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Simple one-pot synthesis of Rh–Fe_3O_4 heterodimer nanocrystals and their applications to a magnetically recyclable catalyst for efficient and selective reduction of nitroarenes and alkenes†

Youngjin Jang,‡[a] Seyoung Kim,‡[b] Samuel Woojoo Jun,[a] Byung Hyo Kim,[a] Sunhwan Hwang,[c] In Kyu Song,[c] B. Moon Kim*[b] and Taeghwan Hyeon*[a]

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A simple synthesis of Rh–Fe_3O_4 heterodimer nanocrystals was achieved by controlled one-pot thermolysis. The nanocrystals exhibited excellent activities for the selective reduction of nitroarenes and alkenes. Furthermore the nanocrystal catalyst could be easily separated by a magnet, and recycled eight times without losing the catalytic activity.

The reduction of nitro compounds to amines is one of the most important chemical reactions because organic amines are essential materials for the production of agrochemicals, dyes, pharmaceuticals, polymers, and rubbers.[1] Numerous catalysts using a variety of metals including Cu, Au, Fe, Pd, Pt, and Rh have been investigated for these reduction reactions.[2,3] For example, Corma and Serna reported that gold nanoparticles supported on TiO_2 catalyzed chemoselective hydrogenation of functionalized nitroarenes with H_2.[3a] The selective reduction of a nitro group in organic compounds containing other reducible functional groups is a very challenging issue in organic synthesis.[3] In addition, the reduction of aromatic nitro compounds is often associated with side products including hydroxylamines, hydrazines, and azoarenes since the reaction can stop at an intermediate stage.[4] Therefore easily-separable, chemoselective, and effective catalysts for the reduction of organic compounds are highly desired.

Because it is difficult to separate a homogeneous catalyst in the mixture solution after reactions, alternative solutions have been explored. The semi-heterogeneous system using well-dispersed nanoparticles is one of the most promising candidates because nanoparticles show a good catalytic activity along with easy separation capability.[5,6] Recently, studies were focused on the magnetic separation of catalysts using magnetic nanocomposite materials.[7] Even though there have been several studies on the immobilization of catalytic metal nanoparticles in magnetic materials, there is no report on the synthesis of Rh–Fe_3O_4 heterostructured nanoparticles for catalytic applications. In this study, we report on the simple and one-pot synthesis of Rh–Fe_3O_4 heterodimer nanocrystals by using "heat-up process,"[8] and demonstrated their applications to magnetically recyclable catalyst for efficient and selective reduction of nitroarenes and alkenes.

We prepared Rh–Fe_3O_4 heterodimer nanocrystals using a consecutive heating approach in one-pot synthesis. $Rh(acac)_3$ (27 mg) and $Fe(acac)_3$ (0.70 g) were mixed with a solution containing 6 mL of oleylamine and 4 mL of oleic acid, and the resulting mixture was slowly heated to 200 °C, then to 300 °C, and aged at 300 °C for 30 min (see the detailed procedure in ESI†). After cooling to room temperature, the mixture solution was precipitated by adding EtOH, and finally the nanocrystals were retrieved by centrifugation. The nanocrystals were dispersible in many organic solvents such as hexane and chloroform. Transmission electron microscopy (TEM) images showed that the Rh–Fe_3O_4 heterodimer nanocrystals are consisted of Rh nanoparticles with an average diameter of 2–3 nm and Fe_3O_4 component of ~16 nm (Fig. 1a and b). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis revealed that the catalyst is composed of 1.09 wt% of Rh and 63.3 wt% of Fe atoms. X-Ray diffraction (XRD) pattern (Fig. 1c) shows that these heterodimer nanocrystals are composed of a face-centered cubic (fcc) Rh (JPCDS 05-0685) and fcc Fe_3O_4 (JCPDS 19-0629). X-Ray photoelectron spectroscopy (XPS) analysis (Fig. 1d and Fig. S1, ESI†) showed that iron oxide component is magnetite (Fe_3O_4) and Rh species is Rh^0. No peak corresponding to

