

Cite this: *Chem. Commun.*, 2011, **47**, 6308–6310

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## COMMUNICATION

## Bifunctional catalytic/magnetic Ni@Ru core-shell nanoparticles†

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Received 31st January 2011, Accepted 1st April 2011

DOI: 10.1039/c1cc10619h

**Core-shell structured Ni@Ru bimetallic nanoparticles are demonstrated as a bifunctional nanoplatform system for the hydrolysis reaction of ammonia-borane and also for magnetic separation.**

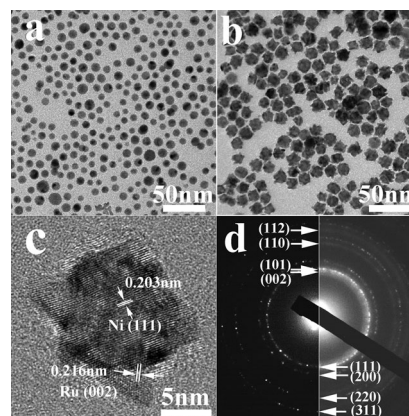
Bimetallic transition metal core-shell nanoparticles (NPs) exhibit promising catalytic, magnetic and optical properties, quite distinct from those of their monometallic counterparts.<sup>1</sup> It has been shown, in particular, that core-shell NPs can be specifically designed and realized to exploit synergistic effects between individual (core and shell) properties of the elemental metals, towards new classes of multifunctional materials.<sup>2</sup> Using noble metals as shell materials in a core-shell NP configuration is a promising strategy with significant economic advantages because it maximizes the precious element's surface to volume ratio.<sup>3</sup> In addition, using magnetic elements (such as Fe, Co and Ni) as a core metal, is expected to confer magnetic properties to noble shell NPs, in turn providing distinct advantages, *e.g.* for material recovery and in biomedical applications.<sup>2a,b,4</sup> However, the synthesis of multifunctional bimetallic structures is still a challenge since several different physical-chemical factors (such as cohesive energy, surface energy) influence the core-shell preferential arrangement.<sup>1c</sup>

Ruthenium is an important, active noble catalytic component for many reactions;<sup>5</sup> yet, research on bimetallic NPs containing ruthenium has been mostly limited so far, to the Pt–Ru system.<sup>6</sup> Further attempts at synthesizing other Ru-based bimetallic core-shell NPs with a view to optimize their properties, therefore, are of fundamental interest as well as promising for applications.

The incorporation of a magnetic element (*e.g.* Ni) in the core-shell architecture adds a second functionality to the material. Consequently, the combination of Ni and Ru is expected to exhibit multifunctional features. Recently, the synthesis of Ru@Ni core-shell NPs (Ru = core metal,

Ni = shell metal by the spray-pyrolysis method) has been reported.<sup>7</sup> However, owing to the difference in cohesive energy between Ru and Ni, this approach yields particles with Ru in the core and Ni shells. Since catalytic reactions mainly occur at NPs' surfaces, this geometry does not make use of the specific Ru catalytic properties, while the 'reversed' NPs Ni@Ru (with Ni cores and Ru shells), are expected to optimize the activity in Ru-related catalytic reactions. Here, we report the synthesis and detailed characterization of new core-shell NPs (Ni@Ru), where the more expensive and catalytically active metal (Ru) is deposited as a shell on a magnetic Ni core. To the best of our knowledge, Ni@Ru core-shell NPs have not been reported so far. This system is of interest because of its multi-functionality, combining catalytic and magnetic properties.

Transmission electron microscopy (TEM) images of Ni NP seeds and of those further decorated with Ru NPs (*i.e.* covered by a Ru shell) are shown in Fig. 1. The average size of Ni and Ni@Ru NPs is 12.5 and 15.0 nm, respectively. After Ru deposition, most Ni@Ru NPs do not inherit the initial spherical shape of the Ni NPs, but exhibit irregular shapes, with rough surfaces presenting some tips (Fig. 1b and Fig. S1†). The rounded contour of the Ni seed particle below the Ru NPs attached on its surface is still visible (see Fig. S2†). In the high-resolution TEM image (Fig. 1c), the measured *d* spacing of 0.203 nm in the center of the particle is assigned to



**Fig. 1** TEM images of (a) oleic acid-capped Ni and (b, c) Ni@Ru core-shell NPs: (b) low resolution, (c) high resolution. (d) SAED patterns of Ni (left) and Ni@Ru (right) core-shell NPs, respectively. The indexes of crystal planes in the upper left refer to Ru and those in the lower right to Ni.

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† Electronic supplementary information (ESI) available: Experimental procedures, XRD, TEM, XPS, EDS and magnetic results of the as-prepared Ni@Ru samples. See DOI: 10.1039/c1cc10619h

the lattice spacing of the (111) plane of Ni, and the interlayer distance of 0.216 nm in the outer region can be indexed with certainty to the lattice spacing of (002) of Ru. The selected area electron diffraction (SAED) pattern for Ni@Ru NPs (Fig. 1d) exhibits two sets of diffraction rings, one set corresponding to the fcc structure of Ni, the other corresponding to the hcp structure of Ru in the Ni@Ru core-shell NPs.

