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Magnetically recyclable hollow nanocomposite catalysts for heterogeneous reduction of nitroarenes and Suzuki reactions[†]

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Highly active magnetically recyclable hollow nanocomposite catalysts with a permeable carbon surface have been prepared by a simple, economical and scalable process. The designed nanocomposite exhibited excellent catalytic activities in the selective reduction of nitroarenes and Suzuki cross-coupling reactions. The catalysts could be easily separated by a magnet, and recycled consecutively.

The fabrication of hollow nanostructures has recently attracted significant attention and has been widely applied in many important research fields such as adsorption and energy storage.¹ Hollow metal nanocapsules provide increased surface area, low density, and selfsupporting capacity compared to their solid counterparts.² Hollow mesoporous structures incorporated with catalytically active nanoparticles (NPs) present powerful catalytic activity and therefore produce promising applications as nanoreactors for catalytic reactions.³ These hollow nanostructures are typically prepared by coating the surface of colloidal particles (e.g., silica or polymer beads) with thin layers of the desired transition metal precursors, followed by selective removal of the colloidal templates through calcination or wet chemical etching.⁴ However, these complicated approaches are not practical from the viewpoint of large scale production which is particularly important for industrial applications. Hollow nanostructure catalysts are generally unstable, and structural collapse occurs after a single use in catalytic reactions causing rapid catalytic activity decay. Furthermore, these catalytic systems require a filtration or centrifugation step or a tedious workup of the final reaction mixture to recover the catalyst.5 Therefore, exploring facile economical methods to prepare stable, scalable, and recyclable hollow nanostructures as catalyst supports is an important issue. A strategy to circumvent this problem is the exploitation of self-assembly processes. Among the various methods of separating catalysts,

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magnetic NPs eliminate the necessity of catalyst filtration after completion of reactions, and offer a convenient approach for recycling catalyst NPs by applying an appropriate magnetic field.⁶

This procedure can prevent the aggregation of the nanocatalyst during recovery, and increase the durability of the catalysts.⁷ Herein, we report an economical and scalable method developed by combining magnetic and hollow structural properties for the synthesis of magnetically recyclable hollow nanocomposite catalysts. The designed nanocomposite catalysts provide excellent catalytic activities for reduction of nitroarenes and Suzuki cross-coupling reactions. The overall synthetic procedure is represented in Scheme 1.

The hollow iron hydroxide nanostructure (β-FeOOH) was prepared by a simple one-pot reaction. A carbon precursor, pyrrole, was introduced in the ongoing reaction and chemically polymerized by palladium(II) nitrate as an oxidant. Then, the magnetically recyclable hollow nanostructure catalyst was prepared via calcination of the synthesized nanocomposites. In a typical synthesis, iron(m) chloride hexahydrate (FeCl₃·6H₂O, 5.4 g) was added to sodium dodecyl sulfate (SDS) solution (400 mL, 0.5 wt% in a 1:1 mixture of water and ethanol). After stirring for 1 h, the resulting mixture was heated to 80 °C for 5 h and stirred for another 12 h at room temperature. To this solution, 0.5 g of palladium(II) nitrate hydrate was directly added without any isolation or washing step. With vigorous stirring, 0.2 mL of pyrrole was added, and the mixture was stirred for 12 h at room temperature. The resulting mixture was filtered and washed to yield a black solid. Then, the sample was heated at a rate of 0.9 $^{\circ}$ C min⁻¹ to 300 °C under an Ar atmosphere and maintained at that temperature for 5 h. Finally the product was calcined at 200 °C for 2 h under hydrogen gas flow to produce the highly active magnetically recyclable hollow nanocomposite Pd catalyst.

The intermediate and final products were characterized using transmission electron microscopy (TEM), and X-ray diffraction



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(XRD). The low- and high-resolution TEM images of iron hydroxide nanostructures (Fig. S1a and b, ESI[†]) show that they are spherical with diameters ranging from 300 nm to 500 nm with hollow interiors. As shown in Fig. S2a and b, ESI[†], the TEM image of the Pd NPs on the magnetically recyclable hollow nanocomposite reveals that they are loaded uniformly with an average size of \sim 3 nm on the carbon shell. The field emission-scanning electron microscopy (FE-SEM) image also demonstrates the hollow interior of the nanocomposite with a rough surface (Fig. S3, ESI[†]).

