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Recent developments in hybrid iron oxide–noble metal nanocatalysts for organic reactions

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ABSTRACT

A review of recent developments in the synthesis of hybrid iron oxide–noble metal nanocomposites and their application to various organic reactions is presented herein. Focus is placed on various strategies for achieving (1) Au nanoparticles (NPs) on Fe_3O_4 @polymer catalysts, (2) optimized dispersion and stability of Fe_3O_4 /Pd catalysts, (3) Au NPs supported on Fe_2O_3 –graphene oxide hybrid nanosheets and (4) rose-like Pd– Fe_3O_4 hybrid nanocomposite-supported Au nanocatalysts. Further application of such hybrid nanocomposites as catalysts for various organic reactions is discussed in brief.

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1. Introduction

In recent years, numerous strategies have been attempted for the design of hybrid nanostructures that combine the physical and chemical properties of each component [1–9]. Many studies have discussed the syntheses of such multicomponent nanostructures with increased functionality [10–20]. The multicomponent functions combined with the enhanced chemical and physical properties make the hybrid nanostructures suitable research targets for magnetic, plasmonic and semiconducting explorations [21–25].

The design of iron oxide nanoparticles (IONPs) has gained particular attention because of fundamental scientific interest in various cutting-edge technological applications of these species, including their use as magnetic storage media, [26] in biosensing [27] and medical applications [28,29] and as contrast agents in magnetic resonance imaging [30–33]. Thus, there has been a drive toward the synthesis of IONPs with controlled size, composition and surface properties in the subjects of extensive interdisciplinary research [34,35]. It is well known that IONPs exhibit the tendency to cluster, aggregate and lose their magnetic properties when applied in solution and in biological systems. To enhance the stability of these nanoparticles (NPs), intensive effort has been devoted to the

development of hybrid nanocomposites to enable functionalization of the surfaces of IONPs and develop new design strategies for hybrid nanocomposites [36–42].

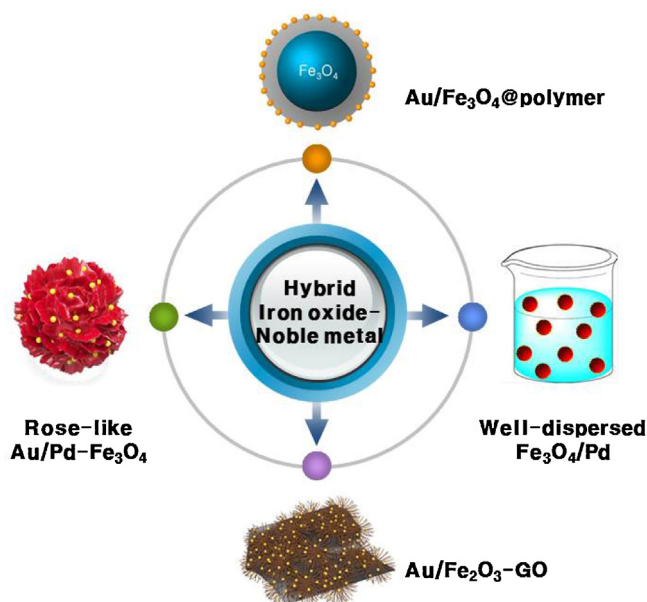
Hybrid nanocomposites are efficient catalysts for a wide range of industrially relevant organic transformations. For example, palladium and gold NPs have attracted attention as catalysts for carbon–carbon coupling reactions, reduction of 4-nitrophenol and a series of other reactions [43–53]. Magnetic NPs or nanocomposites are considered as ideal supports because they efficiently immobilize metal NPs and circumvent the complications of filtration (such as loss of catalyst, oxidation of sensitive metal complexes and usage of additional solvents for precipitation steps).

In this review, we focus on recent developments in the synthesis of hybrid iron oxide–noble metal nanocomposites and various strategies for achieving (1) Au NPs on Fe_3O_4 @polymer catalysts, (2) optimized dispersion and stability of Fe_3O_4 /Pd catalysts, (3) Au NPs supported on Fe_2O_3 –graphene oxide (GO) hybrid nanosheets and (4) rose-like Pd– Fe_3O_4 hybrid nanocomposite-supported Au nanocatalysts (Scheme 1). Further application of such hybrid nanocomposites as catalysts to various organic reactions is also discussed in brief.

2. Au NPs on Fe_3O_4 @polymer catalysts [54]

Core–shell nanocomposites have recently emerged as promising catalysts, where the shell not only protects the core from oxidation, but also facilitates surface modification and

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Scheme 1. Hybrid iron oxide–noble metal nanocomposites.

functionalization to overcome problems caused by oxidation and aggregation of IONPs. These catalysts include metal oxides such as SiO_2 , TiO_2 , and Al_2O_3 , organic monolayers, and polymers [55–66]. We synthesized hybrid Au NPs on Fe_3O_4 microspheres, and then coated these Fe_3O_4 microspheres with a polymer to facilitate loading of the Au NPs and to prevent aggregation and oxidation of the Fe_3O_4 microspheres (Scheme 2) [54].

