. Xu  
Department of Physics  
The Chinese University of Hong Kong  
Shatin, New Territories, Hong Kong (P. R. China)

tions, such as active-material encapsulation, drug delivery, ionic intercalation, surface functionalization, robust catalysts/carriers, and chemical reactors.<sup>[12]</sup> As reported previously,<sup>[13]</sup> the Se-core composites can be used as precursors to yield hollow capsules by subsequent removal of the sacrificial Se cores; this is because Se exhibits high solubility in various solvents (e.g., CS<sub>2</sub> and N<sub>2</sub>H<sub>4</sub>) and a relatively low melting point (~217 °C).<sup>[10]</sup> To the best of our knowledge, there is no report on the preparation of hollow carbon capsules from Se-core composite precursors. In the present work, we demonstrate that hollow carbon capsules can be formed easily from the core-shell Se/C particles. We believe that this is a much more effective approach as the conventional synthesis of carbon materials often requires very harsh conditions (e.g., high-energy input by electric-arc discharge techniques, catalytic chemical vapor deposition, or catalytic pyrolysis of organic compounds).<sup>[14]</sup>

## Results and Discussion

### Synthesis of core-shell Se/C colloids and hollow C capsules:

Chemical synthesis by microwave heating is often very efficient, since it offers rapid volumetric heating, high reaction rates and selectivities, high yields of products, and is energy saving.<sup>[15]</sup> Based on the procedures reported previously,<sup>[16]</sup> a newly developed microwave-assisted hydrothermal reduction/carbonization (MAHRC) approach<sup>[15c]</sup> was used to prepare core-shell Se/C colloids. After removing the Se core by thermal treatment,<sup>[13]</sup> hollow C capsules were formed. Figure 1 shows a schematic outline of our approach. Since the starting materials are natural and cheap, this route is ideal for large-scale industrial production and may also be extended to create other core-shell structures and hollow interiors.

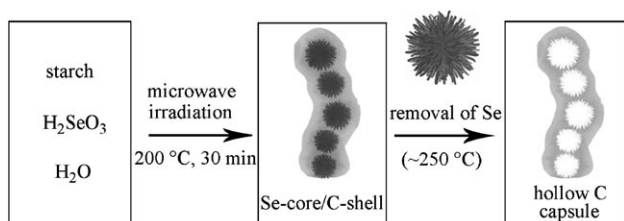


Figure 1. Schematic representation of Se/C composite and hollow C capsule formation.

**Core-shell Se/C structures:** Figure 2 displays a typical XRD pattern of the as-synthesized Se/C composite. All the reflections can be readily indexed to trigonal Se (*t*-Se) with calculated lattice constants of  $a = 4.36 \text{ \AA}$  and  $c = 4.95 \text{ \AA}$ , which are in good agreement with the literature values (JCPDS No. 6–362). The crystal dimension estimated from the Scherrer formula based on the (100) reflections matches well with that observed by TEM. Energy-dispersive X-ray (EDX) spectrometry was also used to determine the local chemical

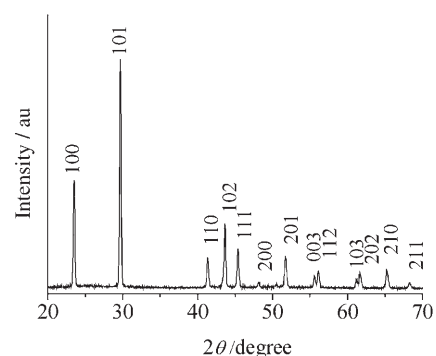


Figure 2. A typical XRD pattern of the as-synthesized Se/C composite.

composition of the product. A typical EDX spectrum is shown in Figure 3. The two major peaks correspond to C and Se and one weak peak at ~0.8 eV indicates the presence of O. These data indicate that the starch reduced H<sub>2</sub>SeO<sub>3</sub> to form *t*-Se, and was also carbonized to amorphous carbon (*a*-C).

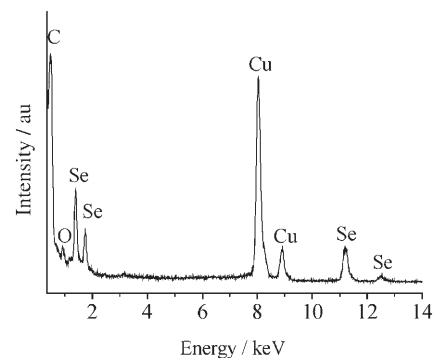


Figure 3. EDX spectrum of the as-synthesized Se/C.

