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Preparation of Bimetallic Core-shell Nanoparticles with Magnetically Recyclable and High Catalytic Abilities

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Abstract

In this work, we report the preparation of bimetallic core-shell nanoparticles (NPs) using a simple solution synthetic route. A typical example is the Ag@Ni NPs that are synthesized using oleylamine as solvent and reducing agent. The as-obtained Ag@Ni NPs exhibit a spherical morphology and a highly narrow size distribution. Excellent catalytic properties for the H₂ generation from dehydrogenation of sodium borohydride in aqueous solutions are observed. Similar synthetic strategies have also been developed for the preparation of other bimetallic core-shell NPs, such as Ag@Co and Cu@Ni NPs. These bimetallic core-shell NPs are promising candidates for novel optical and magnetic materials as well as high-performance catalysts.

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Keywords: Nanoparticles; core-shell; catalysts

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1. Introduction

Bimetallic core-shell nanoparticles (CSNPs), composed of two distinct metal elements which service as inner core and surface shell respectively, are emerging as a new class of nanomaterials [1-3]. Due to the synergistic effects from bimetallic surfaces, enhanced or even novel properties can be obtained in bimetallic CSNPs. Since the special physical and chemical properties of CSNPs depend on the combination way of the two different metal elements, it is crucial to understand the formation of CSNPs and achieve the control on their size and shape. However, developing a theory which can be applied to control the shape and dimension of both core and shell is still a key challenge [4].

Incorporating magnetic elements in NPs, which may endow NPs with superparamagnetism, is meaningful for their applications on biomedical, information storage and catalytic application [5-8]. Superparamagnetic NPs served as semi-heterogeneous catalysts [9, 10] have great application value in various important reactions such as Suzuki-, and Sonogashira-reactions [10, 11]. Unfortunately, due to the high reduction potential of ions of 3d-transition metal (Fe, Co, Ni), it is not easy to generate magnetic NPs with good crystallinity and monodispersed morphology which may be pivotal to their physical and chemical properties. The noble-metal-induced reduction process plays an interesting and exciting role in tailored synthesis of shell metal with high crystallinity. According to previous research, noble metal clusters usually performance as electron carriers which can induce the growth of 3d-transition metal in a mild condition [12]. At the same time, the strain and ligand effects between the two different metals may also modify the electronic and chemical properties of bimetallic surface [13].

Herein, we present a facile method for the synthesis of Ag@Ni and Ag@Co NPs. Catalytic growth of 3d-transition metal shell with high crystallinity was achieved in one-step reaction using Ag as seeds. The formation mechanism, magnetic properties and catalytic performance of the as-synthesized NPs are also discussed in this paper.

2. Experimental

2.1 Synthesis

In a typical synthesis, a mixture of 6 ml of oleylamine, 0.1 mmol of triphenylphosphine (TPP), 0.4 mmol of nickel(acetylacetonate)₂ (Ni(acac)₂) and 0.1 mmol of AgNO₃ was decanted into a three-necked flask and kept under a flow of high-purity argon gas at room temperature for 20 min. The mixture was then heated to 80 °C and kept at this temperature for 15 min with strong magnetic stirring. The resulting solution was then slowly heated up to a temperature of 190 °C directly and aged for 40 min. After cooling down to room temperature, the synthesized products were purified via centrifugation plus washing with mixed organic solvents and dried in a vacuum. Ag@Co NPs were prepared following the same process excepting that the aging temperature was raised to 240 °C and cobalt acetate was used as metal precursor.

2.2 Characterization

X-ray diffraction (XRD) patterns were recorded using a PANalytical X'pert PRO x-ray diffractometer with Cu K_α radiation. Transmission electron microscopy (TEM) was performed on a TECNAI F-30 transmission electron microscope operating at 300 kV. UV-vis spectra were recorded using a Shimadzu UV-2550 Ultraviolet Visible Spectrophotometer. Magnetic measurements were carried out with a superconducting quantum interference device magnetometer (MPMS-5).

2.3 Catalysis Test

In a typical experiment, 4 ml of alkaline NaBH_4 solution (containing 10 wt% NaOH and 10 wt% NaBH_4) was added to the respective catalyst (25 mg) kept in a batch reactor as a sudden supply through a syringe. After 30 s of sonic oscillation the reaction vessel was kept in a thermostat with magnetic stirring at 30 ± 1 °C. The volume of hydrogen gas generated from the hydrolysis reaction was measured using the water-displacement method.

