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Formation of Hollow Submicrometer Spheres of Nickel Selenides

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Hollow submicrometer spheres of nickel selenides have been successfully prepared via sodium dodecyl sulfate (SDS)-assisted hydrothermal reduction route in which aqueous hydrazine was used as a reducing agent and the surfactant SDS was used as a structure-directing agent.

Over the past decades, hollow spheres with nanometer-to-micrometer dimensions have been the focus of considerable interest because of their unique properties and their wide variety of potential applications in various fields, such as controlled release capsules, artificial cells, chemical sensors, photonic crystals, and biotechnology.[1–4] Considerable effort has been devoted to the design and controlled fabrication of hollow spheres, such as silica,[5] polymers,[6,7] metals,[8] and inorganic materials.[9,10] What is worth noting is that most of the above-mentioned hollow spheres have been based on template-based synthesis. Here, we report a facile strategy for the formation of hollow submicrometer spheres of nickel selenides, which gives a simple and general route to the fabrication of hollow spheres.

Nickel selenides have attracted enormous attention owing to their interesting electrical and magnetic properties and promising applications in, e.g., conductivity, and catalytic fields, etc. Various procedures including solid-state reactions,[11] molecular precursor,[12] elemental reactions,[13] mechanical alloying,[14] and solvothermal methods[15] have been employed for the synthesis of nickel selenides. The properties of nickel selenides sensitively depend on their compositions and morphologies. Thus it is significant challenges to fabricate nickel selenides with different compositions and novel morphologies. Their hollow spheres may provide some immediate advantages over the solid counterparts because of the relatively low densities and large surface areas for their applications. In particular, the catalytic activity is greatly enhanced with increasing the surface area. In this communication, we demonstrate that hollow submicrometer spheres of nickel selenides $\mathrm{Ni_{0.85}Se}$ and $\mathrm{NiSe_2}$ can be selectively prepared in one step via a facile sodium dodecyl sulfate (SDS)-assisted hydrothermal reduction route under mild conditions, and the composition of nickel selenides can be easily controlled by adjusting the molar ratios of the reactants. The employed chemical reaction for synthesis of the hollow submicrometer spheres can be expressed by the following equations:

$$2\mathrm{NiCl_2} + \mathrm{N_2H_4} + 4\mathrm{OH^-} \rightarrow 2\mathrm{Ni}\downarrow + \mathrm{N_2}\uparrow + 4\mathrm{H_2O} + 4\mathrm{Cl^-} \quad (1)$$

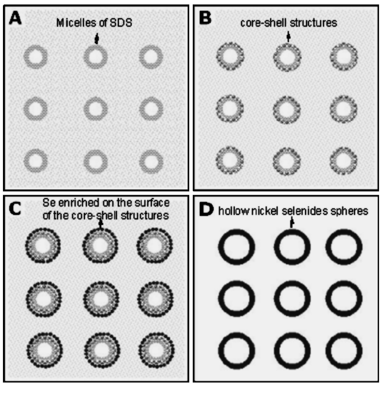
$$x\mathrm{Ni} + y\mathrm{Se} \xrightarrow{\mathrm{N_2H_4}} \mathrm{Ni}_x\mathrm{Se}_y \ (x = 0.85, y = 1 \text{ or } x = 1, y = 2) \quad (2)$$

Soluble nickel chloride firstly reacts with hydrazine to form elemental nickel. Secondly, elemental nickel reacts with Se to form nickel selenides with different compositions according to the molar ratios of reactants.

Our strategies to fabricate the submicrometer spheres are summarized in Scheme 1. Firstly, 0.1 mmol each of sodium dodecyl sulfate was dispersed in deionized water in two Teflon-lined stainless steel autoclaves of 50-mL capacity to form spherical micelles under vigorous stirring. Then, 0.1 mmol of hydrated nickel chloride was added to achive surfactant-stabilized core-shell structures by the electrostatic interactions, and subsequently Se (0.12 or 0.2 mmol) was gradually introduced and enriched on the surface of the core-shell structures. Next, the autoclave was filled with hydrazine hydrate (5 mL, 50 wt % content as reducing agent) up to 75% of the total volume, after 10 min stirring, sealed and maintained at 120 °C for 12 h without shaking or stirring. During the hydrothermal process, elemental nickel was produced and reacted with Se to form nickel selenides and evolved subsequently into hollow submicrometer spheres.

X-ray diffraction (XRD) has been used to characterize the crystal structure of the as-obtained nickel selenides. Figure 1A shows a typical XRD pattern of $\mathrm{Ni_{0.85}Se}$ hollow spheres, and all the peaks could be readily identified as the pure hexagonal phase [space group: $P6_3/mmc$ (194)] with cell constants $a = 3.624$ Å and $c = 5.288$ Å (JCPDS 18-0888). XRD pattern of $\mathrm{NiSe_2}$ hollow spheres is displayed in Figure 1B, and all of the reflection could be indexed to a cubic phase [space group: Pa_3/mmc (205)] with cell constants $a = 5.991$ Å (JCPDS 41-1495). Figure 1 indicates that the two nickel selenides have been successfully synthesized via adjusting the molar ratios of reactants.

