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MINIREVIEW

Magnetically recyclable nanocatalysts (MRNCs): a versatile integration of high catalytic activity and facile recoveryDonghui Zhang,^a Chao Zhou,^a Zhenhua Sun,^b Li-Zhu Wu,^a Chen-Ho Tung^a and Tierui Zhang^{*a}

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Recent advances in wet chemical synthesis of magnetically recyclable nanocatalysts (MRNCs), a versatile integration of high catalytic activity and facile recovery, have led to a dramatic expansion of their potential applications. This review focuses on the recent work in the development of metal and metal oxide based MRNCs for catalytic conversion of organic compounds in solution phase. This will be discussed in detail, according to the two main synthesis methods of MRNCs as classified by us. The two methods are: template-assisted synthetic strategy and direct synthetic strategy. And the template-assisted synthesis is further divided into three subcategories, synthetic strategies assisted by hard-, soft-, and mixed hard-soft coupling layers. At the end, we outline future trends and perspectives in these research areas.

1. Introduction

Recent advances in nanoscience and nanotechnology have led to an enormous number of publications dealing with the discovery and potential applications of nanostructured catalysts in various fields, *e.g.* petroleum, chemical and food processing, nuclear energy, and environmental improvement.^{1–3} These

nanostructured catalysts are usually composed of clusters of atoms, often metals or metal oxide, with particle size varying between 1 and 50 nm. These catalysts represent a new frontier between homogeneous and heterogeneous catalysis and are often regarded as “quasihomogeneous” (or soluble heterogeneous) catalysts.⁴ The beneficial effects of nanostructured catalysts, in terms of enhanced activity, selectivity, resistance to deactivation, and prolonged lifetime of the catalysts have been extensively documented.^{5–7}

However, even though the main focus of catalysis research has been to enhance catalytic activity and selectivity, the recovery and reuse of nanocatalysts by traditional

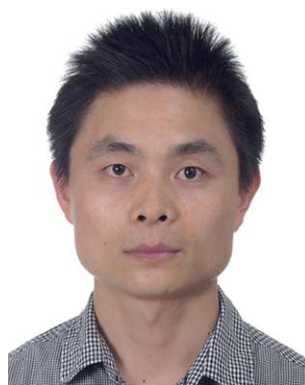
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centrifugation and filtration methods have been given serious consideration due to the ever-growing demands for improving sustainability.^{2,8–10} Towards this end, tremendous efforts have been made in impregnating nanocatalysts on a large variety of conventional supports. However, the sustainable separation and reuse of the nanocatalysts remains a grand challenge.⁸

To meet the long, unmet challenge, magnetically recyclable nanocatalysts (MRNCs) have been studied recently to employ superparamagnetic materials as both catalysts and catalytic supports.^{11–15} The MRNCs possess high surface area, high catalyst loading capacity, high dispersion, high stability, and facile catalyst recyclability and reusability in an external magnetic field. More importantly, the fabrication of MRNCs is generally simple, scalable, safe, cost-effective, and controllable.^{15,16} Recently, several reviews have been dedicated to the general introduction of the recent research progress of

MRNCs^{15–19} leaving a growing need for categorizing the vastly updated synthesis, modifications and applications of MRNCs reported to date, all in order to help us plan new studies in future.

To provide a succinct overview on the recent research progresses and future developments of metal and metal oxide-based MRNCs, this review is organized as follows. First, we will summarize the controllable synthesis of the metal and metal oxide-based MRNCs. According to the types of coupling layers for combining the nanocatalysts with the magnetic components, we will classify the synthetic strategies into two main families: (1) template-assisted synthesis and (2) direct synthesis. And the template-assisted synthesis is further divided into three subcategories, synthetic strategies assisted by hard-, soft-, and mixed hard–soft coupling layers; on this basis, the naturally deduced perspectives on the future work in this field will be discussed.



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2. Template-assisted synthesis strategies

2.1 Synthetic strategies assisted by hard coupling layers^{13,14,20–35}

Robust materials such as silica,^{13,20–24} carbon^{25–33} and polymer^{14,34,35} as coupling layers are often used in the preparation of MRNCs. We call this kind of synthesis “hard coupling layer assisted synthetic strategy”. The hard coupling layers can provide anchoring sites for nanocatalysts or precursors of nanocatalysts to support them, and combine both superparamagnetic components and nanocatalysts.

2.1.1 Silica-based hard coupling layers.^{13,20–24,36–54} Silica is an ideal robust coupling layer material to integrate nanocatalysts and magnetic components because of its excellent chemical affinity and thermal stability.⁵⁵ Moreover, among silica-based coupling layers, porous silica can not only be easily prepared but can provide large surface areas for loading a great number of nanocatalysts and/or act as a protective shell to prevent catalysts from leaching.^{56–60} As such, it is frequently used in assisting in the fabrication of various MRNCs.

In 2007, Hyeon and colleagues reported the preparation of MoO₂-based MRNCs by making use of both solid and mesoporous silica shells as hard coupling layers.¹³ As-synthesized hematite was first covered by a dense layer of silica and then a mesoporous shell of silica in sequence through a sol–gel process. Afterwards, MoO₂ was introduced into the mesoporous layer by impregnation with ammonium molybdate followed by H₂ reduction. The hematite core was transformed simultaneously into magnetite during the course of reduction (Fig. 1a). The excellent catalytic performances of MoO₂-based MRNCs were revealed by an epoxidation reaction of *cis*-cyclooctene (Fig. 1b). Slight decreases of catalytic activity were observed after several cycles of catalysis managed by an external magnetic field. This could have been caused by either incomplete harvest of MRNCs or a slight leaching of active catalytic species. Under otherwise identical conditions, the conversion of *cis*-cyclooctene catalyzed by the MoO₂-based MRNCs only with a dense layer of silica is much lower than that of the MoO₂-based MRNCs with mesoporous silica coating. This is due to the distinct difference in silica surface area. A similar design philosophy has been successfully

put into practice by Yin *et al.* in the preparation of core-satellite like Fe₃O₄/SiO₂/Au/*m*-SiO₂ MRNCs which showed superior catalytic performances for the hydrogenation of *p*-nitrophenol (Fig. 2).²²

The obvious advantages of this protocol are as follows: (1) magnetic cores are fully protected by the solid silica outer layer against the external environment so that MRNCs can be applied in relatively severe reaction conditions (strong acidic, strong oxidizing, *etc.*); (2) the aggregation and leaching of catalytic active species can be effectively inhibited by the outmost layer porous silica; (3) the porous silica layer provides passing channels for the entering of substrates and the leaving of products.

