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Communication

Formation of Hollow Ni$_2$P Nanoparticles Based on the Nanoscale Kirkendall Effect

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Colloidal hollow nanoparticles (NPs) of Ni$_2$P have been prepared by a one-pot reaction from a mixture of nickel acetate, oleylamine, trioctylphosphine (TOP), and 1-octadecene. The mechanism to the hollow structure is related to the nanoscale Kirkendall effect. The process contains two important steps. First, oleylamine-stabilized Ni NPs were formed, which can protect them from TOP etching and slow down the inward diffusion of P atoms. Second, the solid-state reaction between the Ni NPs occurred when the TOP concentration and the reaction temperature were correctly adjusted.

The synthesis of nanostructures with hollow interiors via the assistance of chemical templates has been a very attractive research topic for diverse applications such as encapsulation, ion exchange, drug delivery, and catalyst.[1] The chemical templates, usually stabilized nanoparticles (NPs) or nanowires, participate in the reaction of forming desired materials via a deliberate mechanism such as galvanic replacement[2] and diffusion[3,4] and will not be a removed part for the final structure. In the diffusion methods, the vacancy-hopping model developed by Kirkendall many years ago for the explanation of the observed difference in diffusivities of the composition atoms of a brass−copper couple can be used in the nanoscale for the formation of hollow NPs. While these above methods are generic in principle, apparently, there is still a lack of detailed knowledge for the fabrication of template-free hollow nanostructures with respect to various compositions.

Transition-metal phosphides are generally difficult to prepare in a colloidal form. They are usually prepared via the reduction of phosphates or metathesis at high temperatures[5] or via solvothermal reactions.[6] Recently, organometallic compounds with a metal−P cluster[7] or metal sources (including metal salts, metal alkyl, and metal carbonyl compounds) with organometallic P sources[8,9] have been used as precursors for the solution-phase synthesis of nanostructured metal phosphides. These methods are based on a thermolysis process and generally produce a solid product. To apply the diffusion strategy to the preparation of hollow metal phosphide NPs in a colloidal form, an effective P source remains unknown, while the high-temperature solid-state reactions between metals and phosphines (or elemental

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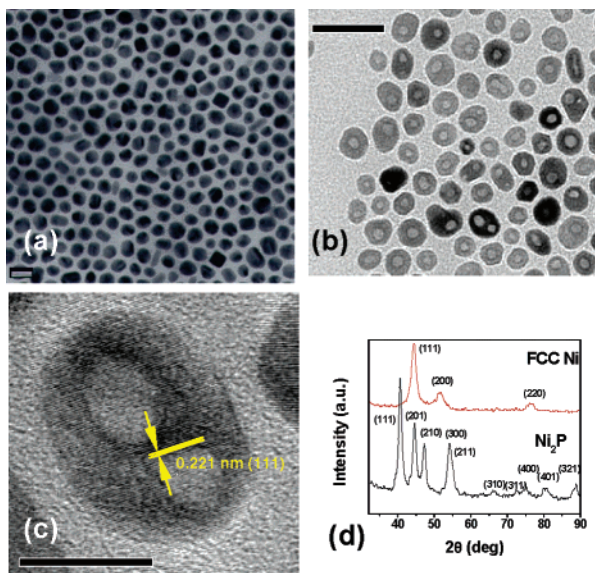

Figure 1. (a) TEM micrograph of the chemical templates, FCC Ni NPs (12.1 ± 3.2 nm). (b) TEM micrograph of the hollow Ni_2P NPs (13.4 ± 3.3 nm) made from phosphidation of the Ni NPs with TOP. (c) HRTEM of a single hollow Ni_2P NP. (d) XRD pattern of the Ni NP templates and the hollow product of Ni_2P NPs. Bar: (a) 20 nm; (b) 50 nm; (c) 10 nm.

P) are well-known.[10] Here we demonstrate how the nanoscale Kirkendall effect can be exploited to prepare hollow Ni_2P NPs using trioctylphosphine (TOP) as a P source in a solution phase at moderate temperatures. Ni_2P has been reported as an important hydrotreating catalyst.[11] Developing an easy synthesis of this material in a hollow form may be beneficial to the manufacture of high-efficiency catalysts.

