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Highly efficient one-step synthesis of carbon encapsulated nanocrystals by the oxidation of metal π -complexes

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Abstract

Various carbon encapsulated nanocrystals, including MnS and MnO, Cr₂O₃, MoO₂, Fe₇S₈ and Fe₃O₄, and ZrO₂, are prepared in one step and *in situ* by a simple and highly efficient synthesis approach. The nanocrystals have an equiaxed morphology and a median size smaller than 30 nm. Tens and hundreds of these nanocrystals are entirely encapsulated by a wormlike amorphous carbon shell. The formation of a core-shell structure depends on the strongly exothermic reaction of metal π -complexes with ammonium persulfate in an autoclave at below 200 °C. During the oxidation process, the generated significant amounts of heat will destroy the molecular structure of the metal π -complex and cleave the ligands into small carbon fragments, which further transform into an amorphous carbon shell. The central metal atoms are oxidized to metal oxide/sulfide nanocrystals. The formation of a core-shell structure is independent of the numbers of ligands and carbon atoms as well as the metal types, implying that any metal π -complex can serve as a precursor and that various carbon encapsulated nanocrystals can be synthesized by this method.

Supplementary material for this article is available [online](#)

Keywords: carbon encapsulated nanocrystals, core-shell, low temperature synthesis, metal π -complex

(Some figures may appear in colour only in the online journal)

1. Introduction

The core-shell structure can generally be defined as comprising an inner core and an external shell with different chemical compositions. The unique structural feature allows the possibility of combining desirable properties of diverse materials and thereby improving physical and chemical properties compared to their single-component counterparts.

Hence, various types of core-shell structures have attracted increasing research interest because of their potentially broad range of applications for drug delivery, bioimaging, sensors and catalysis [1]. Among them, carbon encapsulated nanocrystals are one of the most common classes. This is largely ascribed to the high chemical inertness, ease of surface modification, good conductivity and tensile strength of the carbon shell [2–4].

On the basis of the conventional preparation techniques for carbon nanomaterials, a number of synthetic routes to

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Table 1. Synthesis conditions of carbon encapsulated nanocrystals.

Reactants								
No.	Metal π -complex	mmol	Ammonium persulphate	mmol	Vol. of auto-clave (ml)	Temp. (°C)	Time (min)	Major products
#1	(C ₅ H ₅)Mn(CO) ₃	5	(NH ₄) ₂ S ₂ O ₈	10	50	200	30	MnS and MnO@C
#2	(C ₆ H ₆)Cr(CO) ₃	5		10				Cr ₂ O ₃ @C
#3	(C ₇ H ₈)Mo(CO) ₃	5		10				MoO ₂ @C
#4	(C ₈ H ₈)Fe(CO) ₃	2		8				Fe ₇ S ₈ and Fe ₃ O ₄ @C
#5	(C ₉ H ₇) ₂ ZrCl ₂	2		4				ZrO ₂ @C

these kinds of nanocomposites have been developed over decades. The arc discharge and laser ablation techniques can produce very high temperatures of about 3000 K to evaporate the metal/carbon composite and then effectively form carbon-encapsulated metal or metal carbide nanocrystals [5, 6]. Thermal decomposition of carbon-containing precursors through chemical vapor deposition, pyrolysis/carbonization process and flame spray synthesis is commonly employed to achieve a carbon layer on a variety of preformed cores and cores formed *in situ* [7–9]. These processes all involve high-temperature treatment, a vacuum/inert atmosphere, and specific facilities. A hydrothermal carbonization process for a core-shell structure can be carried out in an autoclave at a low temperature of 140–200 °C, using different types of saccharides as carbon precursor [10]. For example, Au-cored carbon spheres could be hydrothermally prepared at 180 °C for 4–20 h from an aqueous glucose solution containing HAuCl₄ [11]. Additionally, elliptical Fe₃O₄/C core-shell nanorings were prepared by a multi-step hydrothermal route at 180 °C for 9–18 h using iron glycolate nanosheets as templates [12]. LiFePO₄/C submicron rods were also synthesized via a hydrothermal process at 200 °C for 10.5 h following heat treatment in an N₂ atmosphere at 500 °C for 2 h [13]. Although the synthesis temperature is low, a hydrothermal treatment time as long as tens of hours and multiple steps are usually required to form the carbon shell, which is time-consuming and inefficient. It is therefore worth developing an alternative method featuring simple experimental procedures and providing a fast and reliable protocol for the synthesis of carbon encapsulated nanocrystals.