TiO₂ is the first and also the most studied photocatalyst adopted to combine with magnetic materials as recyclable photocatalysts for water splitting or degradation of pollutants.^{47,61} However, direct contact of TiO₂ with magnetic components can result in the photodissolution of magnetic components under light irradiation.^{48–50} In order to solve this problem, silica employed as an insulator layer and the coupling layer was implanted between photocatalytic active TiO₂ and magnetic components to inhibit charge transfer between magnetic components and TiO₂. In these studies,^{20,21,23,47,61} the general synthesis process is as follows: magnetic nanoparticles were first synthesized by wet-chemical methods such as co-precipitation, thermal decomposition, sol–gel, *etc.* Afterwards, silica as a coupling layer was coated on magnetic particles through modified Stöber methods. Lastly, TiO₂ encapsulation was achieved *via* a sol–gel process. Interestingly, in some cases the silica coupling layer also can improve the photocatalytic efficiency of TiO₂ probably owing to a higher surface acidity.^{20,23}

Another obvious advantage of silica coating on magnetic materials is that the silica layer can be conveniently functionalized with various silane coupling agents with rich functional groups, which in turn provides vast opportunities for coupling nanocatalysts of various types.^{22,57–59} This approach is named mixed hard and soft coupling layer assisted synthetic strategy and will be discussed in part 4.

2.1.2 Carbon-based hard coupling layers.^{25–33,62–65} Some properties of carbon are very similar as those of silica such as

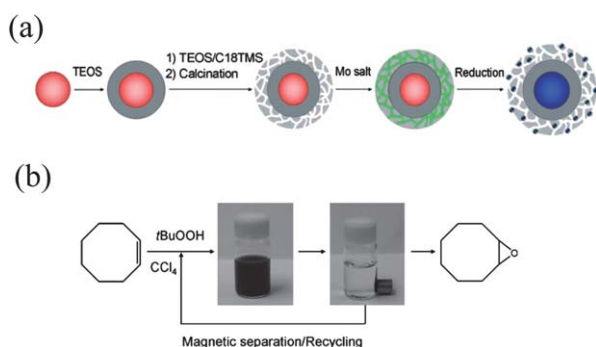


Fig. 1 (a) Synthesis procedure of MoO₂-based MRNCs; (b) schematic illustration of magnetic separation and recycling of MoO₂-based MRNCs. Reprinted from ref. 13 with permission. Copyright (2007) John Wiley & Sons.

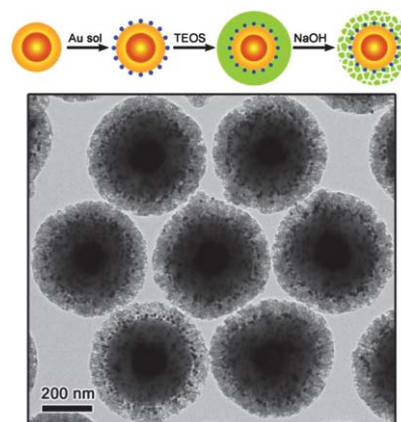


Fig. 2 Synthesis procedure and a typical TEM image of core-satellite like Fe₃O₄/SiO₂/Au/*m*-SiO₂ MRNCs. Reprinted from ref. 22 with permission. Copyright (2008) John Wiley & Sons.

inertness and stability. Therefore, carbon can also serve as a robust hard coupling layer in the preparation of MRNCs.^{25–33,62–65} The carbon with functional groups, such as –OH and –COOH on the surface is ordinarily obtained by the carbonation of organic precursors at high temperature. These functional groups are very beneficial for the subsequent anchoring of catalytic active species and/or magnetic components.

de Groot and colleagues reported a Pd-based MRNC with carbon as a coupling layer.²⁸ Magnetic FeNi alloy was first deposited on γ -Al₂O₃ by reducing a γ -Al₂O₃/NiFe-oxide composite in H₂ flow. Carbon encapsulation was achieved by treating the γ -Al₂O₃/NiFe alloy in a mixture of methane/Ar at more than 700 °C, followed by a removal of Al₂O₃ and any nm Pd nanoparticles were immobilized to the outside of magnetic FeNi@C composites by incipient wetness impregnation and incomplete covered particles with an acid treatment. Finally, 5 nm Pd nanoparticles were immobilized to the outside of magnetic FeNi@C composites by incipient wetness impregnation and hydrogen reduction. However, magnetic properties and catalytic performances were not indicated.

Some other robust hard coupling layers, including hydroxyapatite,^{66–70} layered double hydroxides,⁷¹ and Al₂O₃,⁷² have also been studied for the multifunctional coating on the surface of magnetic Fe₃O₄ to load nanocatalysts for new-typed MRNCs.

