

# First application of core-shell Ag@Ni magnetic nanocatalyst for transfer hydrogenation reactions of aromatic nitro and carbonyl compounds†

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Manoj B. Gawande,<sup>\*a</sup> Huizhang Guo,<sup>b</sup> Anuj K. Rathj,<sup>c</sup> Paula S. Branco,<sup>a</sup>  
Yuanzhi Chen,<sup>b</sup> Rajender S. Varma<sup>d</sup> and Dong-Liang Peng<sup>\*b</sup>

**A magnetically separable core-shell Ag@Ni nanocatalyst was prepared by a simple one-pot synthetic route using oleylamine both as solvent and reducing agent and triphenylphosphine as surfactant. The synthesized nanoparticles were characterized by several techniques such as X-ray diffraction pattern (XRD), high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED) pattern, and energy dispersive X-ray spectroscopy (EDS). The core-shell Ag@Ni nanocatalyst was found to have very excellent activity for the transfer hydrogenation reactions of aromatic nitro and carbonyl compounds under mild conditions using isopropyl alcohol as hydrogen donor. Excellent chemoselectivity and regioselectivity for the nitro group reduction was demonstrated.**

## Introduction

The development and design of core-shell nanomaterials has emerged in recent years because of their multifaceted applications utilizing their electronic, magnetic, and optical properties and as catalysts for organic reactions.<sup>1</sup> These bimetallic core-shell nanomaterials have gained much attention due to their distinctive properties and impending scope in multiple fields. There are various reports on core-shell nanomaterials and their applications in catalysis, such as core-shell Au@SnO<sub>2</sub> used for CO oxidation,<sup>2</sup> thermally stable Pt/mesoporous silica core-shell nanocatalyst for high-temperature reactions,<sup>3</sup> Pd/FePt nanoparticles for reduction reactions,<sup>4</sup> gold-containing core-shell catalyst for a fuel cell

nanocatalyst,<sup>5</sup> Pd-Pt core-shell nanowire catalysts for the oxygen reduction reaction,<sup>6</sup> Pd metal-containing core-shell catalysts for oxidation reaction,<sup>7</sup> and Ag-CeO<sub>2</sub> core-shell nanocatalyst for reduction reactions,<sup>8</sup> etc.

Magnetically separable nanocatalysts is an important class of the core-shell nanocatalyst family. In recent years, they have been used in various important organic transformations because they are robust, air stable, avoid traditional filtration processes, are reusable, and are recyclable for several reaction runs.

These important features make them versatile, and inexpensive heterogeneous catalysts. However, the scope of magnetically separable core-shell nanocatalysts is largely untapped. There are only some reports on magnetically separable core-shell nanocatalysts, such as Fe@Pt core-shell structures used as electrocatalysts for ammonia borane oxidation,<sup>9</sup> mesoporous-silica-protected core-satellite nanocomposite catalysts,<sup>10</sup> core-shell magnetic gold nanocatalyst Fe<sub>3</sub>O<sub>4</sub>@MgAl-LDH@Au for oxidation reactions,<sup>11</sup> dendron-functionalized core-shell nanocatalyst for C-C coupling reactions,<sup>12</sup> core-shell nanoparticle-supported TEMPO catalyst for oxidation of alcohols,<sup>13</sup> Au@Co core-shell nanocatalyst for dehydrogenation of ammonia borane,<sup>14</sup> and some other important core-shell nanocatalyst.<sup>15</sup>

In continuation of our efforts for the development of greener protocols, heterogeneous catalysis<sup>16</sup> and nanomaterials and their applications,<sup>17</sup> a facile, simple, and inexpensive Ag@Ni core-shell magnetically separable catalyst is presented for hydrogen transfer reactions using IPA (isopropyl alcohol) as hydrogen donor. Very recently, Ag@Ni core-shell nanocatalyst have been designed by simple one-pot synthetic route.<sup>18</sup> (Scheme 1, ESI†). To the best of our knowledge this is the first report of Ag@Ni core-shell magnetically separable nanocatalyst for hydrogen transfer reactions of aromatic nitro and carbonyl compounds.