The carbon coating with a thickness of ~ 25 nm keeps the hollow nanocomposite stable from structural collapse during the calcination step and catalytic reactions. In addition, the porous carbon layer is permeable to organic reagents and improves the diffusion of substrates/products. Nitrogen-containing carbon also enhances the interaction between catalyst NPs and the carbon surface. The welldefined carbon matrix can serve as a shield and stabilize catalyst NPs for maintaining their activity under harsh reaction conditions such as temperature alteration, stirring and shaking.⁸ TEM studies show that aggregation of Pd NPs is inevitable if they are directly loaded on a hydroxide platform (Fig. S4, ESI⁺). CHN elemental analysis provided the composition of C (19%), and N (4.1%). The microtomesectioned TEM images of the hollow nanocomposite catalyst (Fig. 1) clearly show the hollow interior and Pd NPs on the carbon layer. The XRD patterns (Fig. S5, ESI⁺) revealed that β -FeOOH was transformed to magnetite through the calcination. The magnetic behavior of the nanocomposite catalyst was investigated using a superconducting quantum interference device (SQUID) magnetometer. The fielddependent magnetization curve at 300 K represents superparamagnetic characteristics (Fig. S6, ESI⁺). The existence of Pd NPs in the hollow nanocomposite was confirmed using X-ray photoelectron spectroscopy (XPS) analysis (Fig. S7, ESI⁺). Energy-dispersive X-ray spectroscopy (EDX) data ascertained the composition of the magnetically recyclable hollow nanocomposite catalyst (Fig. S8, ESI⁺). The nitrogen adsorption-desorption isotherms and pore size distributions (Fig. S9, ESI⁺) of the hollow nanocomposite catalyst reveal the slit shaped pores between plate-like particles in the Fe₃O₄ layer, which are identified in TEM images (Fig. 1a and b). The BET surface area and total pore volume of the nanocomposite are 77.4 $m^2 g^{-1}$ and 0.3405 cm³ g⁻¹, respectively. Considering the high density of iron oxide, the designed hollow nanocomposite provides a high surface area and accommodates a large amount of small Pd catalyst NPs, thus making the catalyst highly active.

To verify the potential and efficiency of the designed nanocomposite as an active catalyst, the Suzuki cross-coupling reaction was chosen as a model reaction.⁹ The Pd loading on the nanocomposite,



Fig. 1 Low (a) and high (b) resolution TEM images of the sectioned magnetically recyclable hollow nanocomposite catalyst.

measured by ICP-AES, was found to be ~ 1.7 wt%. We first investigated the use of various solvents in order to find the most appropriate conditions for the heterogeneous Suzuki coupling of iodobenzene with phenylboronic acid using 1 mol% of the Pd catalyst. The yield of reaction proved to be significantly solventdependent, with 3:1 volume ratio of DMF-H2O giving the best results (Table S1, ESI⁺). To extend the scope of this heterogeneous catalytic reaction, we screened the coupling of several representative arylhalides with phenylboronic acid under the optimized conditions. As shown in Table 1, the reaction of aryliodides and bromides with phenylboronic acid gave almost quantitative yields in 1.5 and 4 h, respectively. The nanocomposite Pd catalyst presented higher catalytic activity than the commercially available Pd/C catalyst with polydisperse particle size distribution (Fig. S10, ESI⁺). The commercial catalyst provided a much lower yield (39%) when it was used in the Suzuki reaction of iodobenzene with phenylboronic acid under identical reaction conditions. We further examined the reactions of various arylboronic acids with iodobenzene in DMF-H2O (Table S2, ESI[†]). The reactions proceeded readily to afford the respective biaryls with high yields within 1.5 h. The hydrolysis of arylboronic acids generally occurs in Suzuki cross coupling reactions and causes decrease in the product yields.¹⁰ However, the reactions of the arylboronic acids with iodobenzene using the nanocomposite Pd catalyst were performed successfully in DMF-H₂O.

The designed magnetically recyclable nanocomposite can be easily used as a general platform to load other noble metal catalyst NPs

R \xrightarrow{r} X + \xrightarrow{r} B(OH) 2 Catalyst R \xrightarrow{r} Catalyst R \xrightarrow{r}					
Entry	Aryl halides	Product	Time (h)	Yield ^b (%)	
1		\sim	1.5	97	
2			1.5	96	
3		$\bigcirc - \bigcirc$	1.5	93	
4	H ₃ CO	H3CO-	1.5	92	
5	\mathbf{v}'	$\rightarrow \sim$	1.5	93	
6	t-Bu	t-Bu	1.5	91	
7	€ Br	$\bigcirc - \bigcirc$	4	97	
8	L Br		4	95	
9	C	$\bigcirc - \bigcirc$	4	91	
10	Ç ₽ ^{Br}	$\bigcirc - \bigcirc$	4	93	
11	NC		4	95	
12	P ^{Br}	$\supset -\bigcirc$	4	92	

 Table 1
 Heterogeneous
 Suzuki
 cross-coupling
 reaction
 of
 aryl
 halides
 with
 phenylboronic acid^a

^{*a*} Aryl halides (0.5 mmol), phenylboronic acid (0.6 mmol), Pd catalyst (1 mol%), K_2CO_3 (2 mmol), DMF-H₂O (3:1), 100 °C. ^{*b*} The yields were determined by gas chromatography mass spectrometry (GC-MS) analysis using internal standard (decane).