2.1.3 Polymer-based hard (semi-soft) coupling layers.^{14,34,35,73,74} Robust polymers with abundant functional groups, such as carboxylated polypyrrole, poly(styrene-acrylic acid) (PSA), poly(ethyleneglycol dimethacrylate), *etc.*, have been widely used in the design and synthesis of novel type MRNCs. This is mainly because of the strong affinities of those functional groups with magnetic components and catalytic species, as well as their facile elimination by post treatment.^{14,34,35,73,74}

Ko and Jang prepared a Pd-based MRNC with the assistance of a carboxylated polypyrrole buffer layer.³⁴ The carboxylated polypyrrole nanotube was formed by vapor deposition polymerization of pyrrole-3-carboxylic acid monomers catalyzed by Fe³⁺ adsorbed on to an anodic aluminum oxide template. The subsequent template removal treated with NaOH led to the transformation of Fe³⁺ to magnetite nanoparticles embedded in the polymer. Pd precursors were then immobilized onto the polymer by strong electrostatic interactions. Finally small Pd nanoparticles bounded on magnetic polymer nanotube were obtained by H₂ reduction (Fig. 3). Here, Fe³⁺ acted as both a catalyst for polymerization and a precursor of magnetite. The pyrrole-3-carboxylic acid played a dual role in being the polymer precursor and providing strong anchoring sites for Pd nanoparticles.

The Pd-based MRNCs showed very high catalytic activity in the olefination of both activated and non-activated aryl iodides with yields all around 100%. The yield for the olefination of non-activated aryl iodides was about two times higher than that of conventional carbon-based Pd catalysts. This could be ascribed to the high surface area of Pd nanoparticles with abundant edge and vertex sites. Both the catalytic activity and morphology of Pd-based MRNCs were maintained due to the strong interaction between carboxylate groups of the polymer coupling layer and Pd nanoparticles after five tests of recycle and reuse. The

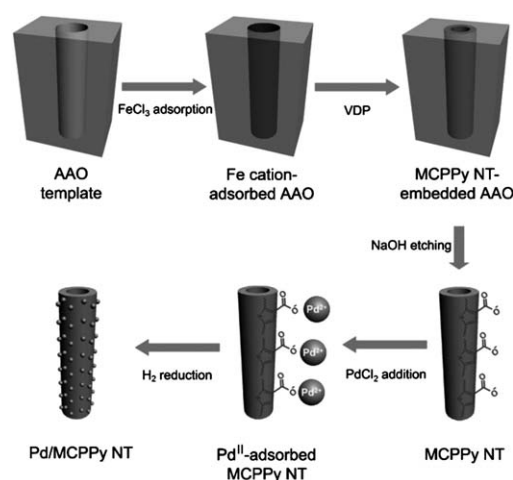


Fig. 3 Synthesis procedure for Pd-based MRNCs. Reprinted from ref. 34 with permission. Copyright (2006) John Wiley & Sons.

Pd-based MRNCs exhibited a strong magnetic response and could be rapidly separated from the suspension within 10 s by an external magnet.

The sacrificial template effect is another advantage of robust polymers as coupling layers. Its effect has been explored in the fabrication of hollow recyclable magnetic photocatalysts for the high efficient decomposition of organic dyes by Hu *et al.* (Fig. 4).¹⁴ Specifically, PSA latex spheres were chosen as a hard template to support Fe₃O₄ particles produced *via* partial reduction of Fe³⁺. TiO₂ was then coated on the surface of PSA/Fe₃O₄ nanocomposites *via* a modified sol–gel process. Subsequently, well-crystallized hollow Fe₃O₄/TiO₂ hybrid spheres were obtained by a sequential dissolution of the PSA core and a sol–thermal treatment.

The Fe₃O₄/TiO₂ MRNCs are superparamagnetic originating from the small-sized magnetite components. The saturation magnetization is as high as 12.8 emu g^{−1} at room temperature. It makes the magnetic separation of MRNCs feasible to complete in 30 s by simply applying an external magnetic field. The hollow magnetic catalysts showed higher catalytic activity than the solid TiO₂ spheres and P25 due to the higher surface area of hollow structures. However, lower photocatalytic degradation efficiency was observed for Fe₃O₄/TiO₂ MRNCs as compared with TiO₂

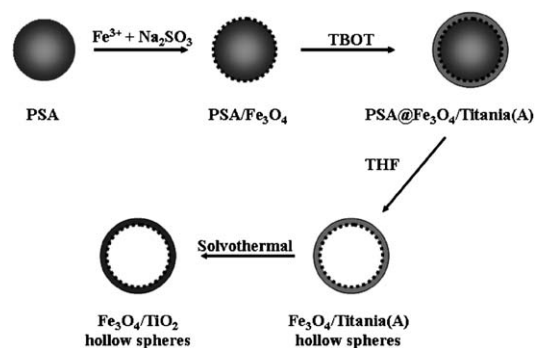


Fig. 4 Synthesis procedure for hollow spherical magnetic Fe₃O₄/TiO₂ photocatalysts (A: amorphous). Reprinted from ref. 14 with permission. Copyright (2009) American Chemical Society.

hollow spheres reported previously. This was generally attributed to the photodissolution of magnetic components.^{48–50} Although the catalytic activity can maintain 93% after six cycles of photocatalytic reactions, the efficiency of decolorization gradually decreased, which could be attributed to both the continual photodissolution and the incomplete magnetic separation of the catalysts.

2.2 Synthetic strategies assisted by soft coupling layers^{75–89}

As compared with hard coupling layer materials mentioned above, soft organic molecules with multiple functional groups such as $-SH$, $-COOH$, $-OH$, $-NH_2$ and pyrrole ring^{75–89} can be more easily attached to the surface of magnetic components as well as catalytic active species *via* covalent bond, coordination bond, electrostatic interaction, and so forth. It is our position that the rational selection and combination of different types of soft organic molecules can lead to a high efficient integration of magnetic components and nanocatalysts.

Dopamine and their derivatives, with two neighboring hydroxyl groups and one amino group, have been proven to be excellent soft molecules in assisting the preparation of MRNCs.^{75,76} In 2009, Varma *et al.* prepared a Ni-based MRNC with the aid of 3-hydroxytyramine.⁷⁶ Magnetic Fe_3O_4 nanoparticles were obtained by co-precipitation. These were then functionalized with dopamine through the strong anchoring effect of neighboring hydroxyl groups. Ni nanoparticles were subsequently formed by the reduction of Ni^{2+} coordinated with amino groups (Fig. 5a). The inexpensive Ni-based MRNCs showed very good catalytic performances towards hydrogenation of alkynes and transfer hydrogenation of ketone which are usually catalyzed by precious metals Pt and Pd. After five times of recycle and reuse tests, the Ni-based MRNCs still performed well and only negligible Ni nanoparticles fell off due to the strong interaction between soft organic coupling layers and Ni nanoparticles (Fig. 5b).