The synthesized nanoparticles (NPs) were characterized by several techniques, such as X-ray diffraction pattern (XRD), high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED) pattern, and energy dispersive X-ray spectroscopy (EDS) (ESI†).

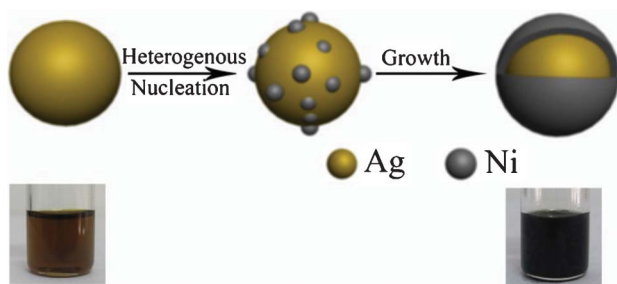
<sup>a</sup>REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.

E-mail: [mbgawande@yahoo.co.in](mailto:mbgawande@yahoo.co.in); [m.gawande@fct.unl.pt](mailto:m.gawande@fct.unl.pt); Fax: +351 21 2948550; Tel: +351 21 2948300

<sup>b</sup>Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, People's Republic of China. E-mail: [dipeng@xmu.edu.cn](mailto:dipeng@xmu.edu.cn)  
<sup>c</sup>Jubilant Chemsys Ltd., B-34, Sector-58, Noida-201301, New Delhi, India

<sup>d</sup>Sustainable Technology Division, National Risk Management Research Laboratory, US Environmental Protection Agency, MS 443, 26 West Martin Luther King Drive, Cincinnati, Ohio, 45268, USA

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**Scheme 1** Synthesis of Ag@Ni core-shell magnetic nanocatalyst.

## Results and discussion

The TEM image of Ag@Ni core-shell NPs shows a spherical morphology with a diameter of 14.9 nm (Fig. 1a). These NPs have a very narrow size distribution with a standard deviation of 1.14 nm. The selected area electron diffraction (SAED) pattern (Fig. 1b) acquired from these NPs displays diffraction rings which can be indexed to both face-centered cubic (fcc) Ni and Ag, respectively. The XRD patterns conform well with SAED analysis. The SAED and XRD analysis results indicate that Ni and Ag exhibit as two separated crystalline phases instead of an alloy or intermetallic in the products.<sup>18</sup> This is because Ni and Ag are phase separated at room temperature, which is very important to maintain the catalytic property of these NPs. To characterize the core-shell structure of the as-synthesized NPs, high-resolution TEM (HRTEM) was conducted on a single nanoparticle. As shown in Fig. 1c in the center area of a single NP, clear lattice fringes with a spacing of 2.33 Å corresponding to the (111) planes of Ag can be observed, while in the edge area lattice fringes with a spacing of

1.78 Å corresponding to the (200) planes of Ni can be observed. In order to further confirm the formation of core-shell structure, high-angle annular dark-field (HAADF) imaging along with EDS line scan performed using scanning TEM (STEM) was used to characterize the distribution of elements in single NPs. The compositional scan profile (red line marked in the HAADF image in Fig. 1d) on a single particle clearly shows strong Ni signals at the particle edge and strong Ag signals in the particle center, which reveals a typical core-shell structure. Both HRTEM and line scan analysis results give convincing proof of the formation of Ag–Ni core-shell structure. The synthesized Ag@Ni core-shell NPs are equipped with a spherical core with a diameter of about 8.1 nm and shell with a thickness of about 3.3 nm.