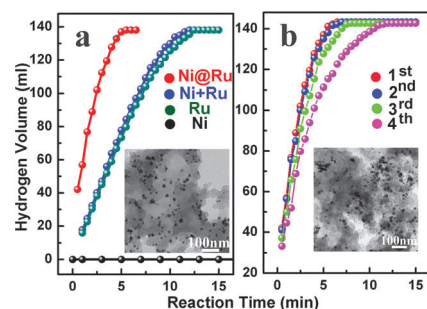
To further confirm the core-shell morphology of the NPs, the as-prepared sample was fully characterized by a combination of X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) (see ESI†). The XRD pattern (Fig. S3†) of the NPs after deposition of Ru on the Ni surface shows individual diffraction peaks matching those of the fcc structure of Ni and of the hcp structure of Ru. The larger full width at half maximum of Ru(110) in the core-shell NPs as compared to that of Ru NPs synthesized without the presence of Ni seeds indicates that the crystal size of Ru in the core-shell structure is smaller than that of monometallic Ru NPs. Additionally, the local composition acquired from EDS point spectra in different regions within a single NP reveals the larger abundance of Ru at the surface, and of Ni in the center (Fig. S4†). XPS is used to detect the surface composition of samples and to provide a proof of the core-shell structures, by etching the sample.<sup>8</sup> Well-defined peaks of metallic Ni 2p and Ru 3d species are clearly detected in the XPS profile before etching (Fig. S5†). The Ni/Ru intensity ratio of the spectra increases with the etching depth, demonstrating the Ni enrichment of the core, further indicating the Ni@Ru core-shell structure in the as-prepared sample.

Oleylamine was found to play a key role in the formation of the Ru shell and thus in the realization of the desired hetero-structure. Using the same method, monometallic Ru NPs with high crystallinity and edged surface were synthesized in oleylamine in the absence of Ni seeds. The resulting Ru NPs show a certain degree of aggregation (Fig. S6†). Oleylamine acts as both a solvent for  $\text{Ru}_3(\text{CO})_{12}$  and a capping ligand that bonds to the Ru NP surface after thermal decomposition of the precursor. For comparison, syntheses were also carried out where diphenyl ether or octadecene were employed, instead of oleylamine, as dispersants for Ni NPs before the deposition of the Ru shell. Under the same synthetic conditions, the as-formed NPs exhibit severe agglomeration, and the Ru NPs prefer homogeneous nucleation to heterogeneous nucleation on the surface of the Ni seeds (Fig. S7a, b†). The electrostatic attraction between amine-capped Ru NPs and oleic acid-capped Ni NPs may account for their effective interaction.<sup>9</sup> This speculation was proved by the formation of similar Ni@Ru core-shell NPs when oleylamine was replaced by 1-hexadecylamine as solvent and ligand (Fig. S8†).

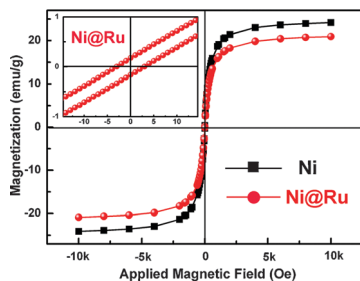
In another synthesis procedure, trioctylphosphine (TOP)-capped Ni NPs were first synthesized, instead of oleic acid-capped Ni NPs, before the decomposition of  $\text{Ru}_3(\text{CO})_{12}$  in oleylamine. The weak interaction between TOP-capped Ni seeds and Ru NPs may be attributed to the large steric effect of TOP, which prevents the Ru NPs deposition on the Ni surface (Fig. S7c†), leading to separate particles. The comparison with the above alternative synthesis paths reveals that the oleylamine-oleic acid system is essential for the establishment

of nucleation sites for Ru on the preformed Ni NPs, and the subsequent growth of Ru is influenced by oleylamine, which leads to the formation of Ni@Ru hetero-nanostructures, as further demonstrated by their morphology evolution at different reaction times (Fig. S9†).