A similar synthetic route has been adopted by the same authors in the synthesis of ruthenium hydroxide based MRNCs for the hydration of nitriles in a mild aqueous solution.⁷⁷ Likewise, the MRNCs were magnetically recovered and reused for three times with no obvious decrease of catalytic activity.

The soft organic molecule with phosphate functional groups has been studied by Zhu *et al.* in immobilizing ultra-small Pd nanocatalysts on a magnetic support.⁸¹ Pd^{2+} can be strongly absorbed by phosphate groups *via* electrostatic interactions and subsequently reduced into less than 1 nm Pd nanoparticles (Fig. 6). The Pd nanoparticles were well dispersed on the surface of about 5 nm magnetic cores, which endowed the Pd-based MRNCs with high surface area and thus exhibited high catalytic activities.

For a Suzuki cross-coupling reaction between bromobenzene and phenylboronic acid, the production yield obtained from Pd-based MRNCs is higher than that from a catalyst composed of a homogeneous Pd(II) complex grafted on a magnetic support.⁹⁰ No obvious aggregation of Pd nanoparticles in MRNCs was detected after three cycles of catalytic reactions because of the presence of soft coupling layers with strong anchoring groups phosphate which improve the stability of Pd nanoparticles. For a Heck coupling reaction between bromobenzene and styrene, a

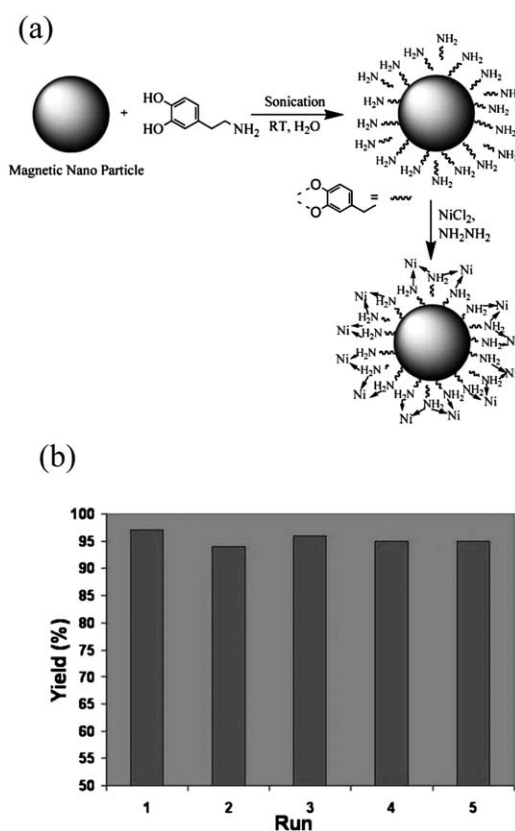


Fig. 5 (a) Synthesis procedure, and (b) recyclability and reusability of Ni-based MRNCs. Reprinted from ref. 76 with permission. Copyright (2008) Royal Society of Chemistry.

higher production yield was obtained as compared with nano-Pd(0) catalysts on other supports (MgO , ZrO_2 and TiO_2).⁹¹ Positive support effect of magnetic components was supposed to be responsible for the enhanced yield although solid data was not obtained.

Citric acid, with three $-COOH$ groups, has been employed as soft coupling layers in the preparation of TiO_2 -based MRNCs by Tyrpekl and colleagues for the decomposition of organic impurities. The surface zeta-potential of $\gamma-Fe_2O_3$ nanoparticles was first modified by citric acid, and were then coated by TiO_2 through heterogeneous nucleation.⁸² The use of soft coupling layer makes the procedure more environmentally benign and also

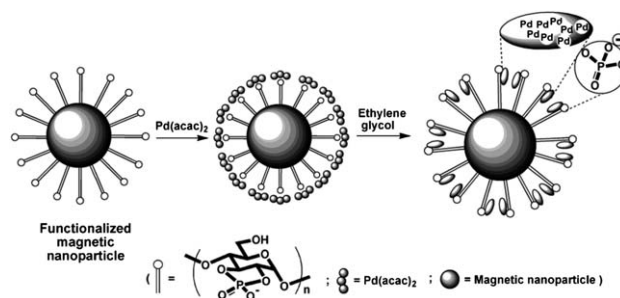


Fig. 6 Synthesis procedure of Pd-based MRNCs using organic molecules with phosphate groups as a coupling layer. Reprinted from ref. 81 with permission. Copyright (2007) John Wiley & Sons.

minimizes the production costs. The $\gamma\text{-Fe}_2\text{O}_3\text{@TiO}_2$ MRNCs exhibited high photocatalytic performances in the degradation of chlorophenol, but the recycling and reusing ability of MRNCs was not shown.

Besides organic molecules mentioned above, ionic liquid,⁷⁹ polyelectrolyte,^{80,85} chitosan,⁸⁹ *etc.* were also studied as soft coupling layers in the preparation of novel type MRNCs.

2.3 Synthetic strategies assisted by mixed hard-soft coupling layers^{22,57–59,90–112}

Most of the time hard and soft coupling layers were used together for the convenient fabrication of MRNCs. The hard coupling layers mainly serve as a protective shell for magnetic components, while the soft coupling layers with multiple functional groups act as anchoring sites for catalytic active species.^{22,57–59,90–112}

The most frequent used combination of hard and soft buffer layers is silica and silane coupling agents or polymers. Hyeon *et al.* demonstrated an ingenious combination of hard and soft coupling layers for the fabrication of MRNCs (Fig. 7a).⁹⁰ Magnetic Fe_3O_4 nanoparticles were attached onto the surface of silica spheres through the nucleophilic substitution reaction between (3-aminopropyl)trimethoxysilane and 2-bromo-2-methylpropionic acid. The residual amino groups on the surface of silica spheres were ideal anchoring sites for nanoparticles such as catalytic active Pd (Fig. 7b).