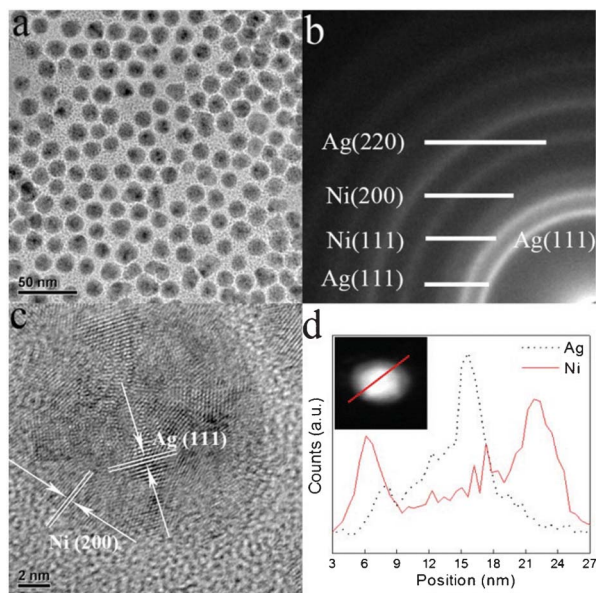
The Ag@Ni core-shell nanoparticles were explored as a catalyst for the hydrogen transfer reactions of aromatic nitro compounds (**1**) using isopropyl alcohol (IPA) as the hydrogen donor (Table 1).

First, catalytic activity of Ag@Ni was tested for the reduction of 4-hydroxy nitrobenzene (**1i**) to yield 4-hydroxyaniline (**2i**) under various reaction conditions (Scheme 2). After optimization of the reaction conditions (ESI†), the catalytic activity of Ag@Ni core-shell MNPs with other nitro substrates was further explored (Table 1).

The catalytic performance of Ag@Ni core-shell nanocatalyst, was not significantly influenced by the nature and position of the substituents on the aromatic nitro compounds. Electron-donating as well as -withdrawing groups such as –Cl, –F, –Br, and –OCH<sub>3</sub> did not have significant influence on the reaction (Table 1). Notably, transfer hydrogenation over Ag@Ni core-shell nanocatalysts exhibits excellent activity and selectivity for the hydrogenation of a series of halogenated nitrobenzenes to the corresponding halogenated amines, without any dehalogenation (Table 1, entries **2c** to **2g**). Ag@Ni core-shell magnetic nanocatalysts also show excellent regio- and chemoselectivity (Table 1, entries **2l** to **2o**). All the nitro arenes were reduced in excellent yields affording a single product, which minimizes the efforts to separate unreacted starting compounds.

To further explore the versatility of the catalyst, the catalytic performance was tested for the hydrogen transfer reactions of carbonyl compounds **3** (Scheme 3). The general reaction proved to be widely applicable as the corresponding alcohols were obtained in good to excellent yields (Table 2, yield 90–94%). Interestingly, no dehalogenation of the halogen derivatives of acetophenones was observed (Table 2, entries **4b** and **4c**). Cyclohexanone was successfully converted to cyclohexanol in good yield (Table 2, entry **4d**).

A proposed mechanism for the reduction of aromatic nitro compounds is depicted in Scheme 4. As a result of the adsorption of IPA on the NPs surface, a hydride is transferred to the nitro group with concomitant formation of acetone.<sup>17c</sup> Meanwhile, the rate of reaction can show dependence on the strength of adsorption of both isopropanol and the nitro compound. The nitroso intermediate **III**, formed on elimination of water, adsorbed on the Ag@Ni core-shell nanocatalyst, is again reduced by the hydride transfer from IPA to the hydroxylamine **IV** which is further reduced to the aniline **V**.

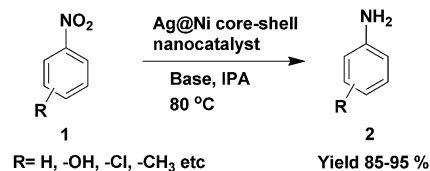


**Fig. 1** Ag–Ni core-shell nanoparticles. (a) Low-magnification TEM image (at 50 nm); (b) SAED pattern; (c) HRTEM image of a single nanoparticle; (d) EDS spectra recorded from the center.

