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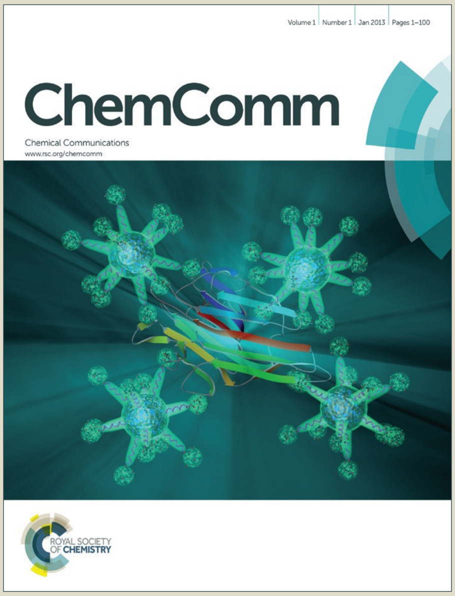

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ARTICLE TYPE

Facile synthesis of Pt@Ir zigzag bimetallic nanocomplexes for the hydrogenation application

Jiaqing Wang,[a] Danhua Ge,[a] Xueqin Cao,[a] Minghua Tang,[b] Yue Pan,*[a] Hongwei Gu*[a]

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Bimetallic Pt@Ir zigzag nanocomplexes were successfully synthesized with uniform morphology by simple reduction of $Ir(acac)_3$ on the surface of Pt nanorods. The novel Pt@Ir nanocomplexes exhibited good catalytic activity in the hydrogenation application under mild conditions, such as the hydrogenation of nitroaromatic compounds. The highest yield of the obtained product achieves ~99.9% using H_2 as the sole reductant.

In recent years, nanomaterials have been extensively studied in academic and applied research because of their interesting properties.[1] Nanostructured materials can exhibit excellent activity and selectivity in catalytic reactions.[2] Hybrid nanomaterials containing well-defined components prepared through solution-growth have attracted much attention.[3] Hybrid bimetallic nanomaterials can exhibit better optical,[4] electriconic[5] and chemical[6] properties than single element-containing nanomaterials due to the incorporation of two distinct nanostructures into a single material.

Pt-based nanomaterials have been extensively studied in recent years.[7] Pt nanowires (Pt NWs) have been used as heterogeneous catalysts for hydrogenation and cross-coupling reactions. Our group has previously reported Pt NWs as efficient catalysts for the controlled hydrogenation of aromatic compounds,[8] N-N coupling,[9] C-N coupling[10] and reductive amidation.[11] Sun et al. synthesized star-like Pt NWs for use in proton exchange membrane (PEM) fuel cells.[12] Sun et al. reported Pt NWs on carbon nanospheres for electrocatalysts in PEM fuel cells.[13] Ir nanostructures have also received much recent interest.[14] Lin et al. reported the high performance of a Ir_1/FeO_x single-atom catalyst in water gas shift reactions.[14(a)] Sarina et al. reported supported nonplasmonic transition metal (Pt and Ir) nanoparticles as photocatalysts under solar irradiation.[14(b)] Li et al. prepared Ir@Pt core-shell nanoparticles supported on high surface area carbon black.[14(c)] These nanomaterial catalysts were all easily separated from the liquid phase, and so could be recycled many times.[15]

Herein, we report hybrid nanostructures of Pt nanorods supporting Ir (Pt@Ir nanocomplexes). To the best of our knowledge, this morphology nanostructure with the same chemical composition has not been reported. Pt@Ir nanocomplexes were prepared by the synthesis of Pt nanorods, and subsequent growth of Ir on the Pt nanorods. Pt@Ir nanocomplexes exhibit good catalytic activity and selectivity when catalysing the hydrogenation of nitroaromatic compounds with H_2 as the sole reductant. The resulting amine compounds ar intermediates in the industrial production of many pharmaceuticals, agrochemicals, dyes, polymers and rubbers.[16]

Scheme 1 shows the formation of the Pt@Ir nanocomplexes. Pt nanorods of average diameter 4 nm and length 50 nm were prepared according to Wang et al,[17] and dispersed in 1 mL of toluene and 10 mL of oleylamine by magnetic stirring. 122.5 mg of Ir(III) acetylacetonate was added, and the temperature was raised to 280 °C for 30 min. The reaction mixture was then cooled to room temperature under Ar atmosphere. Pt@Ir nanocomplexes were precipitated by ethanol and collected by centrifugation. The black precipitate was thoroughly washed with ethanol, and redispersed in hexane for further use.