[a] *National Creative Research Initiative Center for Oxide Nanocrystalline Materials, World Class University Program of Chemical Convergence for Energy & Environment, and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Korea. E-mail: thyeon@snu.ac.kr; Fax: +82 2-886-8457; Tel: +82 2-880-7150*
[b] *Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea. E-mail: kimbm@snu.ac.kr; Fax: +82 2-872-7505; Tel: +82-2-880-6644*
[c] *School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Seoul 151-744, Korea*

† Electronic supplementary information (ESI) available: Detailed experimental procedures, XPS and TPR spectrum, SQUID diagram of Rh–Fe_3O_4 heterodimer nanocrystals, TEM image of Rh–Fe_3O_4 heterodimer nanocrystals after 8 cycles of the catalytic reaction and photographs showing the magnetic separation of the catalyst, and catalytic result on the reduction of nitrobenzene and *trans*-stilbene using various catalysts. See DOI: 10.1039/c0cc04816j

‡ These authors contributed equally to this work.

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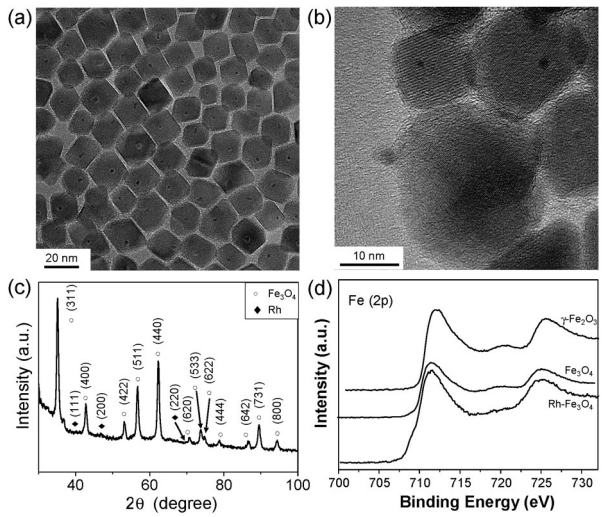


Fig. 1 (a) TEM image, (b) HRTEM image, (c) XRD pattern and (d) XPS spectra of Rh–Fe_3O_4 heterodimer nanocrystals, and Fe_3O_4 and γ-Fe_2O_3 powder references.

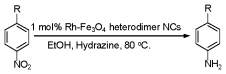
the reduction of RhO_x was observed in the temperature-programmed reduction (TPR) spectrum (Fig. S2, ESI†), confirming that the oxidation state of Rh species is zero.

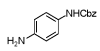
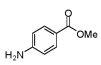
The magnetic properties of Rh–Fe_3O_4 heterodimer nanocrystals were examined by superconducting quantum interference device (SQUID) measurement at 5 K and 300 K (Fig. S3, ESI†). It indicates that the heterodimer nanocrystals exhibit soft ferrimagnetic behavior. It was observed that the heterodimer nanocrystals have a saturation magnetization value of 105.1 emu g^{-1} (Fe) and 95.9 emu g^{-1} (Fe), and a coercivity value of 212.7 Oe and 8.7 Oe at 5 K and 300 K, respectively. A high saturation magnetization value at 300 K demonstrates that the Rh–Fe_3O_4 heterodimer nanocrystals can be used for magnetic separation.

When we tested the catalytic activity of the Rh–Fe_3O_4 heterodimer nanocrystals for the reduction of nitrobenzene using hydrazine, the reaction was finished in 1 h yielding exclusively aniline (Table 1, entry 1). To examine the scope of the reduction reaction using the Rh–Fe_3O_4 heterodimer nanocrystals, we investigated the reduction of structurally diverse nitro compounds. Table 1 shows that the heterodimer nanocrystals have excellent activity for nitro reduction. Arene with more than one nitro group can be reduced with good efficiency; the reduction of 2,6-dinitrotoluene gave 2,6-diaminotoluene as a single product (Table 1, entry 2). The nitro group of nitroarenes with different functional groups was selectively reduced to the amino moiety (Table 1, entries 4–9). No reduction of benzyloxy, *N*-carbobenzyloxy (Cbz), ester, and amide groups was observed by Rh–Fe_3O_4 heterodimer nanocrystals (Table 1, entries 4–7). It is clear that halogen atoms remained intact under the reaction conditions (Table 1, entries 8 and 9). In all cases examined in Table 1, excellent yields of amine products were obtained as exclusive products.