In preliminary experiments, we found that TOP is very reactive with nanosized Ni metal NPs and the protecting surfactants play an important role in modifying the types of reactions. Well-dispersed FCC Ni NPs with an average size of approximately 12 nm were prepared first (Figure 1a). They were collected and used as chemical templates for the initial experiments of the formation of hollow NPs. TOP is a strong ligand toward metals. It was found that the Ni NPs were seriously etched, and both solid and hollow Ni_2P NPs were obtained as the product when concentrated TOP was used (Figure 1S in the Supporting Information). This implies that TOP is capable of dissolving some surface atoms of Ni NPs and forming Ni−TOP complexes. The dense Ni_2P NPs were probably formed from decomposition of these complexes. When we diluted TOP with solvent such as 1-octadecene and used oleylamine as a protecting surfactant for the same reaction, only hollow NPs were found (Figure 1b). High-resolution transmission electron microscopy (HRTEM) images and X-ray diffraction (XRD) of the hollow product are shown in parts c and d of Figure 1, respectively. All of the prominent peaks in XRD of the hollow sample can be matched to the hexagonal Ni_2P (JCPDS 3-953). Magnetic measurement indicates that there is no ferromagnetic Ni left. The small shoulder peaks around the (201) and (300) planes
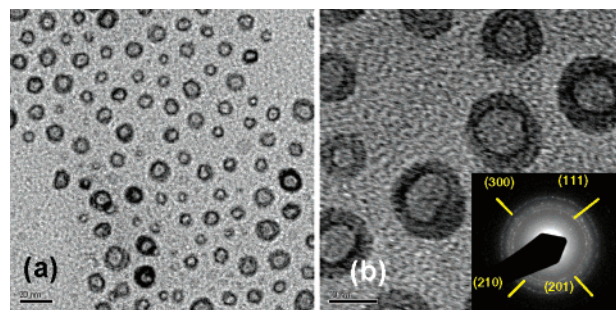
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Figure 2. (a) TEM micrographs of the hollow Ni_2P product from a one-pot sythesis (bar: 20 nm). (b) HRTEM and SAED (inset) for the hollow Ni_2P NPs from the one-pot method (bar: 10 nm).

are probably from other nickel phosphide compounds, most likely $Ni_{12}P_5$ and Ni_5P_6. The regularity of the lattice image of a single hollow NP revealed by the HRTEM indicates that the hollow NP is a single crystal. The space between the adjacent planes is 2.12 Å, corresponding to the (111) planes of Ni_2P. The formation of hollow Ni_2P NPs implied that a solid-state reaction occurred between the Ni NPs and P. The diffusion of Ni in the core crossing the preliminarily formed Ni_2P layer is faster than that of P atoms formed by the decomposition of TOP near the interface at enough high temperature. The void is roughly located at the center because the net inward flow of vacancies was converged in a small spherical NP. However, double and elongated voids were also observed in NPs with a shape deviated from spherical. The diffusion reaction goes to completion very quickly. A core−shell intermediate was not observed in the diffusion process; however, an increased amount of hollow NPs with increased reaction time was observed. For runs with chemical templates of Ni NPs of a smaller size, the voids formed more homogeneously in the center (Figure S2 in the Supporting Information).

The results gathered from the preliminary success on phosphidation of Ni NPs with TOP are quite informative. To obtain a hollow product, one has to limit the reaction to a solid-state one. It appeared that the Ni NP stabilized with a proper capping agent at a lower TOP concentration is essential to avoid TOP dissolution. With this information in mind, an effort to develop a one-pot method for the formation of hollow nanospheres of Ni_2P was made. After testing several sets of reaction parameters, a proper condition was found. In a typical reaction, nickel acetate (anhydrous, 1 mmol), 1-octadecene (15 mL), oleylamine (10 mmole, and TOP (5 mmol) were stirred magnetically under a flow of Ar. The mixture was heated to 320 °C over 15 min and kept at this temperature for 1 h. The color of the solution changed from green to dark green to black. After cooling to room temperature, 30 mL of acetone was added to the solution to give a black precipitate, which was separated from the solution by centrifugation (5000 rpm, 15 min) and dried under vacuum. The recovered NPs could be redispersed in hexane easily. TEM micrographs of the one-pot sample (Figure 2) also revealed the hollow and single-crystalline features on each NP. The hollow structures have diameters distributed between 5 and 15 nm with a wall thickness of 2−3 nm. The diameter-to-wall thickness ratio is roughly 4,