The hydrolysis of ammonia-borane (AB) was chosen as a model reaction to evaluate the catalytic property of the as-prepared Ni@Ru core-shell NPs. Recently, the AB complex was identified as an attractive candidate for hydrogen storage, because of its 19.6 wt% hydrogen content. The release of hydrogen from AB can be obtained through either hydrolysis or pyrolysis. The former process yields 3 mol of hydrogen per mol of AB at room temperature, in the presence of a suitable catalyst, while the latter only releases 6.5 wt% of hydrogen even at 85 °C.<sup>10</sup> Among a number of catalysts reported, ruthenium NPs have been identified as one of the most effective to accelerate this reaction.<sup>11</sup> In our tests, the amount of generated  $\text{H}_2$  was measured by an inverted and graduated burette filled with water. All the tested NPs were first loaded onto electroconductive carbon black (Ketjenblack EC-300J) with high specific surface area ( $\sim 800 \text{ m}^2 \text{ g}^{-1}$ ), then dispersed in water without any special treatment to remove the surface capping ligands. A typical TEM image (Fig. 2a, inset) shows that core-shell NPs have an even dispersion on the support and maintain their original size and morphology. Fig. 2a shows the hydrogen evolution vs. time from an aqueous solution of AB in the presence of monometallic Ni, Ru, a physical mixture of Ni and Ru, and Ni@Ru NPs. There is no gas release for Ni NPs even after 1 h, indicating that the 12.5 nm, oleic acid-capped Ni NPs prepared in this work are inactive. Monometallic Ru NPs exhibit significant catalytic activity, completing the hydrolysis reaction of AB within 12.5 min. The physical mixture of Ni and Ru shows similar activity to that of monometallic Ru, further proving that the Ru is the active component. Remarkably, when Ni@Ru NP is used, keeping the same amount of Ru as in the monometallic Ru and in the physical mixture, the release of  $\text{H}_2$  is completed within 6 min. The activity in terms of turnover frequency (TOF) is  $114 \text{ (mol H}_2 \text{ min}^{-1} \text{ (mol Ru)}^{-1})$  for Ni@Ru NPs; this value is higher than that of monometallic Ru NPs (31.5) and



**Fig. 2** (a) Comparison of catalytic activities of monometallic Ni, monometallic Ru, a physical mixture of Ni and Ru, and Ni@Ru core-shell NPs for  $\text{H}_2$  generation at room temperature. (b) Comparison of Ni@Ru core-shell NPs during a four-cycle reusability test. Inset in (a): TEM image of as-prepared Ni@Ru NPs deposited on Ketjen carbon black. Inset in (b): TEM image of the Ni@Ru NPs after four catalytic cycles. ([Ni]: 5.16 mM; [Ru]: 1.89 mM; [AB]: 200 mM; volume of dispersion: 10 mL).



**Fig. 3** Magnetization curves obtained at 300 K, normalized to the mass of Ni in the Ni@Ru core-shell NPs and monometallic Ni NPs.

even of most reported Pt-based bimetallic NPs, if the TOF is normalized in terms of mol Pt (see ESI† for details).<sup>12</sup> The less costly Ru-based catalysts thus provide a promising alternative in the AB hydrolysis reaction, since Pt was the best catalyst so far.<sup>11d</sup>

We interpret the high catalytic activity of the Ni@Ru core-shell NPs as follows. The Ni seeds provide sites for the heterogeneous nucleation of Ru NPs, so that the size of the deposited Ru NPs ( $\sim 2.5$  nm) is smaller than that of the monometallic Ru ( $\sim 8$  nm) synthesized by the same method. In addition, the Ni seeds can stabilize the deposited Ru NPs and prevent their aggregation in solution, while slight agglomeration was observed for pure Ru NPs. Therefore, for a given mass of Ru, the Ni@Ru core-shell NPs possess a higher surface area, which directly contributes to enhance the catalytic activity. Finally, an influence of the interaction between Ni and Ru on the electronic structure of the active metal, arising from their intimate contact, cannot be excluded. A reusability test shows that the as-prepared Ni@Ru catalysts still exhibit high catalytic activity after four cycles of reaction. The observed activity loss is likely to result from the agglomeration of NPs on the support (Fig. 2b).

Macroscopic magnetic hysteresis loops were also measured at room temperature to investigate the magnetic properties of the Ni@Ru core-shell NPs, as shown in Fig. 3. It is observed that both Ni and Ni@Ru NPs exhibit a weak hysteresis (*i.e.*, near-zero coercivity and remanence), indicating that most of the NPs exhibit superparamagnetic behavior. This could be attributed to the fact that the nickel NPs are so small that they may be considered to have a single magnetic domain. As expected, the Ni@Ru NPs, like other magnetic core-shell NPs,<sup>2a,b,13</sup> exhibit the magnetic feature of the core. The saturation magnetizations are measured as  $20.9 \pm 0.4$  emu g<sup>-1</sup> for Ni@Ru NPs and  $24.1 \pm 0.5$  emu g<sup>-1</sup> for Ni NPs. Therefore, the magnetic Ni@Ru core-shell NPs can be removed and recycled upon application of an external magnetic field (Fig. S10†).

In summary, bifunctional catalytic and magnetic Ni@Ru core-shell NPs were synthesized for the first time, by means of a seeded growth method. The structure of the nanohybrids has been clearly identified by microscopy, diffraction and spectroscopic techniques. Oleylamine was demonstrated to be a key factor for the creation of uniform Ni@Ru NPs with a jagged Ru shell. The ultra-small Ru NPs stabilized on the Ni surface show enhanced activity in the hydrolysis of AB. This novel Ni@Ru core-shell structure may open the pathway for other

applications in heterogeneous catalysis reactions in which Ru NPs are involved and/or magnetic recycling is desired.

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) through a Strategic Grant and Discovery Grants is greatly appreciated. F. Rosei is grateful to MDEIE and to MAE (Italy) for partial funding of the Italy–Quebec Joint Laboratory in Nanostructured Materials for Energy, Catalysis and Biomedical Applications.

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