Figure 4a shows a typical low-magnification bright-field TEM image of the same product shown in Figure 2. The dark/light contrast is clearly observed. The different contrast suggests a different phase composition, indicating the core-shell structure. The dark contrast indicates that Se has a larger mass thickness in the core region. Outside of the core region, the light contrast suggests that C is in the shell layer. The selected area electron diffraction (SAED) pattern from a Se/C composite sphere shows diffraction rings of *t*-Se (inset of Figure 4a). Inelastic scattering from the amorphous carbon in the external layer interfered with the as-obtained electron diffraction (ED) pattern, resulting in a highly diffrused background. Figure 4b and 4c show high-magnification bright-field TEM images of the product. These results indicate that the dandelion-like Se architectures are completely encapsulated in the intestine-like structure of C. Higher-magnification TEM observations clearly reveal that the entire structure of the Se “dandelions” is built from a spherical assembly of centrally oriented Se nanorods with diameters mostly ranging from 5 to 15 nm, and with lengths up to

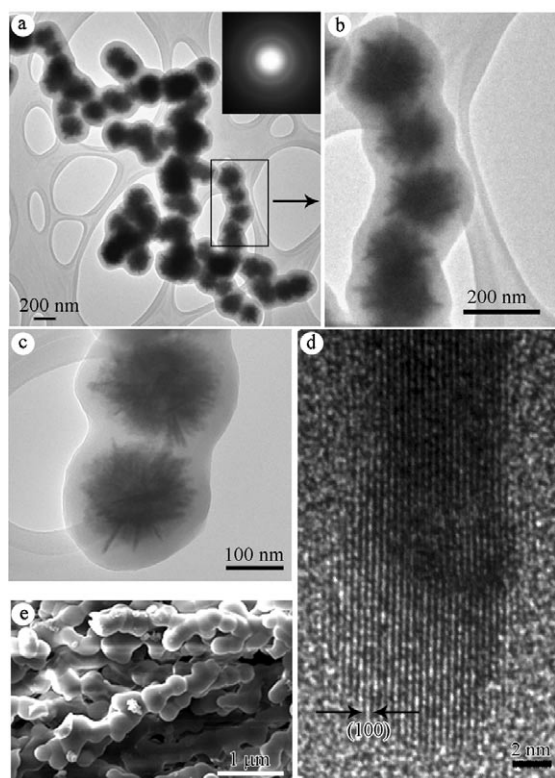


Figure 4. a) Low-magnification bright-field TEM image of Se nanorod assemblies encapsulated in C; b) and c) high-magnification TEM images of the core-shell structured Se/C composite; d) HRTEM image of an individual Se nanorod embedded in the carbon matrix (labeled by an arrow) as shown in (c); e) SEM image of the as-prepared composite.

100 nm. The intestine-like or spherical shells of C have an average wall thickness of  $\sim 40$  nm. Figure 4d shows a high-resolution TEM (HRTEM) image of an individual Se nanorod. This HRTEM image provides more detailed structural information on the nanorods, and shows that the nanorod has a single-crystal structure. Along the radial direction of the nanorod, the periodic fringe spacing of  $3.7 \text{ \AA}$  corresponds to the interplanar spacing between the (100) planes of the *t*-Se. In addition, not graphitic but disordered carbon layers are observed outside of the single-crystalline Se. Figure 4e shows an SEM image of the Se/C capsules. The average outer diameter of the C intestines along the radial direction is about 200 nm.

The spatial distribution of different compositional elements was determined by electron energy loss (EEL) mappings using the C K-edge (284 eV) and Se L-edge (1436 eV). Figure 5a shows the same bright-field TEM image of the Se/C composite as shown in Figure 4c. The corresponding Se and C elemental mappings (Figure 5b and 5c) reveal that Se and C are located in the core and shell region, respectively. This agrees well with the structural analysis shown in Figure 4.