High yields of aryl substituted phenyl acetylene, no less than 95%, were obtained by catalyzing the Sonogashira coupling reactions between several aryl iodides or aryl bromides and phenylacetylene using Pd-based MRNCs. However, the Pd-based MRNCs were not robust enough so that the abrupt decrease of catalytic activity from 99.5% to 16.9% was observed in the first four cycles of catalytic experiments due to the detachment of Pd nanoparticles.

Yin's group took use of silica nanoparticles, thermosensitive polymer and silane coupling agent as hard and soft coupling layers for the synthesis of Au-based MRNCs.⁹¹ In their preparation, $\text{Fe}_3\text{O}_4\text{@silica}$ core and satellite silica nanoparticles were held together by poly(*N*-isopropylacrylamide) (NIPAM). Thereafter, with the assistance of 3-aminopropyl-triethoxysilane Au nanoparticles can be easily loaded on the surface of satellite silica particles (Fig. 8). The reduction of 4-nitrophenol was taken as a model catalytic system to demonstrate the catalytic performances of Au-based MRNCs. The conversion of 4-nitrophenol into 4-aminophenol proved excellent because of the high density loading of Au nanocatalysts. There was almost no change after eight cycles of catalytic experiments. The decreased conversion was observed only after about ten cycles likely due to the gradual loss of catalytic assemblies with repeated magnetic separation.

Ying *et al.* demonstrated the combination of silica and 3-mercaptopropyl-trimethoxysilane (MPS) or *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPS) as hard and soft coupling layers, respectively, for the fabrication of Pd-HS-SiO₂/Fe₂O₃ and Pd-H₂N-SiO₂/Fe₂O₃ MRNCs, taking advantage of the strong affinity between -NH₂ or -SH and transition metal nanoparticles to provide for higher nanoparticles dispersion.⁹² The AAPS soft coupling layers might have stronger affinity with Pd nanoparticles than MPS soft coupling layers to more

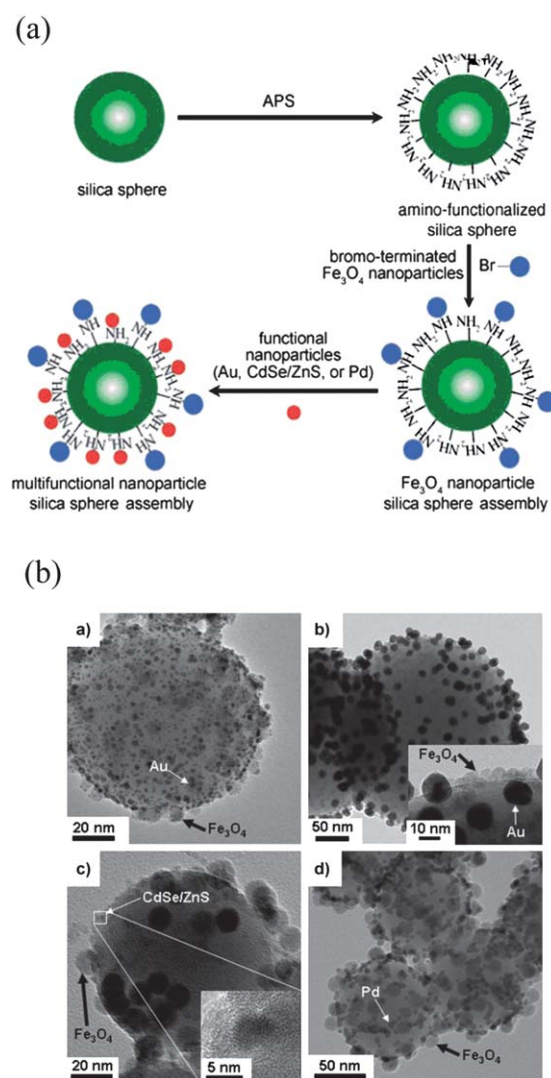


Fig. 7 (a) Synthesis procedure and (b) TEM images of multifunctional magnetic nanocomposites. Reprinted from ref. 90 with permission. Copyright (2006) John Wiley & Sons.

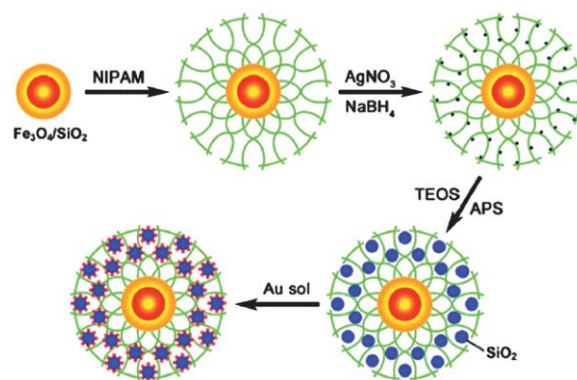


Fig. 8 Schematic illustration of the synthetic procedure of Au-based MRNCs. Reprinted from ref. 91 with permission. Copyright (2008) American Chemical Society.

effectively suppress the agglomeration, aggregation, and growth of Pd nanoparticles, which resulted in better catalytic performances of Pd–H₂N–SiO₂/Fe₂O₃ MRNCs during the test of recycling and reuse for the catalytic hydrogenation of nitrobenzene.

Besides the combination of silica and soft organic molecules, the combination of carbon and soft organic molecules with carboxyl groups was also proven to be very effective in the fabrication of robust MRNCs.⁹⁸ Ni(C) was generated by a laser-assisted heating process. The thin layer of carbon was then functionalized with carboxyl groups by free radical addition of peroxides, succinic acid peroxide or glutaric acid peroxide (Fig. 9a). The carboxyl groups played a critical role in integrating Ni(C) and catalytically active Pt nanoparticles (Fig. 9b). Catalytic hydrogenation of nitrobenzene was carried out for three runs without obvious decrease in yield.

