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A one-pot protocol for synthesis of non-noble metal-based core–shell nanoparticles under ambient conditions: toward highly active and cost-effective catalysts for hydrolytic dehydrogenation of NH_3BH_3†

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A one-pot synthesis of non-noble transition metal-based core–shell nanoparticles (NPs) has been developed under ambient conditions. The obtained Cu@M (M = Co, Fe, Ni) NPs exhibit superior catalytic activity for hydrolytic dehydrogenation of NH_3BH_3, compared to the alloy and monometallic counterparts.

Bimetallic core–shell nanoparticles (NPs) have attracted considerable interest owing to their unique physical and chemical properties and potential applications in contrast to monometallic counterparts and alloys.[1,2] Although there are numerous reports on the preparation of core–shell NPs with various compositions and their diverse applications, especially in heterogeneous catalysis, almost all catalysts are noble metal-based and their high cost and limited reserve greatly inhibit the applications in an industrial scale. By contrast, low-cost transition metal-based core–shell NPs have been rarely reported. To the best of our knowledge, so far, only Co@Cu core–shell NPs were obtained based on a two-step reaction[3] and very large Cu@Ni NPs[4a] (>100 nm) and Ni@Co NPs[4b] (>60 nm) were recently synthesized with precise temperature controlling in a polyol-type reaction and under microwave irradiation, respectively. There is no investigation on the synergistic performance of both non-noble metal species in these reports. Therefore, exploiting a facile and general strategy to obtain low-cost transition metal-based bimetallic core–shell NPs with synergistic/enhanced performances (such as, catalysis) still remains undeveloped.

On the other hand, hydrogen is a globally accepted clean fuel. The development of effective hydrogen-storage materials is imperative but challenging to establish a future hydrogen economy.[5] Ammonia borane (AB, NH_3BH_3) has a hydrogen content of 19.6 wt%, which exceeds that of gasoline and makes it one of the most attractive candidates for chemical hydrogen storage application.[6,7] Hydrogen generation from hydrolysis of NH_3BH_3 is a promising alternative approach in addition to thermolysis. However, the search for suitable catalysts that meet performance, cost and safe requirements to further improve kinetic properties under moderate conditions is crucial for the practical application of this system.[8]

Herein, we present a facile one-step and general route for *in situ* synthesis of a series of Cu@M (M = Co, Fe, Ni) core–shell NPs under ambient conditions in very short time (within several to tens of minutes). In contrast to the monometallic and alloy counterparts, the *in situ* generated bimetallic core–shell NPs have exhibited synergistic and superior catalytic activity for hydrolytic dehydrogenation of ammonia borane.

In a typical synthesis of Cu@M (M = Co, Fe, Ni) core–shell NPs, to the round-bottom flask containing ammonia borane, a mixture of copper(II) chloride, cobalt(II) or nickel(II) chloride or iron(II) sulfate aqueous solution, and polyvinylpyrrolidone K 30 (PVP) as a capping agent was introduced. The Cu^{2+} and M^{2+} were reduced in sequence to produce core–shell structured NPs during the reduction process, in which Cu^{2+} with high reduction potentials ($E^{o}_{Cu(II)/Cu(I)}$ = +0.159 eV *vs.* SHE; $E^{o}_{Cu(I)/Cu}$ = +0.520 eV *vs.* SHE) was first reduced by NH_3BH_3. The generated Cu–H or/and subsequent M–H species with a strong reducing ability can further reduce M^{2+} although they cannot be directly reduced by NH_3BH_3 due to their lower reduction potentials ($E^{o}_{Co(II)/Co}$ = −0.28 eV *vs.* SHE; $E^{o}_{Fe(II)/Fe}$ = −0.44 eV *vs.* SHE; $E^{o}_{Ni(II)/Ni}$ = −0.25 eV *vs.* SHE),[1a] during which the pre-formed Cu^0 NPs, serving as *in situ* seeds/core NPs, could induce the successive growth of M^0 as a shell to thus yield Cu@M core–shell NPs. Such *in situ* reduction and one-pot synthetic protocol for core–shell NPs is to take advantage of the differences in the reduction potentials of core and shell metal salts, where the key point is to employ a suitable reducing agent. NH_3BH_3 is a desirable reducing agent based on its following merits: (1) with weak reduction ability, it can only reduce the metal cations with high reduction potential; (2) during the first metal reduction to be core/seed NPs, the hydrolysis of NH_3BH_3 catalyzed by these NPs produces M–H species as a stronger reducing agent to further reduce the second metal cation with lower reduction potential as a shell.