Our previous study proposed a general *in situ* synthesis approach for different carbon encapsulated oxide/sulfide nanocrystals with a core-shell structure by a solid-state explosive reaction between metallocene complexes and high-oxidative ammonium salts in an autoclave at 200 °C [14, 15]. Compared to the conventional preparation techniques, the oxidizing agent is indispensable for the formation of carbon [16], implying that the effect of the presence of oxygen in the reaction apparatus on the product can be negligible, and that only a sealed reactor is sufficient for the synthesis. As no other specific apparatus or operating steps are needed, this method shows distinct advantages such as its simple procedure, low temperature, and high efficiency and yield, which is attractive for lithium-ion batteries [17–19]. Until now, most

metallocene complexes, typically consisting of cyclopentadienyl ligand with the formula C₅H₅ bound to central metal atoms, have been proved to be promising precursors for the preparation of carbon encapsulated nanocrystals by this method. Although the cyclopentadienyl ligand is among the most frequently utilized π ligand in organometallic chemistry, other cyclic ligands such as benzene (C₆H₆), cycloheptatriene (C₇H₈), cyclooctatetraene (C₈H₈) and indenyl (C₉H₇) can serve as metal-binding platforms as well, to form metal π -complexes. These complexes have similar electronic structures and properties to metallocenes, which are conceived to undergo the same oxidation process to produce carbon encapsulated nanocrystals. Consequently, in this work, several metal π -complexes including cyclopentadienyl manganese tricarbonyl ((C₅H₅)Mn(CO)₃), benzene chromium tricarbonyl ((C₆H₆)Cr(CO)₃), cycloheptatriene molybdenum tricarbonyl ((C₇H₈)Mo(CO)₃), cyclooctatetraene iron tricarbonyl ((C₈H₈)Fe(CO)₃) and bis(indenyl)zirconium dichloride ((C₉H₇)₂ZrCl₂) are used to react with ammonium persulfate ((NH₄)₂S₂O₈), and various carbon encapsulated nanocrystals with core-shell structures are successfully fabricated (denoted as ‘formula of inner core’@C, such as MnS and MnO@C, Cr₂O₃@C, etc).

2. Experimental details

2.1. Materials and preparation

All the chemicals, of analytically pure grade, were received from Amethyst Chemicals (J&K Scientific Ltd, China). Several carbon encapsulated nanocrystals were prepared by the oxidation of metal π -complexes in an autoclave, and the synthesis conditions are presented in table 1. Typically, the metal π -complex and (NH₄)₂S₂O₈ were roughly milled in a mortar and subsequently heated at 200 °C for 30 min. After cooling to room temperature, the as-prepared black powder was washed with deionized water and carbon encapsulated nanocrystals were eventually obtained after drying overnight at 120 °C. It is worth noting that the simple and highly efficient synthesis process performed in a sealed reactor is based on the rapid reaction of metal π -complexes with (NH₄)₂S₂O₈ without any solvent, which is completely different than the hydrothermal method depending on high solvent vapour pressure and long reaction times. The purpose of the use of

Figure 1. (a) XRD patterns of the powder in sample #1 in different positions in the autoclave: (I) top; (II) bottom; (III) washed bottom. (b), (c) SEM images of the top powder at different magnifications. (d)–(f) TEM and HRTEM images of the top powder.

the autoclave was to prevent the escape of vaporized metal π -complexes before the reaction temperature and the gaseous intermediate products.

2.2. Characterization

X-ray diffraction (XRD) was performed on a PANalytical X'Pert PRO diffractometer with $\text{Cu K}\alpha$ radiation for phase identification. A Raman spectrum was recorded by a Bruker Senterra micro Raman spectrometer with an excitation wavelength of 633 nm at 2 mW. The morphology and microstructure of the samples were analyzed by scanning electron microscopy (SEM, JEOL JSM 7500F) and transmission electron microscopy (TEM, JEOL JEM 2010) equipped with an x-ray energy-dispersive spectroscopy system (EDS, EDAX) for composition analysis. Differential scanning calorimetry (DSC) was carried out on a Netzsch DSC 204F1 at a heating rate of $10^\circ\text{C min}^{-1}$ using a sealed aluminum pan.