Very recently, Chen *et al.* developed a Au-based MRNC, Fe₃O₄/C/Au/PVP/*p*-SiO₂, for the reduction of *o*-nitroaniline to benzenediamine by using carbon and mesoporous silica as hard coupling layers and PVP as soft coupling layers.⁹⁹ The mesoporous silica hard coupling layers prevent aggregation of neighboring nanoparticles and offer a large surface area for mass and heat transfer which significantly improved the catalytic efficiency and changed the reaction kinetics as compared with the catalysts without mesoporous shells.

Other combinations of hard and soft coupling layers, such as silica and polyelectrolytes or ionic liquid,^{103–199} and polymer and soft organic molecules with functional groups,^{104,105} have also been successfully demonstrated.

3. Direct synthesis strategies^{48,113–161}

In all the strategies reviewed above, at least three to five reaction steps were generally required to obtain a MRNC, which in the end was tedious, time consuming and costly. Therefore, direct

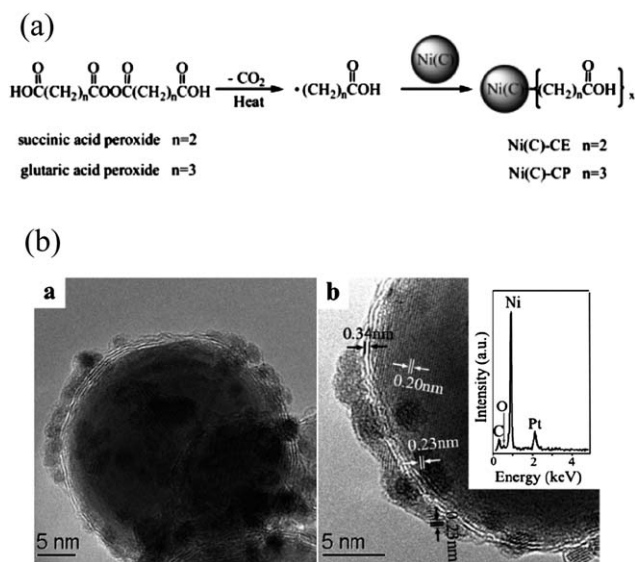


Fig. 9 (a) Free radical addition route to functionalize Ni (C) with carboxylic acid end groups; (b) TEM images of Pt/Ni(C) MRNCs with a corresponding EDX spectrum. Reprinted from ref. 98 with permission. Copyright (2008) American Chemical Society.

synthesis strategy without any coupling layers is desirable. In the last two years, some ingeniously designed MRNCs were fabricated through the direct synthesis strategy.^{48,113–161}

A smart direct synthesis strategy has been reported by Cheon *et al.* in the preparation of Pt-based bimetallic MRNCs through a transmetalation reaction.¹¹⁷ Co colloid was prepared by thermal decomposition of Co₂(CO)₈, and then refluxed with Pt(hfac)₂ in a nonane solution containing C₁₂H₂₅NC as a stabilizer. The formed superparamagnetic Pt@Co core-shell nanoparticles with 6.4 nm diameter has a high surface area, and thus high activity can be achieved with the use of a very low amount of Pt (Fig. 10). Catalytic hydrogenation of 1-decene by Pt@Co MRNCs was carried out under very mild conditions (room temperature and atmospheric hydrogen pressure). Complete conversion of 1-decene into *n*-decane was achieved within 4 h. 100% conversion was then still well retained after seven runs of recycling and reusing, thus outperforming the commercial Pt/C catalyst. The Pt@Co MRNCs also performed well in the catalytic hydrogenation of terminal, internal, conjugated and isolated olefins, alkynes as well as aldehydes.

A similar protocol has been employed by Liu *et al.* in preparing Fe@Co core/shell MRNCs.¹²² Besides core/shell structure, magnetic FeCo alloy nanoparticles were also produced. The Fe@Co MRNCs demonstrated a higher catalytic activity than that of FeCo MRNCs in the hydrolysis of NaBH₄, indicating the position of Fe appearance could influence the catalytic ability.

What is noteworthy is that many novel metal-based MRNCs have also been obtained by direct synthesis strategy.^{127,132,134–138,140,145,154–158}

In 2008, Sun *et al.* reported the synthesis of Pd/Fe₃O₄ through sequentially impregnating Fe₃O₄ with NaPdCl₄ aqueous solution, alkalizing the suspension, and reducing the precursor with KBH₄.¹⁵⁴ The Pd/Fe₃O₄ exhibited higher catalytic activity than homogeneous palladium catalyst for the coupling reaction of aryl iodides with alkynes under phosphine-free conditions and only slight activity decrease was observed during seven cycles of catalytic test. With a similar wet impregnation protocol, Glorius *et al.*, in 2010, prepared Pd/Fe₃O₄ nanoparticles with chiral, enantiomerically pure imidazolium salts to modify their surface for asymmetric catalysis.¹⁵⁵ Up to 85% ee was achieved in catalyzing the challenging intramolecular asymmetric α -arylation reactions with the resulting nanocatalyst. Moreover, the

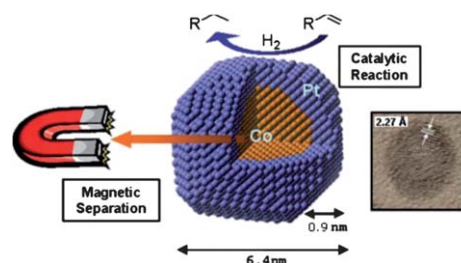


Fig. 10 Schematic illustration of the catalytic activity and magnetic separation of the Pt@Co core-shell MRNCs. Inset is a HRTEM image of a single MRNC with a lattice constant of Pt. Reprinted from ref. 117 with permission. Copyright (2006) Royal Society of Chemistry.

catalyst can be reused for five times without significant loss in either activity or selectivity.