3. Results and Discussion

In the typically synthetic process, Ag^+ with low reduction potential will be reduced at a mild temperature and then serving as seeds for the catalytic growth of the shell components. This process can be confirmed by the color change of the solution. During the temperature increasing process, the color of the reaction mixtures began to change from green to yellow at approximately 130 °C, indicating that Ag^+ cations were preferentially reduced to Ag NPs. When the temperature reached 190 °C, the color started to turn black, which indicated that 3d-transition metal cations were reduced to metallic atoms.

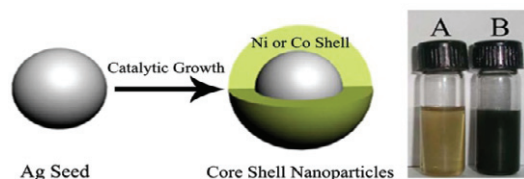


Fig. 1 Schematic illustration of the formation process of Ag-3d transition metal CSNPs.

According to this color evolution (Fig. 1), it is clear that Ag^+ , Ni^{2+} and Co^{2+} are reduced sequentially and therefore it is conducive to the formation of a core-shell structure. Ag seeds can transfer electrons to the 3d-transition metal ions covering at the surface of the noble metal clusters so as to induce the growth of shell metal. Because transferring electrons from the clusters to the 3d-transition metal ions is much easier in solution, the ions can be reduced at a lower temperature in which no isolated 3d-transition metal NPs can be generated. However, because of the large surface mismatch of silver and 3d-transition metals, it is not easy to grow homogeneous shell on the surface of Ag seeds. The generated CSNPs would exhibit a somewhat irregular-shaped morphology, if no additional surfactant such as TPP was added. It is possible that some TPP molecules may complex with silver ions, and then, adsorb on the surface of Ag nanoparticles after the seeds growing fully. The benzene-containing ligands that have comparatively large density electron cloud can enhance the electron-storage ability of the seed, and therefore help to form uniform 3d-transition metal shells. The current seed-growth synthetic strategy can also be modified for the synthesis of other bimetallic CSNPs, such as Cu@Ni NPs (data not shown here).

Figure 2 presents the TEM analytic results of the as-prepared Ag@Co and Ag@Ni NPs. Both Ag@Co and Ag@Ni NPs have near monodisperse spherical morphology and a very narrow size distribution with mean sizes of about 10 and 15 nm, respectively. From the HRTEM (Fig. 2b and 2e), it can be seen that the particle cores appear darker while the shells appear lighter, which is due to the large difference in electron scattering ability between Ag and Ni or Co. The estimated shell thickness of the Ag@Ni NPs is about 2.5 nm, while the inner core diameter is 9 nm. On the other hand, Ag@Co NPs have smaller scale with a core of 4 nm surrounded by a shell around 2 nm in thickness. The shell thickness can be easily tuned by adjusting the metal precursor and reaction temperature. Increased metal precursor and reaction temperature lead to thicker shells. High-angle annular dark-field (HAADF) imaging along with the EDS line scan performed using scanning TEM (STEM) is applied to verify the core-shell structure. As shown

in Fig. 2c and 2f, the compositional scan profile (dot line marked in the HAADF image) on a single particle clearly shows strong Ni and Co signals at the particle edge and strong Ag signals in the particle center, which reveals a typical core-shell structure. All these microscopic analytic results give convincing proof of the formation of Ag-3d transition metal core-shell structure.

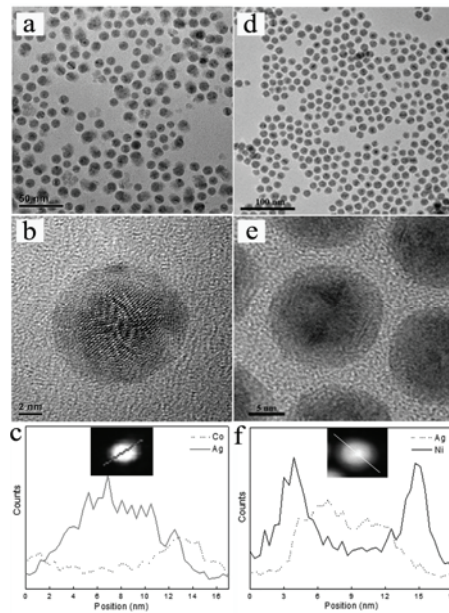


Fig. 2 Low-magnification TEM image (a and d), HRTEM image (b and e) and STEM-EDS line-scan analysis along with the HAADF image (c and f) for the as-prepared Ag@Co (a, b and c) and Ag@Ni (d, e and f) NPs.