X-ray photoelectron spectroscopy (XPS) was used to determine the surface electronic states and the composition of the core-shell Se/C structures. The XPS spectra show strong

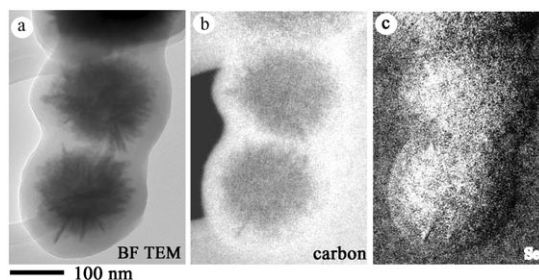


Figure 5. a) Bright-field image of the Se/C composite as shown in Figure 4c; b) and c) electron energy loss (EEL) elemental maps of C and Se taken by using the C K edge and Se L edge, respectively.

peaks for C 1s but the peak at 55.6 eV for Se 3d is barely detectable. This confirms that the Se nanorod assemblies are encapsulated within the carbon shell with a wall thickness larger than 20 nm. Figure 6 shows the C 1s peaks in a high-

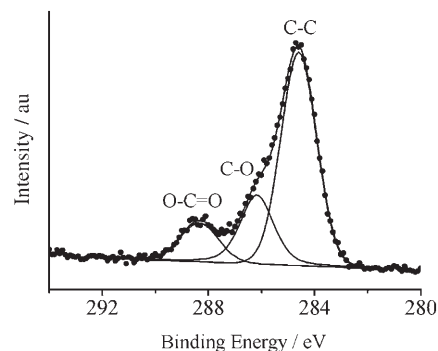


Figure 6. High-resolution XPS spectrum showing the C 1s peaks.

resolution XPS spectrum of the Se/C composite. The broad C 1s peak consists of three peaks at 284.5, 286.0, and 288.4 eV. The peak at 284.5 eV is assigned to the C–C bonds in the disordered carbon frameworks, while those at 286.0 and 288.4 eV suggest the existence of residual groups such as OH and CHO.<sup>[17]</sup> The partially dehydrated residuals in which OH or CHO groups are covalently bonded to the carbon frameworks improve the hydrophilicity and stability of the Se/C particles in aqueous systems, and greatly widen their range of applications in biochemistry, diagnostics, and drug delivery.<sup>[16b]</sup>

Both the diameter of spherical Se nanorod assemblies and thickness of the C shells can be controlled by changing the reaction conditions, such as the reactant concentrations and the reactant ratios (Figure 7). Our experimental results show that a thicker C layer can be deposited on the surfaces of Se nanorod assemblies by using a higher mass ratio of starch/selenious acid. We also investigated the influence of different heating methods on the final products. When a conventional heating method (oil bath) was used, only Se nano- and microspheres were obtained after heating at  $200^\circ\text{C}$  for 30 min. Even if the heating time was increased to 4 h, no trace of carbon-encapsulated Se spheres could be

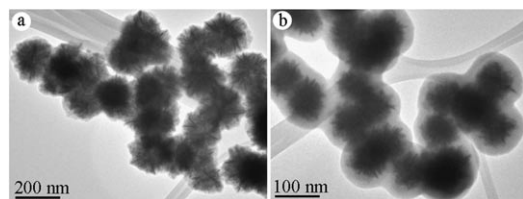


Figure 7. TEM images of the products prepared at 200°C for 30 min by microwave-hydrothermally treating a mixture of: a) Starch (2 g), selenious acid (3 mmol), and DI-water (30 mL); b) starch (3 g), selenious acid (2 mmol), and DI-water (30 mL).

found by TEM. After a conventional hydrothermal reaction at 200°C for 48 h, the carbonization yield was only about 46%. In contrast, the yield of the Se/C hybrids can reach as high as 70% by microwave heating at 200°C for 30 min. The heating time for the fabrication of Se/C hybrids can be shortened by more than one order of magnitude by using microwave heating instead of conventional heating. The higher yield and shorter microwave-heating time leads to enhanced efficiency and significant energy savings.

In our approach, two main reactions are believed to occur simultaneously during the one-pot microwave-induced hydrothermal process. One is the reduction of selenious acid by starch and the other is the carbonization of starch. A formation mechanism is proposed for the growth of the Se/C composites. The 1D Se nanorods probably grow from a precursor particle, as in the case of sonochemical formation of Se nanowires.<sup>[18]</sup> The growth of the core/shell Se/C composites can be roughly divided into two stages. In the first stage, starch-encapsulated spherical amorphous Se (or *t*-Se or both) particles are produced by reducing selenious acid under microwave irradiation. Meanwhile, the shell layer of starch is carbonized, due to localized “hot surfaces” as well as “hot spots” created by the microwave energy.<sup>[15]</sup> Our experimental results show that a thicker carbon layer can be deposited on the surfaces of Se nanorods by using a higher initial concentration of starch. In the second stage, 1D Se nanostructures grow from the surface of the Se cores, for which the newly-formed *t*-Se crystallites may serve as seeds. It is well known that 1D Se nanostructures can be preferentially generated, because the trigonal phase contains infinite spiral chains of Se atoms along the *c* axis and has a lower free energy relative to *a*-Se.<sup>[18]</sup> The growth process continues until all the spherical Se particles in the core region are depleted, leaving behind a pure assembly of *t*-Se nanorods encapsulated in an external layer of amorphous carbon. Furthermore, the thermal and nonthermal effects induced by microwave irradiation probably contribute to the final morphologies and structures of products. These local thermal effects may simultaneously accelerate the reduction and carbonization reactions leading to the formation of clusters of single-crystalline Se nanorods surrounded by amorphous carbon. Of course, a detailed formation mechanism for these novel core-shell Se/C architectures formed under microwave heating needs to be investigated further.