Oxide-based MRNCs can also be obtained without using coupling layers by a heterogeneous nucleation process in the presence of magnetic nanoparticles in a weak alkaline environment.^{48,113,116,118–121,126,128,139} The weak alkaline environment is suitable for the formation of alkaline oxides. In addition, it cannot destroy magnetic iron oxides. In 2000, Amal *et al.* prepared a titania coated magnetite MRNC by heterogeneous nucleation of TiO_2 on magnetite *via* a sol–gel process.⁴⁸ However, as compared with bare TiO_2 , decreased photocatalytic activity was observed ascribing to the photodissolution. A similar route was adopted by Su *et al.* in the synthesis of ZnO-based MRNCs by immobilizing ZnO onto the surface of Fe_3O_4 *via* hydrolysis of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ in an alkaline solution.¹²¹ The ZnO-MRNCs had excellent photocatalytic activity in the decomposition of methyl orange and the activity only decreased slightly after five cycles of usage owing to the active sites gradually blocked by the deposited photoinsensitive hydroxides and the loss of catalysts.

Some other oxide-based MRNCs prepared by direct synthesis strategy have also been reported by means of co-decomposition, impregnation, co-precipitation, *etc.*^{130,131,133,159–161}

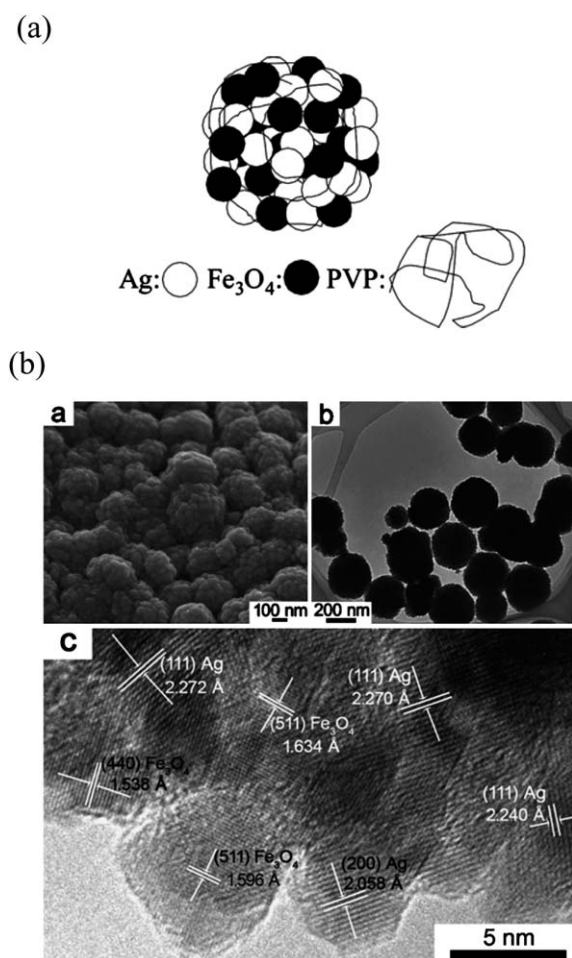


Fig. 11 (a) Schematic illustration of the structure of the one-pot synthesized Ag-based MRNCs, and (b) their SEM, TEM and HRTEM images. Reprinted from ref. 124 with permission. Copyright (2008) Royal Society of Chemistry.

Although numerous reports emerged on a facile synthesis of MRNCs, a one-step preparation of MRNCs is still a challenge because magnetic components and/or catalytic active species usually have to be synthesized and/or modified separately in advance before integrating them together.

In 2008, we developed a one-pot synthesis of Ag-based MRNCs and studied their catalytic performances in epoxidation of styrene (Fig. 11).¹²⁴ The Ag-based MRNCs can be easily obtained by the solvothermal treatment of a mixed ethylene glycol solution containing silver nitrate, iron(III) chloride, PVP and anhydrous sodium acetate. The formation of Ag and Fe_3O_4 nanoparticles and their assembly into one integrated Ag– Fe_3O_4 nanocomposite were successfully achieved in the same reaction system. A high yield of 84% for styrene oxide was achieved partially because of the support effect of Fe_3O_4 particles interacting with Ag particles directly and then acting as co-catalysts to assist the supply of active oxygen (Fig. 12a). No obvious decrease of catalytic activity or morphological change of MRNCs was detected after five cycles of catalytic reactions, confirming the superior stability of Ag-based MRNCs. The magnetic separation process can be quickly finished within one minute due to the

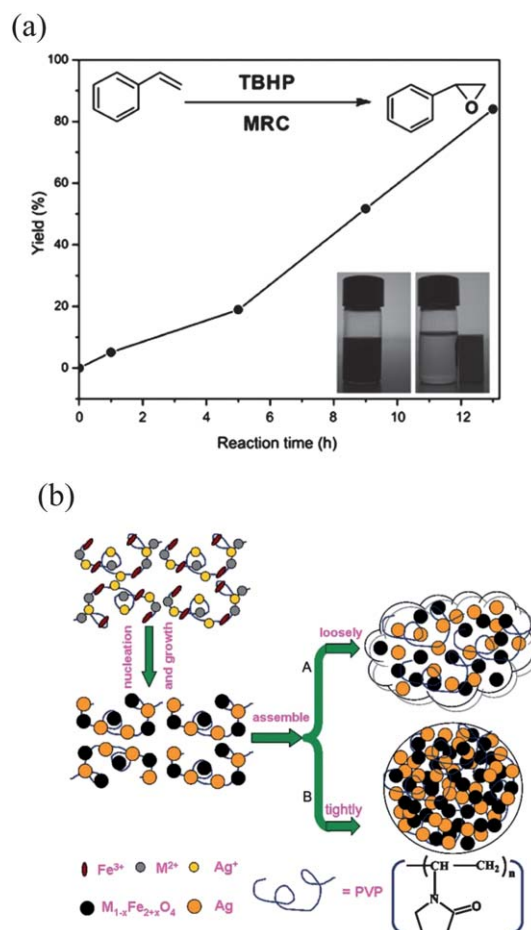


Fig. 12 (a) Yield of styrene epoxide *versus* reaction time catalyzed by Ag-based MRNCs. The photographs demonstrate the separation of MRNCs by a magnet; and (b) the formation mechanism of Ag-based MRNCs. Reprinted from ref. 123 and ref. 124 with permission. Copyright (2008 and 2009) Royal Society of Chemistry.

