One-Step Seeding Growth of Magnetically Recyclable Au@Co Core−Shell Nanoparticles: Highly Efficient Catalyst for Hydrolytic Dehydrogenation of Ammonia Borane

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Bimetallic NPs with core−shell architecture have attracted growing research interest in recent years due to their unique and novel optical, electrical, and catalytic properties compared with their monometallic counterparts and alloys.[1] Containing a magnetic element in NPs is additionally attractive owing to their applications on biomedical, information storage, technological, and catalytic applications.[2] Therefore, investigations on the synthesis and application of magnetic core−shell NPs are of great interest for harvesting the combined advantages of synergistic structural/electronic effects of core−shell structure and the intrinsic property of the magnetic element. Up to now, magnetic core−shell NPs have been successfully synthesized via the two-step seeding growth (seeds are prepared beforehand), gas condensation, or thermal decomposition methods, wherein either complicated process or strict reaction conditions (such as high temperature and high vacuum) are employed.[3] On the other hand, to the best of our knowledge, exploring and tuning their application performance of the synthesized magnetic core−shell NPs has rarely been mentioned.[3] Compared to these complicated and subeconomic methods, development of a facile and general strategy for one-step synthesis of magnetic core−shell NPs under mild conditions in a short time and exploring their potential applications, such as in catalysis, is of great importance.

Currently, finding effective hydrogen storage materials is one of the most difficult challenges toward a hydrogen powered society as a long-term solution for a secure energy future.[4] Ammonia borane (NH_3BH_3, AB) has a hydrogen capacity of 19.6 wt %, exceeding that of gasoline and making itself an attractive candidate for chemical hydrogen-storage applications.[5,6] One of the major obstacles of the practical application of this system is to develop efficient, economical, and easily recyclable catalysts for further improving the kinetic and thermodynamic properties under moderate conditions.[6,7]

Herein, we report a rational and general strategy for preparing magnetically recyclable Au@Co core−shell NPs through the one-step seeding-growth route at room temperature under ambient atmosphere within a few minutes. Unexpectedly, in contrast to its monometallic and alloy counterparts, the resultant magnetically recyclable Au@Co NPs exert excellent catalytic activity and long-term stability toward the hydrolytic dehydrogenation of aqueous AB under ambient atmosphere at room temperature.

This one-step synthetic method was achieved by exposing a mixture of Au^{3+} and Co^{2+} precursors to the reducing agent at the same time,[8] where the core Au NPs can be formed first and served as the *in situ* seeds for the successive catalytic reduction leading to the growth of outer Co NPs (Figure 1a). The basic concept of this one-step synthesis of the Au@Co core−shell NPs is to take advantage of the difference in reduction potentials of the two soluble metal salts ($E°_{Co^{2+}/Co} = -0.28$ eV vs SHE; $E°_{Au^{3+}/Au} = +0.93$ eV vs SHE), where a suitable reducing agent is essential. Alcohol has been used as the reducing agent for the one-step synthesis of core−shell NPs of dual noble metals,[1h,i] but this is difficult for non-noble metal containing core−shell NPs.[2f] Here, to fulfill the requirement of the non-noble metal system, AB is employed as a suitable reducing agent, with which magnetic Au@Co NPs are successfully synthesized within 2 min. On the contrary, a relative stronger reduction agent, $NaBH_4$, instead causes the formation of Au−Co alloy NPs.[8]

The synthesis progress can be visibly monitored by the evolution of the solution color (Figure 1b). Once the aqueous solution of $HAuCl_4$ and $CoCl_2$ with a molar ratio of 0.06:0.94 in the presence of polyvinylpyrrolidone K 30 (PVP, 1 wt %) as the stabilizing agent is mixed with the AB solid,[8] the color of the mixture suddenly changes from its light-pink color to orange-red in a few seconds, indicating Au^{3+} cations are preferentially reduced to Au^0 NPs prior to Co^{2+} cations. Then the color became darker and darker and finally changed to pure black within 2 min. Based on this color evolution and their intrinsic difference in reduction potentials, we can reasonably assume that the obtained particles are in the core−shell architecture.
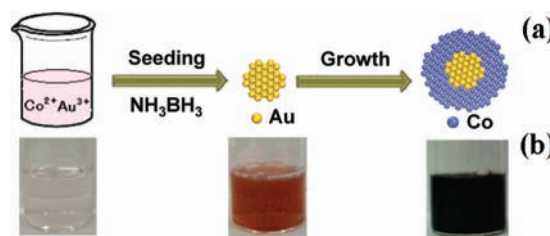

Figure 1. (a) Schematic illustration, (b) color evolution in the formation process of Au@Co core−shell NPs via a one-step seeding-growth method at room temperature.

This assumption has immediately been confirmed by monitoring the UV−vis spectra.[8] To further confirm the core−shell architecture, X-ray photoelectron spectroscopy (XPS) with Ar etching was also applied to the prepared NPs.[8] Well-defined peaks of metallic Au specie can be detected only after Ar etching, while those of metallic Co can be found both before and after Ar etching and the intensities are slightly decreased, indicating all the Au ions are reduced prior to the Co ions. This means that the atomic ratio of Au/Co increases from the surface to the inner part of the prepared NPs, which, combined with the UV−vis spectra results, gives convincing evidence for the homogeneous core−shell structures, with the cores mainly composed of Au and the shells mainly composed of Co, of the whole specimen particles.