Table 2 Heterogeneous reduction of substituted nitrobenzene with hydrazine^a

$R \xrightarrow{r} NO_2 \xrightarrow{Catalyst} R \xrightarrow{r} NH_2$					
Entry	Aryl halides	Product	Yield ^b (%)		
1	C NO2	\bigcirc ^{NH₂}	99		
2	CI NO2	CI NH2	99		
3	Br NO2	Br NH2	98		
4	NO ₂	NH ₂	99		
5	HO NO2	HO NH2	94		
6	NO ₂	NH ₂	95		
7	\bigcap^{NO_2}	\bigcap^{NH_2}	91		

 a Reaction conditions: 0.5 substituted nitrobenzene, hydrazine (2 equiv.), Rh catalyst (1 mol%), EtOH, 80 °C, 2.5 h. b The yields were determined by GC-MS using an internal standard.

 Table 3
 Magnetic separation and recycling of the catalyst in heterogeneous reduction of nitrobenzene with hydrazine^a



 a Reaction conditions: 0.5 nitrobenzene, hydrazine (2 equiv.), Rh catalyst (1 mol%), EtOH, 80 °C, 2.5 h. b The yields were determined by GC-MS using an internal standard.

such as rhodium, which can be utilized for reduction of nitro compounds to amines. The reduction of nitro aromatics is an important chemical reaction because organic amines are intermediate materials for the production of pharmaceuticals and polymers.¹¹ We synthesized a magnetically recyclable nanocomposite with a Rh catalyst using a similar approach to prepare a nanocomposite Pd catalyst. TEM images of this catalyst show that Rh NPs are uniform with an average size of ~ 2 nm (Fig. S11, ESI⁺). The EDX of the nanocomposite Rh catalyst indicates that the Rh species are successfully immobilized on the nanocomposite (Fig. S12, ESI⁺). The presence of Rh NPs on the nanocomposite was verified using XPS analysis (Fig. S13, ESI[†]). We investigated the catalytic activity of the Rh catalyst in the reduction of structurally diverse nitro compounds. Table 2 confirms that the Rh nanocrystals show excellent activity in nitro reduction. Although the selective reduction of a nitro group in organic compounds containing other reducible functional groups is a challenging reaction, the nitro group of nitroarenes with different functional groups using the nanocomposite Rh catalyst was selectively reduced to the amino moiety (Table 2, entries 2-5). The halogen functional groups remained intact under the reaction conditions. We investigated magnetic separation and recycling of the nanocomposite Rh catalyst, which was successfully reused for five consecutive cycles of the reduction of nitrobenzene with no major loss of activity (Table 3). Upon completion of the reaction, the catalyst was easily separated using a magnet, and reused in the next reaction.

When we examined the magnetic separation and durability of the Pd catalyst in the Suzuki coupling of bromobenzene with phenylboronic acid (Table S3, ESI[†]), there was a small decrease in the activity after each recycling of the catalyst. The viscosity of DMF used as solvent in Suzuki coupling is lower than EtOH. Therefore, the small decline of catalytic activity seems to result from incomplete magnetic separation of the catalyst during the consecutive recycling. The ICP-AES analysis showed that 2.1% of Pd species remained in the reaction solution. The magnetically recyclable hollow nanocomposite catalyst can be readily synthesized on a large scale using a simple process. For example, when larger amounts of starting materials (\times 5) were used, \sim 2.3 g of the nanocomposite catalyst could be obtained by one batch synthesis (Fig. S14, ESI[†]).

In conclusion, we have described a highly active magnetically recyclable hollow nanocomposite catalyst prepared by a simple, economical, and scalable synthetic process. The designed nanocomposite with a high surface area accommodates large amounts of small catalyst NPs providing high catalytic activity. Variable catalyst NPs such as Pd, Pt, and Rh can be loaded on the nanocomposite for different catalytic reactions. The efficiency of the nanocomposite was verified in reduction of nitroarenes and Suzuki reactions providing excellent yields. The magnetic properties of the nanocomposite can be readily utilized for the easy recovery and recycling of the catalyst. The catalysts could be reused for five consecutive cycles in reduction of nitrobenzene and Suzuki coupling of bromobenzene.

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