3. Results and discussion

The macroscopic morphology of as-prepared sample #1 shows an obvious stratification phenomenon. Fluffy powder and soft powder agglomerates are yielded in the top and bottom of the autoclave, respectively. The XRD patterns in figure 1(a) show that the MnS and MnO are the major phases in the top powder, while the $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{Mn}_2(\text{SO}_4)_3$ reside in the bottom powder. When these soluble ammonium salts are eliminated by the washing process, the MnS and MnO diffraction peaks become visible, which is identical with the top powder. The carbon diffraction

peaks are not evident because of its poor crystallinity at low synthesis temperature. The core-shell structure can be directly observed by the SEM images of the top powder, consisting of interconnected nanoparticles with obvious white cores inside (figures 1(b) and (c)). The TEM and high-resolution TEM (HRTEM) images in figures 1(d)–(f) indicate that the turbostratic carbon shell encapsulated tens of MnS and MnO nanocrystals as a whole. The enlarged HRTEM images with clear lattice fringes are shown in the supplementary data (figure S1). These small nanocrystals have a diameter range of 2–32 nm according to the TEM measurement and their median size is 13.34 nm (figure S2). The bottom powder mainly contains core-shell structure despite the emergence of some irregularly-shaped carbon particles (figure S3). In addition, some $(\text{NH}_4)_2\text{Mn}_2(\text{SO}_4)_3$ nanocrystals can also be encapsulated by the carbon shell (figure S4).

In sample #2, only the fluffy top powder is obtained and its XRD pattern reveals that Cr_2O_3 is formed during the oxidation synthesis (figure 2(a)). Under SEM examination, the homogeneous nanoparticles exhibit an equiaxed morphology and aggregate together. However, the semitransparent carbon layer cannot be seen on the surface of these nanoparticles (figures 2(b) and (c)). Thus, Raman spectroscopy is carried out and two typical D and G bands of amorphous carbon are represented, confirming the existence of carbon shell in the specimen (figure S5). The TEM image further displays that the Cr_2O_3 nanocrystals are encapsulated by a very thin carbon shell (figure 2(d)). Single-crystal lattices of one typical Cr_2O_3 nanocrystal can be identified in the enlarged HRTEM image (inset of figure 2(d); the enlarged image is shown in figure S6), and the thickness of the carbon shell is only about 0.5 nm. The diameter of Cr_2O_3 nanocrystals is less than 45 nm and the median size is calculated to

Figure 2. Characterization of $\text{Cr}_2\text{O}_3@\text{C}$: (a) XRD pattern; (b), (c) SEM images; (d) TEM image. Inset is the HRTEM image of the lattice fringes of an individual Cr_2O_3 nanocrystal encapsulated by a thin carbon layer.

Figure 3. Characterization of $\text{MoO}_2@\text{C}$: (a) XRD pattern; (b), (c) SEM images; (d)–(f) TEM and HRTEM images.

be 15.51 nm, according to the size distribution histogram (figure S7).

Similar to sample #2, only the fluffy powder can be found in the top of the autoclave in sample #3 and the XRD pattern shows that the as-prepared powder is predominantly

composed of MoO_2 (figure 3(a)). SEM images indicate that the powder has a homogeneous morphology of nanoparticles, consisting of white cores under the complete coverage of a carbon layer (figures 3(b) and (c)). In fact, it can be seen under TEM observation that these cores are the agglomerate

Figure 4. (a) XRD patterns of the powder in sample #4 in different positions in the autoclave: (I) top; (II) bottom; (III) washed bottom. (b), (c) SEM images of the top powder at different magnifications. (d), (e) TEM and HRTEM images of the top powder. (f) TEM image of the washed bottom powder.

of quantities of ultrafine MoO_2 nanocrystals and the thickness of the amorphous carbon shell is about 2 ~ 3 nm (figures 3(d) and (e); an enlarged figure 3(e) is shown in figure S8). These MoO_2 nanocrystals have a typical diameter of less than 20 nm and a median size of 6.41 nm (figure S9). Moreover, it is worth mentioning that the MoO_2 nanocrystals coexist with a small amount of MoS_2 folded into a few layers (figure 3(f)). The formation mechanism has been discussed elsewhere [18].