Scheme 2 shows the total synthesis of the Fe_3O_4 @polymer/Au catalyst. Fe_3O_4 microspheres were synthesized using the solvothermal method [61,62]. This comprised the partial reduction of FeCl_3 with ethylene glycol as a solvent, sodium acetate as a reducing agent and trisodium citrate (Na_3Cit) as an electrostatic stabilizer at 200°C . The resulting Fe_3O_4 microspheres are shown in Fig. 1a, demonstrating their spherical morphology with a rough surface and an average diameter of 142 nm (Fig. 2b). The Fe_3O_4 microspheres consisted of aggregates of small magnetite particles with a mean size of 3 nm, as observed by transmission electron microscopy (TEM) (Fig. 1b). Au NPs with a diameter of 18 nm (Fig. 2b) were immobilized on the Fe_3O_4 @polymer microspheres through hydrogen bonding between the ester groups in the polymer and the Au precursors (Fig. 1c and d). The polymerization was carried out by using the hydrophobic monomer ethylene glycol dimethacrylate (EGDMA) as a cross-linker with the hydrophilic monomer methacrylic acid (MAA) to increase the hydrophilicity of the Fe_3O_4 @polymer microspheres, thereby generating Fe_3O_4 @P(EGDMA-co-MAA) core–shell microspheres. The TEM image of the Fe_3O_4 @P(EGDMA-co-MAA) microspheres in Fig. 1b shows a well-defined core–shell structure, with a black core and a gray shell, without the appearance of any secondary polymer as shown in Fig. 1b. Because the Fe_3O_4 microspheres had carboxyl groups on their surfaces due to the use of Na_3Cit

in the magnetic synthetic system, the synergetic hydrogen bonds formed between the carboxyl groups and ester groups, as well as between the carbonyl groups and hydroxyl groups, were strong enough to synthesize P(EGDMA-co-MAA) on the magnetite surface. Thus, hydrogen bond interactions played an important role during the coating of the polymer onto the Fe_3O_4 microspheres [61,62]. X-ray diffraction (XRD) (Fig. 2a) was used to identify the crystal phase of the Fe_3O_4 spherical aggregates and Fe_3O_4 @P(EGDMA-co-MAA)/Au. Specifically, the patterns could be assigned to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), and (5 3 3) reflections of the cubic spinel structure of Fe_3O_4 (JCPDS No. 19-0629) and the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) reflections of face centered cubic (fcc) Au (JCPDS No. 04-0784). The elemental compositions of the Fe_3O_4 @P(EGDMA-co-MAA)/Au catalyst were obtained using energy-dispersive X-ray spectroscopy (EDS) (Fig. 2c). The superconducting quantum interference device (SQUID) data (Fig. 2d) shows the magnetic curves as a function of the applied field at 300 K. The saturation magnetization value of Fe_3O_4 @P(EGDMA-co-MAA)/Au was about 45.3 emu g^{-1} , which was a similar to that of Fe_3O_4 @P(EGDMA-co-MAA) at about 46.4 emu g^{-1} . There was no drastic decrease of the magnetization after loading of the Au NPs. Moreover, the remanence and coercivity of the Fe_3O_4 microspheres were both close to zero, indicating superparamagnetism.

The UV/vis absorption of the reaction mixture was monitored with time during the catalytic reduction of 4-nitrophenol (Fig. 3). Notably, the absorption of 4-nitrophenol at 400 nm decreased rapidly with a concomitant increase in the intensity of the peak at 300 nm, which is attributed to the product of the reduction, 4-aminophenol. In control experiments, only the Fe_3O_4 @P(EGDMA-co-MAA) microspheres were used as the catalyst; no reaction was observed (entry 1, Table 1). In the absence of NaBH_4 , the Fe_3O_4 @P(EGDMA-co-MAA)/Au catalyst showed no catalytic activity (entry 2, Table 1). As expected, increasing the temperature enhanced the catalytic activity (entries 3 and 4, Table 1). In Fig. 3a, the reaction rate constant (k) is compared under different temperatures with the use of 2.5 mol% of Fe_3O_4 @P(EGDMA-co-MAA)/Au and 100 equiv. of NaBH_4 . The highest catalytic efficiency (0.330 min^{-1}) was obtained at 35°C . The amount of catalyst as well as the amount of NaBH_4 used during the reduction was also optimized (entries 5 and 6, Table 1). The reduction was completed in 45 s when Fe_3O_4 @P(EGDMA-co-MAA)/Au was used as the catalyst (5.0 mol% of catalyst, 300 equiv. of NaBH_4 per equiv. substrate) (Fig. 3b). Fe_3O_4 @P(EGDMA-co-MAA)/Au microspheres with different loadings of Au (11 and 18 wt.%) were also used as catalysts, resulting in lower catalytic activity (entries 7 and 8, Table 1). The Fe_3O_4 @P(EGDMA-co-MAA)/Au catalyst exhibited superior catalytic activity to that previously reported for Au– CeO_2 nanocomposites and hybrid Au nanoparticle–GO nanosheets based on comparison of the turnover frequency (TOF) value [67,68]. APTS-modified Fe_3O_4 @P(EGDMA-co-MAA)/Au and Fe_3O_4 @ SiO_2 /Au catalysts were synthesized and applied in this reaction as catalysts (Fig. 4a and b). Au NPs were immobilized on APTS-modified Fe_3O_4 @P(EGDMA-co-MAA) and Fe_3O_4 @ SiO_2 . However, catalysts with low metal loadings were obtained as compared with the Fe_3O_4 @P(EGDMA-co-MAA)/Au catalyst. The Fe_3O_4 @P(EGDMA-co-MAA)/Au



Scheme 2. An illustration of synthesis for Fe_3O_4 @polymer/Au.

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