Scheme 1. The illustration of the formation of the Pt@Ir zigzag nanocomplexes.

The morphologies of the Pt nanorods and Pt@Ir nanocomplexes were characterized by transmission electron microscopy (TEM). Figure 1A shows that the initial Pt nanorods were ~50 nm long and 4 nm wide. A high-resolution TEM image of the Pt nanorods (Figure 1B) shows that their surface was smooth. Pt@Ir zigzag nanocomplexes were prepared by adding $Ir(acac)_3$ to the Pt nanorod solution. Figures 1C and D show the morphology of the Pt@Ir zigzag nanocomplexes. Ir zigzag nanostructures of 3–5 nm in diameter grew on the nanorods to form Pt@Ir nanocomplexes. Energy dispersive X-ray spectroscopy (EDS) indicated a Ir:P ratio of ~56:44 (Figures 1E and S1). EDS spectra recorded at different regions indicated that Ir was uniformly dispersed on the Pt surface.

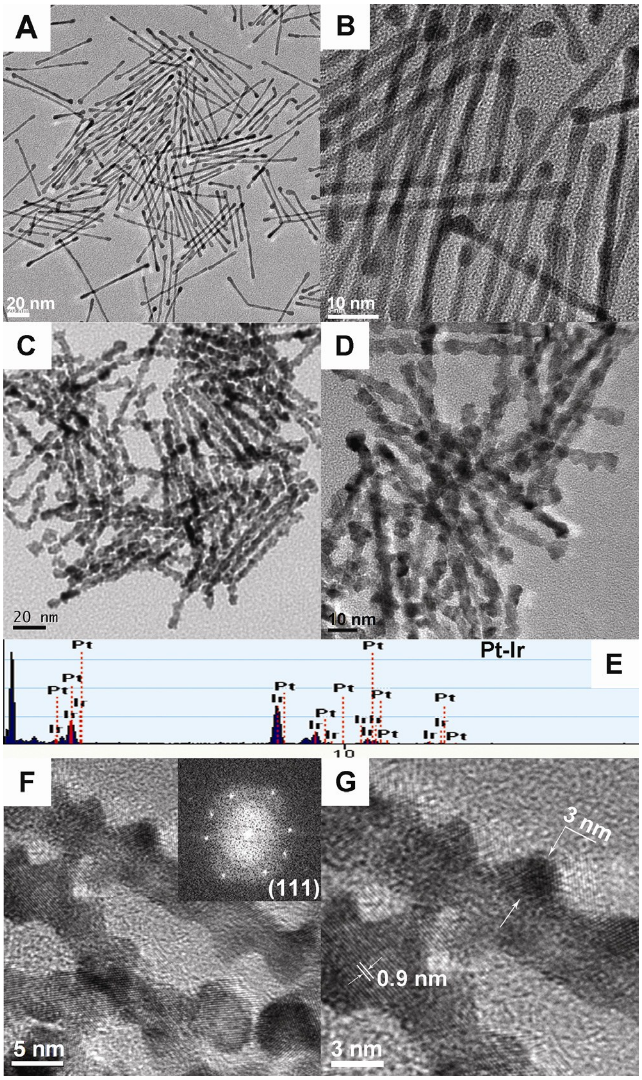


Figure 1. TEM and HRTEM images of the Pt (A, B) and Pt@Ir (C, D) nanocomplexes; EDS analysis of the Pt@Ir nanocomplexes (E); HRTEM images and selected area electron diffraction pattern of the Pt@Ir nanocomplexes (F, G).

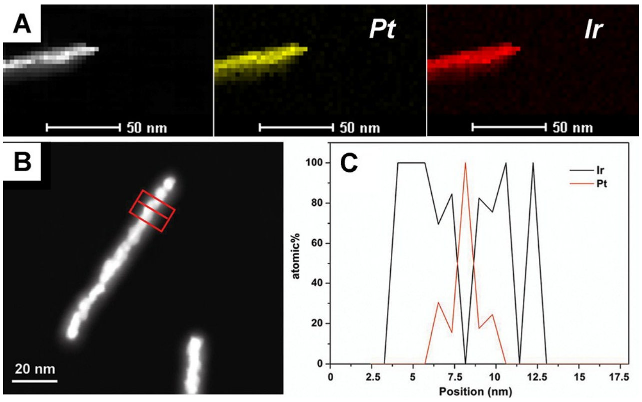


Figure 2. (A) Elemental mapping for the Pt@Ir nanocomplexes; (B) HAADF image of the Pt@Ir nanocomplexes; (C) Cross-sectional elemental composition of the marked area in (B).