The reaction process can be readily monitored by the naked eye due to the obvious color evolution in the solution (Fig. S1, ESI†). The Cu^{2+} and M^{2+} salts were mixed with PVP as a capping agent in water. The solution color instantly changed to khaki upon the addition of NH_3BH_3, indicating the reduction of Cu^{2+} to Cu^{+} prior to the M^{2+} reduction. Subsequently, the color turned darker and darker along with plentiful H_2

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generation, revealing the complete reduction of Cu^{+}/Cu^{2+} and M^{2+}. From the difference of the reduction sequence explained above and the solution color evolution, we can reasonably propose the core–shell nanostructure of the obtained Cu-based bimetallic catalyst. The structure assumption was supported by UV-vis and X-ray photoelectron spectroscopy (XPS) studies. As shown in Fig. 1, the peak at around 570 nm resulting from the surface plasmon resonance (SPR) of Cu NPs disappears after introducing another metal (Co, Fe, Ni) as the main component in shells. The XPS investigation with Ar etching was conducted for the representative Cu@Co NPs. Results show that Cu $2p_{3/2}$ and $2p_{1/2}$ peaks are almost unobservable before Ar etching whereas the peaks appear and increase after Ar etching. However, the metallic Co species can be earlier detected before Ar etching. The slight peak shift of Co $2p_{3/2}$ and $2p_{1/2}$ on the outer shell before Ar etching could be ascribed to the surface oxidation in the Cu@Co sample during the exposure to air.

The transmission electron microscopy (TEM) observation for the representative Cu@Co NPs further verifies the core–shell nanostructure and the core/shell is readily distinguishable (Fig. 2). The Cu@Co NPs are found to be not monodisperse but interconnected to afford a nanochain-like structure possibly owing to the weak wrapping/protecting capability of PVP. The energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) analyses for the selected points in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images clearly show that the white rice-like NPs are Cu whereas the outer gray shell is composed by Co. In addition, the lattice fringes of a Cu core indicate its crystallinity whereas a Co shell could be amorphous from the high resolution TEM (HRTEM) image (Fig. 2a), which are also

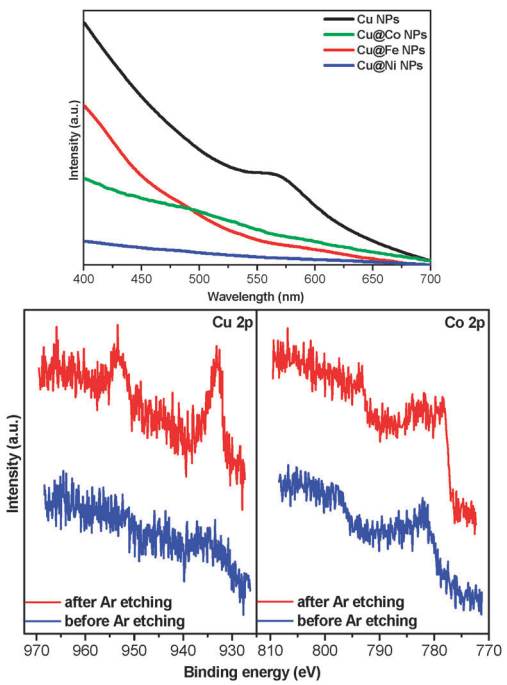

Fig. 1 (Top) UV-vis spectra of Cu and Cu@M (M = Co, Fe, Ni) samples in aqueous PVP solution. (Bottom) XPS spectra of Cu 2p and Co 2p for representative Cu@Co NPs before and after Ar etching for 60 min.

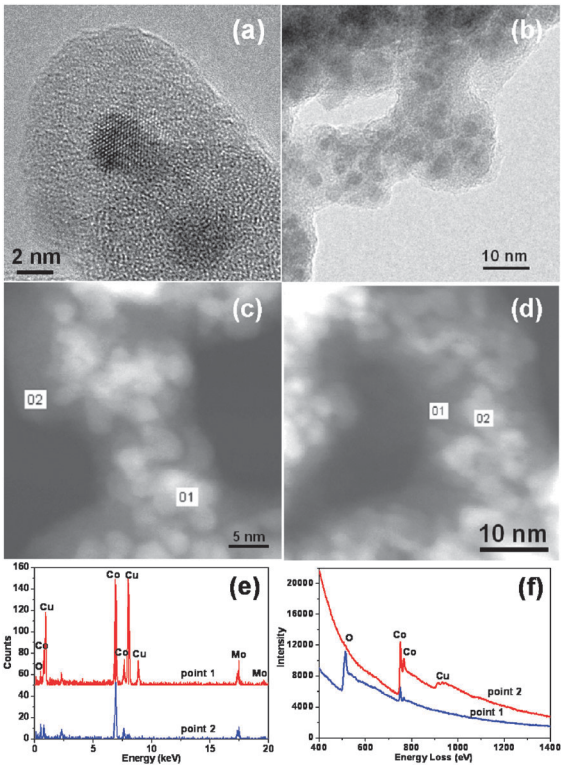

Fig. 2 Microstructure observation for representative Cu@Co NPs. (a) HRTEM and (b) TEM images. (c, d) HAADF-STEM images and (e) the corresponding EDS spectra for selected points 1 and 2 in (c), as well as (f) the corresponding EELS analyses for selected points 1 and 2 in (d). The oxygen signal in (f) is ascribed to the partial oxidation of particle surface.

approved by the absence of Co peaks but gradually increasing Cu peaks along with a larger Cu/Co ratio in the powder XRD patterns (Fig. S2, ESI†).