The transmission electron microscopy (TEM) images with different magnifications of the Au@Co NPs are shown in Figure 2. The NPs are roughly spherical in shape and ∼7 nm in size. A distinct contrast

of core and shell metals can be observed clearly, and the dark cores are Au (ca. 2.5 nm) and the gray shells are Co. The high resolution image (Figure 2c) indicates this sample is basically amorphous, which agrees well with its XRD result.[8] It can be well crystallized into metallic Au and Co while keeping its core−shell architecture after heat treatment at 873 K for 3 h,[8] suggesting the core−shell architecture has good thermal stability. The EDS analysis[8] reveals the Au/Co atomic ratio to be 7/93, which agrees well with the target atomic ratio. In a word, robust Au@Co core−shell NPs have been successfully synthesized with the appointed atomic ratio through a one-step seeding-growth pathway under mild conditions within a few minutes.
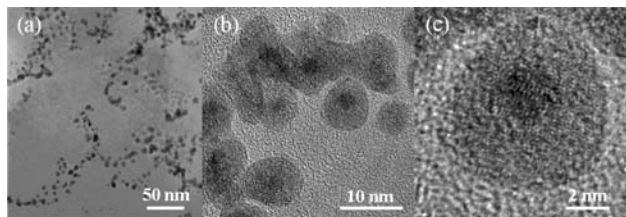

Figure 2. TEM images of Au@Co NPs with (a) low, (b) middle, and (c) high magnifications.

It should be noted that this strategy employed here for preparing Au@Co core−shell NPs can be easily expanded to the other system. For example, changing the core metal from Au to Ag or shell metal from Co to Ni can also lead to core−shell architecture.[8] However, changing the reduction agent of AB to conventional NaBH₄ only leads to the formation of Au−Co alloy[8] with inferior catalytic activity (vide infra), indicating both the relative reduction potentials of the metal ions and the reduction ability of the reduction agent are the key factors for this synthesis strategy.

To compare the catalytic properties of Au@Co NPs with those of pure Au, Co, and AuCo alloy NPs, we evaluated their catalytic activities for the dehydrogenation of AB, which is a promising chemical hydrogen storage material. Figure 3 shows the amount of H_2 generated as a function of reaction time. The core−shell Au@Co NPs exhibit markedly high catalytic activity (Figure 3a) to complete the dehydrogenation reaction of AB within 11 min. This excellent catalytic activity is much higher than that of the AuCo alloy (Figure 3b, 25 min) and Co (Figure 3c, 169 min) with similar morphologies and sizes as those of Au@Co.[8] Au NPs, which are in interlaced branch shapes with diameters less than 10 nm, have the worst activity (Figure 3d; only 70% of H_2 is released even after more than 800 min).[8]

The electronic structure in the bimetallic alloy or core−shell architecture can be modified through the interaction of the two kinds of atoms in relation to the so-called ligand and strain effects.[1c,9] Here, the better catalytic activity of Au@Co core−shell than AuCo alloy NPs might result from the modification of the electronic structure in a core−shell NP which is superior to that in an alloy NP for AB dehydrogenation. Further experimental and theoretical work is needed for elucidating this.
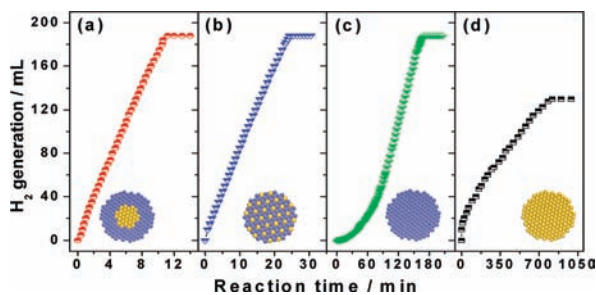

Figure 3. Hydrogen generation from AB aqueous solution (0.26 M, 10 mL) catalyzed by (a) Au@Co, (b) Au−Co, (c) Co, and (d) Au NPs under ambient atmosphere at room temperature. Catalyst/AB = 0.02 (molar ratio).

The lifetime/stability is very important for the practical application of catalysts. We tested the catalytic activity of the Au@Co NPs every 24 h in solution under ambient atmosphere. There was no significant decrease (17% decrease) in catalytic activity even after 120 h.[8] Moreover, this high performance catalyst is magnetic and thus can be easily recovered by an external magnet.[8]

In summary, we have demonstrated a novel methodology for the synthesis of Au@Co magnetic core−shell structured NPs through a one-step seeding-growth method at room temperature under ambient atmosphere within a few minutes. In addition to possessing thermal stability and easy recovery functions, the resultant Au@Co NPs exhibit high catalytic activity and long-term stability for the hydrolytic dehydrogenation of aqueous AB. Moreover, this rational and general method can be easily extended to the other metallic systems, which are used as optical, magnetic, and electrical materials as well as heterogeneous catalysts.

Supporting Information Available: Experimental procedures, XRD, TEM, XPS, UV−vis, stability, and lifetime/stability results of prepared samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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