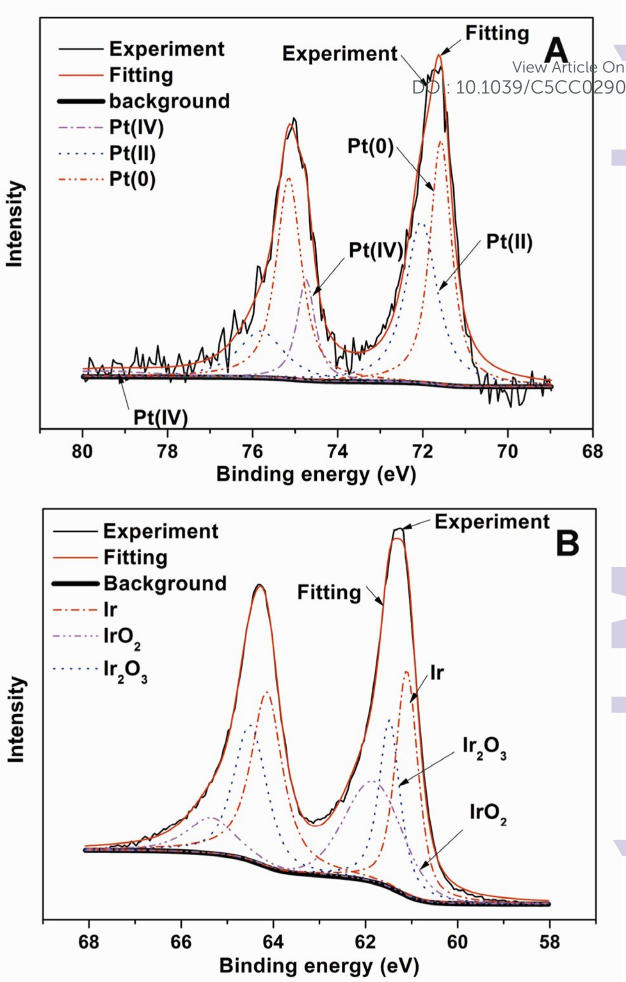


Figure 3. High resolution XPS spectra and fitting of the (A) Pt 4f and (B) Ir 4f (B) spectral regions for the Ir@Pt nanocomplexes.

High resolution EDS mapping using the TEM apparatus was employed to further characterize the nanostructures (Figure 2A). A high-angle annular dark field (HAADF) image is shown in Figure 2B. The cross-sectional elemental profile across the nanostructure indicated that Pt and Ir were well-dispersed, without any observed phase separation (Figure 2C).

The X-ray photoelectron spectra (XPS) of the Pt@Ir nanocomplexes is shown in Figures 3A and B. Figure 3A shows the Pt 4f spectral region, which was deconvoluted into three pairs of doublets.[18(a)] The most intense doublet (71.4 and 75.2 eV) was the Pt (0) signature. The next most intense doublet (72.0 and 75.8 eV) exhibited binding energies (BEs) 0.6 eV higher than those of Pt (0), and was assigned to Pt (II). The weakest doublet exhibited still higher BEs (74.8 and 78.6 eV), and was most likely due to residual surface Pt (IV). Figure 3B shows that the Ir 4f region was also deconvoluted into three pairs of doublets.[18(b)] The most intense doublet at 61.0 and 64.0 eV was due to Ir (0). The corresponding peaks in the XPS spectrum of Ir_2O_3 (61.6 and 64.6 eV) are also shown, and occurred at higher BE than those for Ir (0). Peak shifts to higher BE were expected in the XPS spectrum of IrO_2 (61.8 and 65.4 eV), since Ir had a positive oxidation state in iridium oxide.

Table 1 Hydrogenation of nitrobenzene over Pt@Ir nanocomplexes in different solvents[a]

entry	solvent	T (°C)	t (h)	yield (%)[b]
1	CH_3OH	40	3	85.3
2	C_2H_5OH	40	3	89.5
3	H_2O	40	3	60.1
4	THF	40	17	71.8
5	CH_2Cl_2	40	17	8.5
6	C_2H_5OH	70	3	99.9
7	toluene	80	3	25.1
8	n-heptane	80	3	63.0

[a] Reaction conditions: nitroaromatic compound (1 mmol), solvent (2 mL), sealed H_2 system (1 atm.), Pt@Ir nanocomplexes (2 mg). [b] Determined by GC and GC-MS.