**Hollow carbon capsules:** Figure 8a and b show TEM images of the products after removing Se by thermal evaporation in vacuum at ~250°C for 10 min. The TEM dark/light contrast clearly reveals that nanostructured hollow carbon capsules were formed. The corresponding SEM images are shown in Figure 8c and 8d.

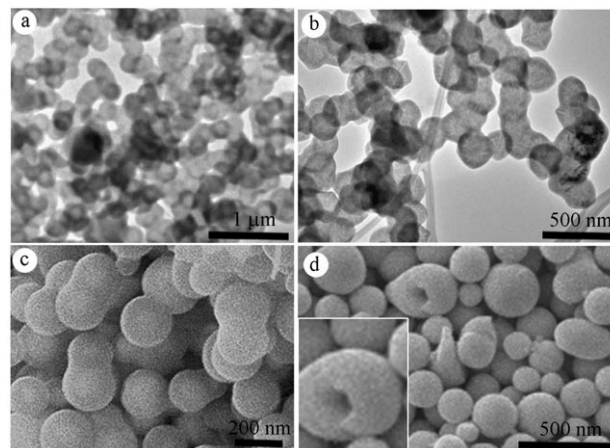


Figure 8. a) and b) TEM images of hollow C capsules after removing *t*-Se cores through evaporation; c) and d) SEM images of hollow C capsules. A higher magnification SEM image for an individual broken C capsule is shown in the inset of (d).

## Conclusion

In summary, core-shell structured nanocomposite particles, that is, *t*-Se nanorod assemblies encapsulated in amorphous carbon have been successfully synthesized through a facile one-step controllable procedure. This work presents a fast, high-yield, and environmental-friendly route for fabrication of Se/C particles that is ideal for large-scale industrial production. Our experiments show that microwave heating plays a crucial role in the formation of the Se/C nanocomposite. By controlling the experimental parameters, the microstructures of the core-shell hybrids can be tailored. The present method will open up possibilities for realizing efficient production of a variety of core-shell nanostructures by preferable “green chemistry” routes. Furthermore, the resultant Se/C composite can be easily transformed into hollow carbon capsules by a simple thermal treatment procedure. The core-shell structured Se/C colloids, as well as the hollow C capsules, inherit functional groups from the starting materials; they also possess hydrophilic surfaces. These properties are potentially useful in biochemistry, diagnostics, and drug delivery applications.

## Experimental Section

**Synthesis:** All chemicals were used as received without further purification. In a typical process, starch (3 g) and H<sub>2</sub>SeO<sub>3</sub> (3 mmol) were dissolved in deionized (DI) water (30 mL). The solution was sealed in a



double-walled digestion vessel. After treating at a controllable temperature of 200 °C for 30 min by using a microwave digestion system (Ethos TC, Milestone), the vessel was then cooled to room temperature. The product was collected, washed with deionized water and alcohol, and dried in vacuum at 40 °C for 4 h. After removing the Se core by thermal evaporation in vacuum at ~250 °C for 10 min, the hollow carbon capsules were obtained.

**Characterization:** The crystallographic phase of the products was determined by powder XRD by using a Bruker D8 Advance diffractometer with high-intensity Cu<sub>Kα1</sub> irradiation ( $\lambda = 1.5406 \text{ \AA}$ ). The general morphology of the products was examined by SEM (LEO, 1045 VP). The size, microstructures, and chemical composition of the products were investigated by TEM by using a Tecnai F20 microscope (FEI, 200 kV) and a CM-120 microscope (Philips, 120 kV) coupled with an EDX spectrometer (Oxford Instrument). EEL elemental mapping was carried out by using a Gatan image filtering (GIF) system coupled to the Tecnai F20 microscope. XPS measurements were performed in a Kratos AXIS-HS spectrometer equipped with a monochromatic Al<sub>Kα</sub> source.

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