The size and morphology of the hollow submicrometer spheres were further examined by transmission electron microscopy (TEM). Figure 2A shows the typical TEM photograph of



Scheme 1. Schematic illustration of the experimental procedure that generates hollow submicrometer spheres of nickel selenides. (A) micelles of SDS; (B) surfactant-stabilized core-shell structures; (C) Se enriched on the surface of the core-shell structures; (D) hollow spheres.

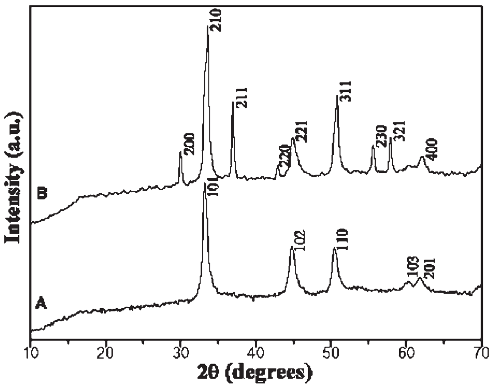


Figure 1. X-ray powder diffraction patterns of nickel selenides as-obtained at 120 °C for 12 h: (A) $Ni_{0.85}Se$, (B) $NiSe_2$.

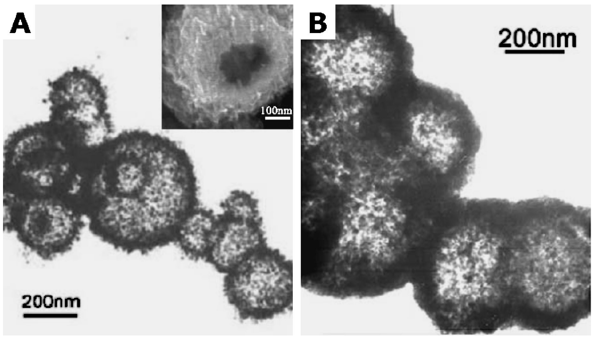


Figure 2. Transmission electron micrograph images of the hollow submicrometer spheres: (A) $Ni_{0.85}Se$, (B) $NiSe_2$. The inset of (A) is scanning electron microscopic image of a single $Ni_{0.85}Se$ hollow sphere.

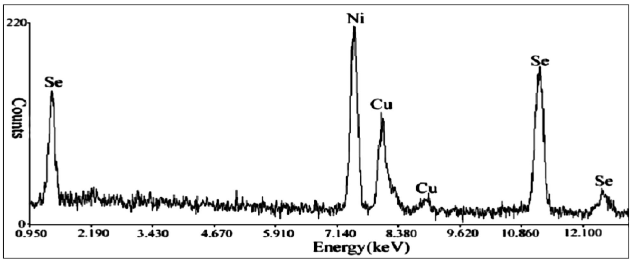


Figure 3. EDXA spectrum of as-prepared $Ni_{0.85}Se$ hollow spheres.

$Ni_{0.85}Se$ hollow submicrometer spheres obtained at 120 °C for 12 h using hydrazine hydrate as a reducing agent and SDS as a structure-directing agent. The scanning electron microscopic (SEM) images (the inset of Figure 2A) distinctly showed $Ni_{0.85}Se$ submicrometer spheres with hollow interiors. The size of $Ni_{0.85}Se$ hollow submicrometer spheres is about 100–300 nm. The composition of the $Ni_{0.85}Se$ hollow submicrometer spheres was performed by energy-dispersive X-ray analysis (EDXA) and revealed that these hollow spheres contained only Ni and Se. Figure 3 shows a typical EDXA spectrum for the $Ni_{0.85}Se$ hollow submicrometer spheres, whose peaks are assigned to Ni and Se (the Cu peaks arise from the copper grid). Relative quantitive analysis shows that the atomic ratio of Ni to Se is about 0.85. It is very interesting that $NiSe_2$ hollow submicrometer spheres were also obtained at 120 °C for 12 h using hydrazine hydrate as a reducing agent and SDS as a structure-directing agent by adjusting the molar ratios of reactants, as indicated in Figure 2B. The transmission electron microscopy photograph (Figure 2B) showed the $NiSe_2$ hollow submicrometer spheres with average diameters about 250 nm.

In summary, we have found a simple route to prepare hollow submicrometer spheres of nickel selenides, $Ni_{0.85}Se$ and $NiSe_2$, by a facile surfactant sodium dodecyl sulfate-assisted hydrothermal treatment, and the composition of nickel selenides could be easily controlled by adjusting the molar ratios of reactants. The synthetic strategy presented here can provide an effective and general route to the formation of other hollow spheres. Owing to the excellent physical properties of the nickel selenides, it is expected that their hollow submicrometer spheres exhibit some important applications in, e.g., thermoelectric cooling, solar cell, conductivity, and catalytic fields, etc.

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