For sample #4, powders with different macroscopic morphologies are separately collected from the different positions of the autoclave. As shown in the XRD patterns in figure 4(a), the top fluffy powder contains a mixture of phases of Fe_7S_8 and Fe_3O_4 , whereas the bottom soft agglomerates are abundant in $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$. This soluble ammonium salt will be removed during the washing process, leaving behind the phases of Fe_7S_8 and Fe_3O_4 , which is the same as the top powder. The top powder also shows a uniform core-shell structure and both Fe_7S_8 and Fe_3O_4 equiaxed nanocrystals are encapsulated by a thin amorphous carbon shell of about 3–5 nm, demonstrated by the SEM and TEM images (figures 4(b)–(e); an enlarged figure 4(e) is shown in figure S10). Most of these nanocrystals have a narrow diameter distribution of 5–25 nm and a median size of 12.6 nm (figure S11). The SEM images of the washed bottom powder also show an evident core-shell structure. However, there is a large amount of hollows in the powder, which should be ascribed to the dissolution of interior $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$ nanocrystals (figures S12 and 4(f)).

According to the XRD patterns of sample #5 (figure 5(a)), besides the tetragonal phase of ZrO_2 (t- ZrO_2), NH_4Cl is formed in the top powder because of the combination of the chlorine in the precursor with ammonium in

$(\text{NH}_4)_2\text{S}_2\text{O}_8$. This byproduct can also be found in the bottom powder, together with some unknown product which may be supposed to be ammonium zirconium sulfate due to its good solubility in water, and the washed bottom powder is mainly composed of t- ZrO_2 . SEM images of the top powder show that the nanoparticles are synthesized and that some of them have white cores, corresponding to the core-shell structure (figures 5(b) and (c)). TEM images clearly show the core-shell structure of carbon encapsulated equiaxed ZrO_2 nanocrystals about 20–35 nm in diameter and an amorphous carbon shell about 20–30 nm in thickness (figures 5(d) and (e); an enlarged figure 5(e) is shown in figure S13). There are some smaller t- ZrO_2 nanocrystals ranging from 5 to 15 nm embedded inside the amorphous wormlike carbon (figure S14). The size distribution histogram of the ZrO_2 nanocrystals is shown in figure S15 and the median size is 22.57 nm. It should be noted that a certain amount of necklace-like solid carbon is simultaneously formed during the synthesis and can be regarded as amorphous owing to the disordered lattice fringes revealed in the magnified image (figure 5(f)). The formation of a thick carbon shell and solid carbon should be attributed to the two C_9H_7 ligands in the precursor, in which the carbon content is relatively high with respect to Zr. The morphology of the washed bottom powder in sample #5 is not uniform, as irregularly-shaped carbonaceous materials can be found together with the core-shell structure (figure S16).

DSC curves of these samples using sealed pans were recorded in order to investigate the reaction behavior of the starting materials, as shown in figure 6. The metal π -complexes can be very stable at low temperature, even with the presence of the strong oxidizing agent, and their following oxidation takes place at 100–200 °C on the basis of the very

Figure 5. (a) XRD patterns of the powder in sample #5 in different positions in the autoclave: (I) top; (II) bottom; (III) washed bottom. (b), (c) SEM images of the top powder at different magnifications. (d)–(f) TEM and HRTEM images of the top powder. Inset is the HRTEM image of the amorphous solid carbon.

Figure 6. DSC curves of different samples in sealed pans.

strong exothermic peak for each sample. The severe oxidation reaction should be caused by the oxidation of cyclic ligands by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and releases large amounts of heat as the hydrogen atoms are transformed into H_2O . As a result, a schematic of the oxidation synthesis process is proposed in figure 7. The mixture of the metal π -complex and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ are unreactive at low temperature and are firstly placed in the bottom of the autoclave (figure 7(a)). When the temperature increases to the reaction temperature, the oxidation reaction takes place rapidly and produces blast water vapour, which can push some reactants to the top of the autoclave (figure 7(b)). Additionally, a large amount of heat is liberated during the reaction, significantly raising the inner temperature

Figure 7. The schematic of the oxidation synthesis process.