The obtained Cu@M (M = Co, Fe, Ni) NPs have been employed as catalysts for hydrolytic dehydrogenation of NH_3BH_3, which has been demonstrated to be a promising chemical hydrogen storage material.[5d,8d,h] As displayed in Fig. 3, $Cu_1@M_4$ approximately shows the best activity among all the catalysts with different Cu/M ratios although $Cu_1@Ni_4$ and $Cu_2@Ni_3$ have similar results, revealing the optimal combination of Cu/M = 1/4. As a whole, the catalytic activity of a $Cu_x@Co_{5-x}$ catalyst is superior to $Cu_x@Fe_{5-x}$ and $Cu_x@Ni_{5-x}$, which could be attributed to the more excellent activity of Co NPs than that of Fe or Ni NPs toward hydrogen generation from aqueous NH_3BH_3 based on the previous reports.[8b,9] In addition, the monometallic and alloyed NP counterparts have also been prepared with a conventional reducing agent $NaBH_4$. The resultant Cu_1M_4 alloy NPs (Fig. 3d) and Cu/Co/Fe/Ni monometallic NPs (Fig. S4, ESI†) display much lower catalytic activities than those of the core–shell $Cu_1@M_4$ NPs, which demonstrates the synergistic effects between Cu and M metals in the core–shell nanostructure. As a result, H_2 generation over $Cu_1@Co_4$ NPs is the fastest among all the catalysts, with which the reaction is completed in 10 min, comparable to or even better than that of Au@Co NPs with an expensive Au core.[2c] Moreover, the magnetism of all the Cu@M NPs benefits their separation from the solution by simply using an external magnet (Fig. S5, ESI†).

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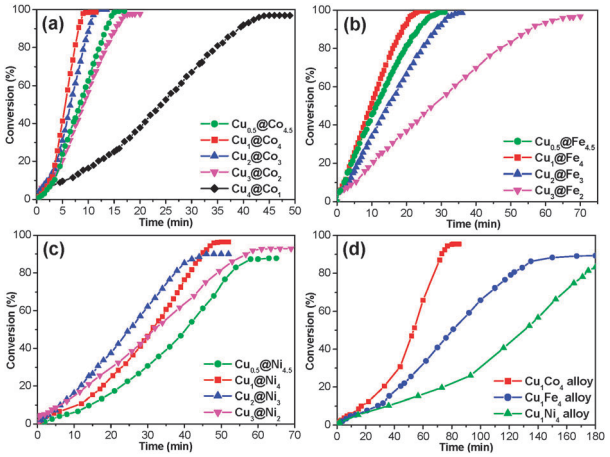

Fig. 3 Hydrogen generation from NH_3BH_3 aqueous solution (0.26 mol L^{-1}, 10 mL) over (a) $Cu_x@Co_{5-x}$, (b) $Cu_x@Fe_{5-x}$, (c) $Cu_x@Ni_{5-x}$ (x = 0.5, 1, 2, 3, 4) core–shell and (d) Cu_1M_4 (M = Co, Fe, Ni) alloy catalysts under ambient conditions. The molar ratio of $(Cu^{2+} + M^{2+})/NH_3BH_3$ = 0.02.

The excellent catalytic activity of core–shell structured NPs and the performance difference among Cu@M catalysts could be explained based on the following considerations: (a) since the catalytic properties are closely correlated with the catalyst surface, the precise modification of the core–shell catalyst surface by introducing different active components as shells could facilitate the tuning of the catalytic performance; (b) the modification of the electronic structure in the Cu@M core–shell architecture through the interaction of Cu and M species in relation to the so-called ligand and strain effects that change the width of the surface d band may benefit the optimization of catalytic performance,[1b,d,2f,10] which results in their superior activity to alloy or monometallic NP counterparts for hydrolytic dehydrogenation from NH_3BH_3. Further experimental and theoretical work is necessary to elucidate the detailed mechanism.

In conclusion, for the first time, we report here a simple one-pot approach to *in situ* and quick synthesis of Cu@M (M = Co, Fe, Ni) core–shell NPs under ambient conditions. The resultant NPs are low-cost and magnetically recyclable and exhibit synergistically enhanced catalytic performance for hydrogen generation from aqueous NH_3BH_3, surpassing that over the monometallic and alloy NP counterparts. The present general room-temperature synthesis approach might open up a new avenue in the development of low-cost transition metal NPs with core–shell architecture, which have important applications not only in heterogeneous catalysis but also in areas of optics, electronics as well as magnetism, and so on.

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