The Rh–Fe_3O_4 heterodimer nanocrystals were easily separated by using a magnet after the reduction of nitrobenzene and reused in the next reaction (Fig. S4, ESI†). It was observed that the catalysts had excellent catalytic activity at least until 8 times of the catalytic reaction (Table 2). ICP results of the

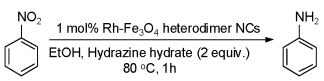
Table 1 Summary on the reduction of various substituted nitrobenzenes



Entry	Substrate	Product	Hydrazine equiv.	Reaction time/h	Yield[a] (%)
1			2	1	99
2			4	2	99
3			4	1	99[b]
4			8	10	99
5			6	5	94
6			6	5	99
7			6	2	97
8			6	1	99[b]
9			6	1	99[b]

[a] Yields of isolated products. [b] Yield was determined by GC analysis.

Table 2 Recycling result on the reduction of nitrobenzene



Run	1st	2nd	3rd	4th	5th	6th	7th	8th
Yield (%)[a]	99	99	99	99	99	99	99	99

[a] All the yields were determined by GC analysis using anisole as an internal standard.

catalyst estimated before the reaction and after 8 cycles were 1.09 wt% and 1.02 wt%, respectively, and no Rh was observed in the filtrate obtained after separating the catalysts in the 1st, 2nd, 4th, 6th, and 8th reactions to the detectable level. These results show no leaching of Rh species during the reaction and recycling. Fig. S5 (ESI†) indicates that the shape and size of catalysts separated after 8 cycles remain almost the same. These results explain the consistently high catalytic efficiency of the catalyst in 8 cycles.

The olefin reductions were also carried out with the Rh–Fe_3O_4 heterodimer nanocrystals, and the results are summarized in Table 3. The catalyst exhibited good catalytic efficiency in the reduction of olefins. The catalyst was also highly chemoselective in the reduction of the double bond. Only the olefinic bonds were reduced without affecting several reducible functional groups including benzyloxy, amide, ether, and ester groups (Table 3, entries 6–9). These results clearly show that the catalyst has remarkable selectivity for the reduction of a variety of nitrobenzene compounds and olefins. As a control experiment, we compared the catalytic activity of

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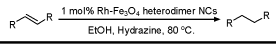
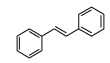
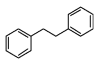
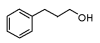
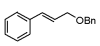
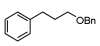
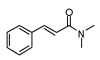
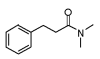
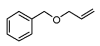
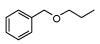
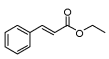
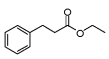
Table 3 Summary on the reduction of various substituted olefins



Entry	Substrate	Product	Hydrazine equiv.	Reaction time/h	Yield[a] (%)
1			10	20	99
2			12	20	99
3			12	22	97
4			8	14	80
5			8	14	99
6			10	23	99
7			8	14	99[b]
8			6	6	90
9			6	20	78

[a] Yields were determined based on GC analysis and ^{1}H NMR integration. [b] Yield of isolated product.

the current catalyst with other related catalysts including Fe_3O_4, Rh_2O_3, and a mixture of Rh_2O_3 and Fe_3O_4. The results (Tables S1 and S2, ESI†) and the initial rate data of the tested catalysts (Fig. S6 and S7, ESI†) show that the Rh–Fe_3O_4 heterodimer nanocrystal catalyst is the most active among the tested catalysts in both nitro and olefin reductions.

In summary, we developed the facile synthesis of Rh–Fe_3O_4 heterodimer nanocrystals using one-pot thermolysis of $M(acac)_3$ (M = Fe, Rh). These heterodimer nanocrystals had excellent catalytic activity and good selectivity for the reduction of nitroarenes and alkenes. The catalyst can be easily separated using a magnet and had good activity until 8 time's recycling.

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