of the sealed reactor, which is much higher than the reaction temperature [15]. The high temperature will inevitably result in the cleavage of metal π -complex, and then the generation of different kinds of clusters and radicals, and eventually the formation of a carbon shell and the metal oxide/sulfide nanocrystals. For samples #1 and #4, both metal oxide and sulfide nanocrystals are found in the products, demonstrating that O and S radicals are simultaneously generated during the drastic exothermic reaction. Therefore, the weight percentage content of metal oxide and sulfide nanocrystals should depend on the ratio of O to S radicals in the autoclave. Otherwise, some oxophilic metal atoms will prefer to bond with oxygen atoms to form stable metal oxides (samples #2, #3 and #5). The carbon clusters from the cleaved cyclic ligands surround these nanocrystals to form a core-shell structure. However, carbon-carbon bonds of benzene are quite stable and consequently unreactive under many reaction conditions [20]. The

strong oxidizing agent and high temperature must be required for the cleavage of benzene rings. The oxidation temperature of sample #2 is as low as about 153 °C, which is insufficient for the complete C–C bond-tearing of the stable benzene ligand into small carbon clusters, leading to the formation of a very thin carbon layer on the Cr₂O₃ nanocrystals. For sample #5, the reaction temperature is only about 139 °C, suggesting that the C₉H₇ ligand is unstable and susceptible to oxidation at low temperature. And the C₉H₇ molecule can be easily cleaved and carbonized, resulting in the formation of a thick carbon shell. After cooling, a fluffy powder consisting of homogeneous nanoparticles with a core–shell structure is collected, which is formed by the gaseous clusters and radicals in the top of the autoclave (figure 7(c)). The quantity of the generated gas in the reaction is not high and mainly limited by the number of H atoms in the ligands. Relative to the weight of the metal π -complex, the generated gas is 22.05–32.11 wt.% for these samples on the assumption that only H₂O vapor is formed in the process. This means most of the solid products are deposited in the bottom of the autoclave, corresponding to the soft agglomerates. It has been proved by the XRD patterns that carbon encapsulated nanocrystals and (NH₄)₃H(SO₄)₂ are the major products in the bottom powder. The (NH₄)₃H(SO₄)₂ may also serve as a reactant for the production of ammonium metal sulfides at the reaction temperature, such as (NH₄)₂Mn₂(SO₄)₃ and (NH₄)₃Fe(SO₄)₃. On the other hand, the byproduct of NH₄Cl in sample #5 is reactive to the metal π -complex in the oxidation atmosphere, leading to the formation of amorphous carbon particles instead of a core–shell structure, sequentially decreasing the uniformity of the bottom powder [15, 16]. For samples #2 and #3, it is suggested that the oxidation reactions are drastic and that most of the metal π -complexes are pushed up to the top of the autoclave, and then only the top fluffy powder is obtained.

In summary, it has been proved that carbon encapsulated nanocrystals with a core–shell structure can be commonly synthesized by the strongly exothermic reaction of the metal π -complex with a strong oxidizing agent, which is independent of the molecular structure of the ligand. More metal π -complexes with varying numbers of ligands and carbon atoms can be chosen for controlling the carbon content in the core–shell structure and the shell thickness for different applications. It is also a meaningful starting point for the practical application of the method because we can further select cheap organics containing metal atoms and more general organic ligands as precursors instead of the high-price metallocene complexes or metal π -complexes.

4. Conclusions

Several carbon encapsulated nanocrystals with core–shell structure, including MnS and MnO@C, Cr₂O₃@C, MoO₂@C, Fe₇S₈ and Fe₃O₄@C, ZrO₂@C, are synthesized by a strong exothermic reaction of metal π -complexes with (NH₄)₂S₂O₈ in an autoclave at below 200 °C. The molecular structure of the metal π -complex can be destroyed by the

generated large amounts of heat during the oxidation of hydrogen atoms in the ligands. The ligands will be cleaved into small carbon fragments, which further transform into an amorphous carbon shell. The central metal atoms are oxidized to metal oxide/sulfide nanocrystals with an equiaxed morphology and small median size. The formation of the core–shell structure is independent of the numbers of ligands and carbon atoms as well as the metal types, implying that any metal π -complex can serve as a precursor. The synthesis method is common for the preparation of various carbon encapsulated metal oxide/sulfide nanocrystals and shows clear advantages with its simple process parameters, low energy consumption, and high efficiency and yield, which may be attractive for practical applications.

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