strong superparamagnetism of Fe_3O_4 clusters (inset of Fig. 12a). Thereafter, we generalized the facile one-pot synthesis method and prepared a series of new type MRNCs, $\text{M}'\text{-M}_{1-x}\text{Fe}_{2+x}\text{O}_4$, by extending the supports and catalysts to series of ferrites and metals, respectively (Fig. 12b).¹²³ Similar routes have recently been reported by Gusevskaya *et al.*¹⁴¹ in the fabrication of cobalt-iron magnetic composites, and their catalytic activity, stability and recyclability were studied in aerobic oxidation of thiols. Very recently $\text{Ni-Fe}_3\text{O}_4$,¹⁴³ Pd-Fe ,¹⁴⁴ and $\text{Ag-Fe}_3\text{O}_4$ ¹⁴² MRNCs were also obtained through one-pot synthesis.

Magnetic materials themselves also can play a dual role in serving as both catalysts and magnetic responsive materials in some heterogeneous catalytic reactions. Moreover, most of them including oxides ($\gamma\text{-Fe}_2\text{O}_3$, ferrites, Mn_3O_4 , *etc.*), metals, *etc.*^{162–204} can be facilely obtained by one-pot synthesis. In 2009, Kantam *et al.* synthesized Fe_3O_4 and three substituted magnetic ferrites catalysts, MFe_2O_4 ($\text{M} = \text{Cu}^{2+}$, Co^{2+} , Ni^{2+}) by coprecipitation, and investigated their catalytic performances in asymmetric hydrosilylation of a variety of ketones.¹⁶⁴ CuFe_2O_4 was identified as the most active one, and the efficiency of the catalysts remained with almost no change up to three cycles. Recently, Sun *et al.* reported a simple preparation of magnetically recoverable CuFe_2O_4 for a successful application in C–O cross coupling of series of phenols and aryl halides.¹⁶⁵ No significant decrease of catalytic selectivity and activity was observed after six runs of recycling and reusing. Ferrites,^{176–182,195–197,202,204} Mn_3O_4 ,¹⁶⁷ magnetic metals,^{199,200} and $\gamma\text{-Fe}_2\text{O}_3$,^{183–186} have also been synthesized and used for the degradation of various pollutants, cyclohexane oxidation, *N*-arylation of heterocycles, Knoevenagel condensation reaction, *etc.* In order to protect the magnetic components from leaching and/or enhance their catalytic activity porous silica, sodium alginate, humic acid, multiwall carbon nanotube, *etc.* were usually used in the synthesis of magnetic catalysts.^{188–194,203} They can also serve as a support to load magnetic catalysts for robust high efficient catalysis.²⁰¹

4. Concluding remarks

Great achievements have been accomplished in the past few years in the development of MRNCs. Various synthetic strategies including template-assisted synthesis in which hard coupling layers, soft coupling layers, and mixed hard-soft coupling layers have been utilized as well as direct synthesis with reaction steps ranging from one to five or so have been developed. In addition, catalytic performances of MRNCs in a variety of catalytic transformation systems have also been studied. However, there are still many challenges towards the practical and industrial applications for MRNCs.

(I) Most of the synthesis approaches of MRNCs involving multistep reactions are tedious and expensive. Direct synthesis of MRNCs with only one reaction step is more efficient and economical, and is also in line with the principles of green chemistry. Therefore, more general, facile and easy to scale-up synthetic strategies are still in great demand.

(II) Types of catalytic active species in MRNCs are mostly limited to noble metals. Moreover, simple model reactions, such as *p*-nitrophenol hydrogenation, coupling, alkene hydrogenation, *etc.*, are often chosen to demonstrate the catalytic

performances of MRNCs. More focused research on non-precious metal-based or metal oxide-based catalysts and important organic transformation processes in industry could speed up the development of MRNCs for practical applications.

(III) The long-term stabilities of MRNCs including the catalytic active species and magnetic components need to be further improved by a rational design and synthesis of robust MRNCs for the need of industrialization process.²⁰⁵ For example, more stable and inert mesoporous and solid shells such as TiO_2 should be developed in order to stabilize the catalytic active species and magnetic components, respectively. This would prevent them from leaking and aggregation, and etching. More rational selection of soft organic molecules with various functional groups for anchoring catalytic active species can increase the interaction between soft coupling layers and catalytic active species, suppress the aggregation of catalytic active species, and thus improve the stability of MRNCs.

(IV) It should be noted that not only the size of the catalysts but the morphologies have an important impact on the catalytic activities because the exposed atomic arrangement of the facets with different Miller indices are sometimes quite distinct. MRNCs composed of nanocatalysts with high ratio exposed high-index facets could improve catalytic activity. Moreover, both geometric and electronic structures of catalytic active species closely related to catalytic activities can be affected by magnetic semiconductor or metal components because of their support effects. Although support effects have been explored, a further and fully understanding of them is still very much in need, which can be achieved by a conjunctive utilization of various advanced research means such as theory calculation, single-molecule analytic technique, *etc.*²⁰⁶ An improved knowledge on the structure–performance relationship of MRNCs is very helpful for the rational design and synthesis of new-typed robust MRNCs from a molecular engineer perspective.

Successful tackling of the above mentioned problems depends upon the cooperative efforts of researchers in fields of nanomaterials, catalysis, organic synthesis, theory calculation, *etc.* The continued need for further and fully research on MRNCs will surely accelerate their practical and industrial applications, and in addition, further boost the development of green chemistry in industry.

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