which is larger than that in the previous process. Selected area electron diffraction (SAED) also revealed the diffraction lines ascribed to Ni_2P. To know more about the mechanism of formation of the hollow structure in this one-pot process, an intermediate sample at 200 °C was taken for TEM. Solid NPs with sizes between 2 and 10 nm were found. It appears that solid NPs were formed first and the hollow NPs were derived from them. The XRD of this intermediate sample revealed a poorly crystalline pattern, with its major peaks consistent with that of FCC Ni. Energy-dispersive analysis of X-rays also suggested that the solid intermediate is Ni-riched with a Ni/P ratio of 4. The poorly crystalline Ni NPs can bear more defects in it. This is probably the reason that the hollow NPs of the one-pot process have a larger portion of voids in particles than those made from well-crystalline templates.

Colloidal NPs stabilized in an organic solvent are frequently protected by a layer of surfactants. The types of surfactants may, therefore, determine the reactivity of the NPs. The long-chain amine used in the reaction is essential for the successful synthesis of hollow Ni_2P. It is at least part of the capped surfactants on the solid Ni NP intermediates based on their diffusive-reflectance Fourier transform IR spectra. Its amount in the reaction also has an effect on the size of the final product; increasing the amount of amine will increase the size of the hollow NPs (Figure S3 in the Supporting Information). Replacing oleylamine with hexadecylamine gave similar Ni_2P hollow NPs as products. However, when oleylamine is replaced with oleic acid, solid nanorods of Ni_2P were obtained (Figure S4 in the Supporting Information). When trioctylphosphine oxide (TOPO) was added as another surfactant in the same reaction, solid spherical Ni_2P NPs were obtained (Figure S5 in the Supporting Information). TOPO may compete with oleylamine on the Ni NP surface; hence, the reactivity of Ni NPs changed. The results remind us that the NPs are very reactive in nature and the ligands at the interface can determine its reactivity. Although the Kirkendall effect is commonly found in bulk materials, we have to pay special attention to the stability of the chemical templates themselves when using them for the synthesis of hollow NPs.

While there have been several reports using TOP as a P source for the synthesis of metal phosphides, there are no examples where hollow structures form as products. In their methods, TOP served as a complexing agent to form metal−
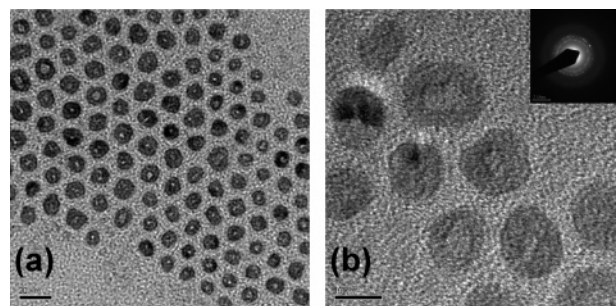

Figure 3. (a) TEM micrographs of the hollow Co_2P product from a one-pot synthesis (bar: 20 nm). (b) HRTEM and SAED (inset) for the hollow Co_2P NPs from the one-pot method (bar: 10 nm).

TOP precursors, and in some cases, it also served as a solvent in the reaction simultaneously. Therefore, these conditions cannot lead to hollow structures, which are consistent with what we found here: the TOP concentration is an important factor in the formation of hollow samples. On the other hand, the reaction temperature also has its effect on the role of TOP. Direct heating of the same reaction mixture to 250 °C for 3 h can also give the hollow Ni_2P NPs as the products. Below that temperature, however, phosphide was not obtained. It appears that TOP will not decompose to a P source on the Ni surfaces for the phosphidation process below that temperature. On the basis of the combined evidence, the solid-state reaction occurred only at a combined control of the stability of the template NP and the role of TOP that is determined by its concentration and the reaction temperature used. Under these circumstances, well-controlled hollow metal phosphide nanostructures are thus preferentially formed. This process can also be extended to prepare hollow Co_2P NPs (Figure 3). Experiments using other trialkylphosphines show that tributylphosphine can replace TOP and give similar hollow products. Further extension of this idea on preparing other metal phosphides with hollow nanostructures is in progress in our group.

Supporting Information Available: Experimental details, TEM, and FTIR. This material is available free of charge via the Internet at http://pubs.acs.org.

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