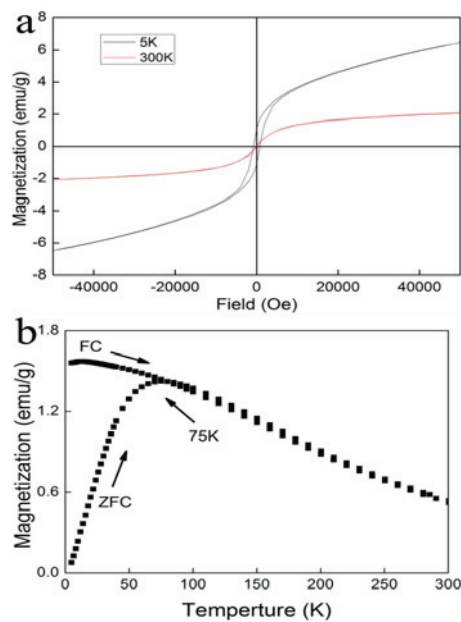


Fig. 3 Magnetic hysteresis loops (a) ZFC-FC curves and (b) of the as-synthesized Ag@Ni NPs.

Figure 3a represents the hysteresis loops of Ag@Ni NPs measured at 300 and 5 K. It indicates that the as-prepared CSNPs are ferromagnetic with a coercivity of 318 Oe at 5 K. However, such magnetic hysteresis disappears at 300 K. The determined blocking temperature (T_B) from the ZFC/FC curve (Fig. 3b) is 75 K. This result indicates that the synthesized core-shell nanoparticles are superparamagnetic at room temperature. Similar magnetic properties were also found for Ag@Co NPs. In the absence of the external magnetic field, superparamagnetic NPs can be well dispersed in a reaction solution, providing large surface area. They can also be efficiently isolated from the product solution through simple magnetic separation process.

The UV-vis spectra analyses (data not shown here) indicate the surface plasmon resonance (SPR) absorption peak of Ag is greatly damped upon coating Ni or Co. Red-shifted SPR absorption peak of Ag is also observed in several samples.

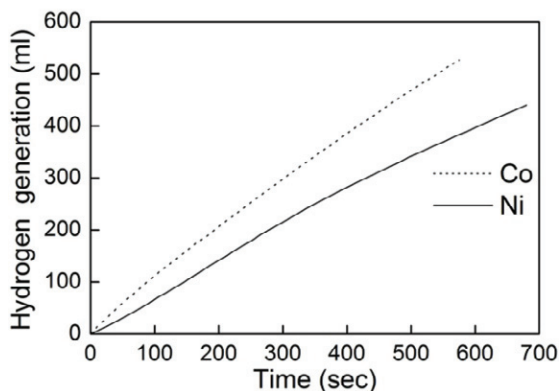


Fig. 4 Hydrogen generation from the hydrolysis of NaBH₄ catalyzed by Ag@Co (dot line) and Ag@Ni NPs (full line) at 303 K.

The as-synthesized Ag@Ni and Ag@Co NPs were used to generate H₂ from dehydrogenation of sodium borohydride in aqueous solutions. When catalysts are added, the release of hydrogen is rapid via the following reaction:



Figure 4 shows the amount of H₂ generated as a function of reaction time. The dot line illustrates the catalytic generation of H₂ by Ag@Co NPs, while the full line indicates the catalytic generation of H₂ by Ag@Ni NPs. They both exhibit highly catalytic activities in the reaction. The H₂ generation rates are 1726 and 2182 ml g⁻¹min⁻¹ for Ag@Ni and Ag@Co NPs, respectively.

4. Conclusions

Following a flexible one-pot seed-growth method, we have synthesized near-monodisperse Ag@Ni and Ag@Co NPs with tunable shell thickness. These NPs are superparamagnetic at room temperature and can be magnetically recycled. Excellent catalytic ability has been found for the generation of H₂ gas from the hydrolysis of sodium borohydride in aqueous solution.

Acknowledgements

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