**Table 1** Ag@Ni core-shell catalyzed hydrogen transfer reactions of aromatic nitroarenes<sup>a</sup>

2	Nitro compound	Amines	Time (h)	Isolated yield (%)
2a			2	96
2b			2.5	91
2c			3	86
2d			2.5	94
2e			2.5	93
2f			3	89
2g			3	88
2h			2	93
2i			2	90
2j			3	85
2k			2	93
2l			2	94
2m			2	91
2n			2	93
2o			2.5	94

<sup>a</sup> Reaction conditions: nitroarene (1 mmol), KOH (1.5 mmol), 80 °C, IPA (3 mL), 50 mg of catalyst.

**Scheme 2** Hydrogen transfer reactions of aromatic nitro compounds on Ag@Ni core-shell nanocatalyst.

A more effective and competitive interaction between the nitro group and the NPs can justify the chemoselectivity observed for the substrates **2m-o**.

In heterogeneous catalysis, the stability of the catalyst is an important issue from the viewpoint of a green sustainable protocol. So, keeping this in mind, the stability of Ag@Ni core shell magnetic nanoparticles was tested by recycling and reusing the catalyst eight times without any significant loss of the catalytic activity. After each cycle Ag@Ni MNPs were separated using an external magnet and used for the next cycle (Fig. 2).

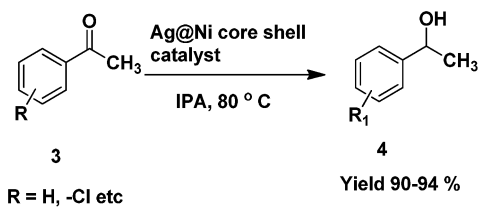
To check the efficiency of this protocol, the reduction of nitrobenzene to aniline was compared to some existing protocol.<sup>19</sup>

In order to prove the reaction is heterogeneous, a standard leaching experiment was conducted by the hot filtration method. The model reaction of the reduction of 4-hydroxynitrobenzene proceeded for 20 min in the presence of Ag@Ni at 80 °C. The hot filtered reaction mixture was then stirred without catalyst for 12 h. Notably, no formation of product was observed even after 12 h indicating that no homogeneous catalyst was involved. Inductively coupled plasma atomic emission spectra (ICP-AES) analysis of the filtrate (hot) revealed the absence of Ag and Ni species in the filtrate.

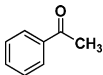
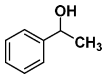
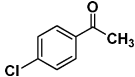
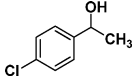
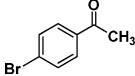
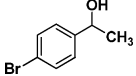


A facile, effective, and magnetic core-shell nanocatalyst has been designed for hydrogen transfer reactions. The reaction was broadly applicable as diverse aromatic nitro and carbonyl compounds were successively converted to the corresponding amines or alcohols in excellent yield (85–94%) and short reaction times. Being magnetically separable, this core-shell catalyst is a promising candidate for other important organic conversions and industrial applications.

## Experimental

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromato-

**Scheme 3** Ag@Ni core-shell catalyst for hydrogenation of carbonyl compounds

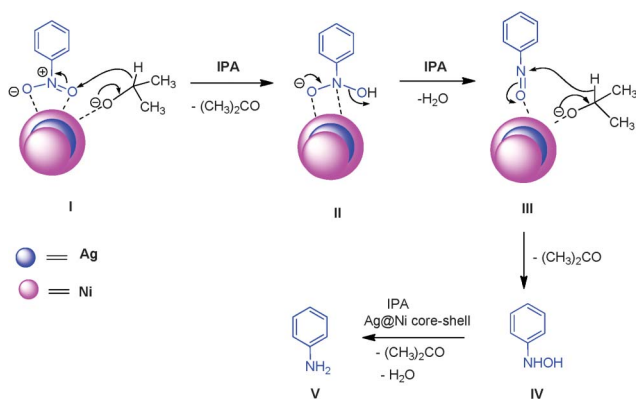
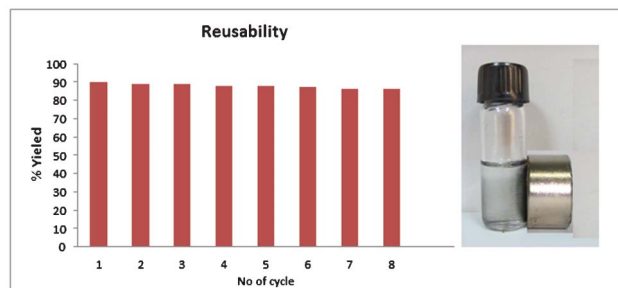
**Table 2** Ag@Ni core-shell catalyzed hydrogen transfer reactions of carbonyl compounds<sup>a</sup>