The Pt@Ir nanocomplexes were used as catalysts for the hydrogenation of nitroaromatic compounds using H_2 as the sole reductant. Table 1 shows the catalytic performance of the Pt@Ir nanocomplexes for nitrobenzene in different solvents. Ethanol was the most suitable solvent for high yields of obtained aniline (Table 1, entries 2 and 6). A reaction temperature of 40–70 °C was also found to be very important. Reaction at 70 °C resulted in a yield of 99.9% (Table 1, entry 6). This zigzag nanocomplex catalysts will precipitate within a few minutes in a solvent when quiescent and is therefore easy to recycle upon completion of the reaction (Figure 4).

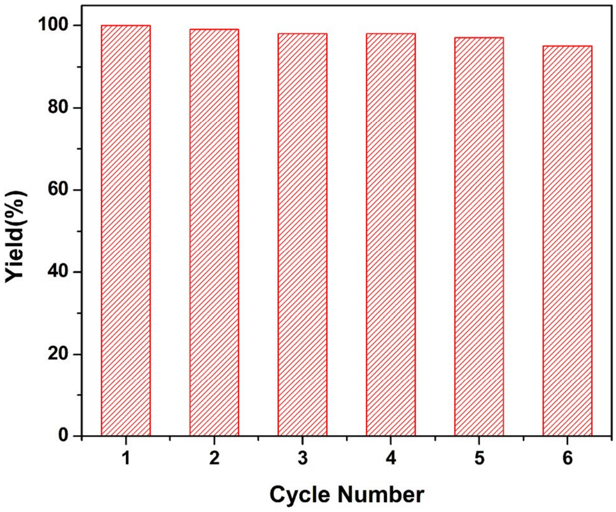
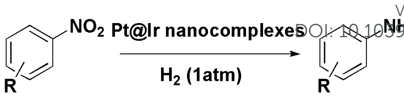
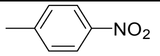
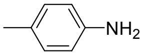
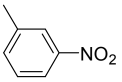
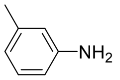
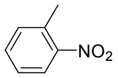
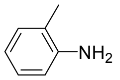
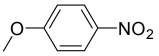
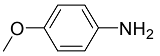
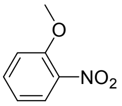
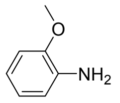
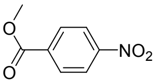
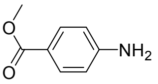
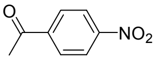
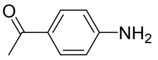
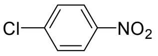
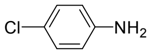


Figure 4. The catalytic stability of Pt@Ir nanocomplexes in the hydrogenation of nitrobenzene in different cycles.

Under the above optimized conditions, treating nitroaromatic compounds with the Pt@Ir nanocomplexes in anhydrous ethanol at 70 °C and 1 atm. H_2 gave good to excellent yields of the corresponding substituted amines. The results are shown in Table 2. Most substrates gave high yields, including *para*-, *meta*- and *ortho*-substituted substrates (Table 2, entries 1–5, 7 and 8). Methyl-4-aminobenzoate was obtained in relatively low yield (Table 2, entry 6) from methyl-4-nitrobenzoate, perhaps due to a low reaction temperature. The reaction conditions were found to be compatible with the functionality of the nitroaromatic compounds. Furthermore, the catalysts have excellent selectivities in carbonyl- and nitro- group. As shown in Table 2, entry 6 and 7, nitro-group could be converted into amino-group, while carbon-oxygen double bonds remained the same.

Table 2 Hydrogenation of nitroaromatic compounds by Pt@Ir nanocomplexes[a]



entry	substrate	product	yield (%)[b]
1			84.7
2			99.1
3			81.8
4			94.6
5			99.0
6[c]			40.2
7			97.2
8			98.7

[a] Reaction conditions: nitroaromatic compound (1 mmol), ethanol (2 mL), sealed H_2 system (1 atm.), Pt@Ir nanocomplexes (2 mg), 70 °C. [b] Determined by GC and GC-MS. [c] $CHCl_3$, 40 °C.

In summary, we here reported a facile approach for the synthesis of Pt@Ir zigzag bimetallic nanocomplexes via simple nucleation. This bimetallic nanomaterial exhibited high catalytic activity for the hydrogenation of nitroaromatic compounds under green reaction conditions. Furthermore, the nanocatalysts were very stable and recyclable after separation from the reaction system. These findings are potential for other bimetallic nanomaterials' synthesis.

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Notes and references

[a] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, P. R. China 215123; Tel:+86-512-65880905;*
Email: panyue@suda.edu.cn; hongwei@suda.edu.cn;
[b] *Analysis and Testing Center, Soochow University, Suzhou, P. R. China.*

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