4	Carbonyl compound	Products	Time	Yield (%)
4a			2	94
4b			2.5	92
4c			2.5	90
4d			2	90

<sup>a</sup> Reaction conditions: carbonyl compound (1 mmol), KOH (1.5 mmol), 80 °C, IPA (3 mL), 50 mg of catalyst.

graphy, Merck 0.2 mm and 0.5 mm Kieselgel GF 254 precoated plates were used, respectively. The spots were visualized using UV light.

X-ray diffraction (XRD) patterns of the synthesized nanoparticles were recorded using a PANalytical X'pert PRO X-ray diffractometer with Cu-K $\alpha$  radiation. Transmission electron microscopy (TEM) was performed on a TECNAI F-30 transmission electron microscope operating at 300 kV. Energy dispersive X-ray spectroscopy (EDS) analyses in both spot and line-scan mode were used to identify the chemical components of single nanoparticles. The TEM samples were prepared by dropping the particle suspensions in toluene onto a copper grid coated with carbon film before drying at room temperature under ambient conditions. Elemental analysis was performed by using ICP-AES using a Horiba Jobin-Yvon, France, Ultima model equipped with a 40.68 MHz RF generator, Czerny–Turner monochromator with 1.00 m (sequential), auto sampler AS500 and CMA (concomitant metals analyzer). Proton NMR spectra were recorded on a Bruker, 300, 5

**Scheme 4** Possible mechanism for hydrogen transfer reactions over Ag@Ni nanocatalysts.**Fig. 2** Reusability of Ag@Ni nanocatalyst (inset: catalyst separated by magnet).

mm probe at 300 MHz. <sup>1</sup>H shifts are reported relative to internal TMS.

### Catalyst preparation

Ag–Ni core-shell nanoparticles were prepared *via* the thermal decomposition of nickel(acetylacetonate)<sub>2</sub> (Ni(acac)<sub>2</sub>, 96%, Acros) and AgNO<sub>3</sub> (99.8%, SCRC) in oleylamine (80–90%, Acros) using a one-pot seed-growth method. In a typical synthesis, a mixture of 6 ml of oleylamine, 0.1 mmol of triphenylphosphine (TPP; CP grade, SCRC), 0.4 mmol of Ni(acac)<sub>2</sub>, and 0.1 mmol of AgNO<sub>3</sub> was decanted into a three necked flask and kept under a flow of high-purity argon gas at room temperature for 20 min. After that, the mixture was 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 (the reaction temperature may range from 180 to 230 °C) directly and aged for 40 min. After cooling down to room temperature naturally, excess acetone was added to the black solution to give a black precipitate, which was isolated *via* centrifugation. The precipitate was then washed thoroughly with a mixture of hexane and acetone and dried in a vacuum.

### General method for the reduction of nitroarenes and carbonyl compounds

The nitroarene **1** or the carbonyl compound **3** (1 mmol), isopropyl alcohol (3 mL), KOH (1.5 mmol), and Ag@Ni (50 mg), were stirred at 80 °C for an appropriate time. After completion of the reaction (monitored by TLC), the catalyst was separated magnetically. The ensuing product was extracted with ethyl acetate and repeatedly washed with water (5 to 7 times) to remove KOH. Then, the organic solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel using n-hexane and ethyl acetate as eluent.

### Acknowledgements

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