Recent Advances in the Nanocatalyst-Assisted NaBH₄ Reduction of Nitroaromatics in Water

Kaiqiang Zhang,†§‡ Jun Min Suh,†‡ Ji-Won Choi,§ Ho Won Jang,*† Mohammadreza Shokouhimehr,*§∥⊥ and Rajender S. Varma*†

† Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 08826, Republic of Korea
§ Electronic Materials Center, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea
∥ Regional Center of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacky University, Šlechtitelů 27, 783 71 Olomouc, Czech Republic
⊥ Water Resources Recovery Branch, Water Systems Division, National Risk Management Research Laboratory, US Environmental Protection Agency, Cincinnati, Ohio 45268, United States

ABSTRACT: In view of the increasing applications of nanocatalysis in chemical transformations, this article illustrates recent advances on the use of nanocatalysts for an important reduction reaction, the hydrogenation of nitroaromatics to significant aminoaromatics with aqueous NaBH₄ solution; the utility of mono- and multimetal nanocatalysts with special emphasis on heterogeneous nanocatalysts is included. A progressive trend on the applicability of nanocatalysts is also incorporated with large-scale application and their sustainable recyclization and reuse utilizing supported and magnetic nanocatalysts; representative methods for the synthesis of such reusable nanocatalysts are featured.

1. INTRODUCTION

Reduction process is a fundamental and important chemical transformation in organic synthesis1−3 and industrial chemistry,4−6 the key step being that the electrons transform from a donor to the target substance. The reduction of nitroaromatics (NAs) is a common and facile route to produce aminoaromatics (AAs), which are very significant intermediates for the synthesis of several nitrogen-containing compounds, such as agrochemicals, pharmaceuticals, polymers, dyes, pesticides, and cosmetics.7−12 Several toxic NAs are responsible for serious environmental pollutions.13 However, they can be transformed into AAs, that is, nitrophenol (NP) conversion into harmless aminophenols (AP), which are potential intermediates for accessing pharmaceuticals and dyes via the reduction process (Figure 1a). Accordingly, various NAs can be reduced to their amino counterparts through the use of catalysts wherein the applied catalysts play a significant role.14−19 Consequently, the suitable design of the catalyst structure and their prudent selection can remarkably improve the reduction efficiency, thus providing better catalytic sustainability and recoverability.

The description of the catalysts these days can be simply and ideally stated as nanoparticles (NPs) with or without supports. Nanosized catalysts with high specific surface area and without supports provide a ready contact with the reactants, thereby improving the catalytic activity.20−22 However, the high surface energy of nanostructures escalates their instability and leads to aggregation, which results in the loss of catalytic activity.23,24 An inevitable loss of nanocatalysts appears during their tedious separation from the products. Therefore, the deployment of supports effectively prevents their aggregation and undesirable

Figure 1. (a) Schematic design for the reduction of nitrobenzene with aqueous NaBH₄ using nanocatalysts. (b) Classification of various nanocatalysts applied for the reduction of NAs to AAs.

Received: November 1, 2018
Accepted: December 24, 2018
Published: January 8, 2019

© 2019 American Chemical Society

DOI: 10.1021/acsomega.8b03051
ACS Omega 2019, 4, 483−495
http://pubs.acs.org/journal/acsoa1

This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.
lose, thereby enlarging the total surface area and assuring their sustained catalytic activity and reusability; the positioning of supports with a high specific surface area generally provides a promoted adhesion to reactants.25−27

Regarding the greener aspect of the catalytic processes, it is highly desirable to develop environmentally benign procedures that can be conducted preferably in aqueous media, thus avoiding the use of volatile organic solvents; sodium borohydride (NaBH4) is one such favored water-soluble reductant for representative reductions.28−30 In the reduction process of NA to AA with aqueous NaBH4, electrons from the reductant for representative reductions.28

Thereafter, these peaks at 400 nm are reduced over time.34 The formation of 4-nitrophenolate ions under alkaline conditions. There occurs immediately from 317 to 400 nm because of the occurrence of 4-nitrophenolate ions under alkaline conditions. Then there, these peaks of 400 nm are reduced over time.34 Moreover, gas chromatography−mass spectrometry is needed for the measurement of accurate conversion percentage and for verifying the ensuing reaction products.39,40

Consequently, the compatibility of the applied catalysts affects the overall reduction productivity.41 In view of their importance, we present recent methods for the synthesis of nanocatalysts as directed for the reduction of NAs with focus on the advances in nanostructured catalysts for the hydrogenation of NA with aqueous NaBH4. The general strategies for the synthesis of representative heterogeneous nanocatalysts, their advantages, limitation, and challenges are also discussed. For the sake of differentiation and ease of understanding, the nanocatalysts are classified with or without supports for monometal and bi- or multimetal nanostructured catalysts. Additionally, we have categorized separately the supported nanocatalysts with and without magnetic properties in view of their ease of separation and reuse (Figure 1b). The first category of nanocatalysts in this article, monometallic nanocatalysts, possesses solely one metal element as the catalyst for expediting the reduction of NAs to AAs. Subsequently, bimetallic and solid supported non-magnetic nanocatalysts are discussed, emphasizing on their designs to overcome the low efficiency and aggregation issues of the monometal nanocatalysts.52 Although these catalysts demonstrate considerably improved catalytic activity, their reusability is still a challenge. Consequently, the magnetic nanostructured catalysts are presented to facilitate easy separation and as sustainable catalysts for reduction of NAs.43

2. MONOMETALLIC NANOCATALYSTS

The decrease in size of metal catalysts having diameters in the nanometer range ensures high surface area, enhancing their catalytic performances. Metal NPs have remarkable catalytic susceptibility because of their adjustable size, shape-associated activity, and selectivity. Monometal nanocatalysts used in NaBH4 reduction of NAs, generally, noble- and transition-metal NPs such as palladium (Pd), platinum (Pt), ruthenium (Ru), and silver (Ag), are synthesized and directly employed as nanocatalysts in the hydrogenation of various NAs using aqueous NaBH4 as the reductant.44−49 Effective catalytic achievement can be attained using monometallic NPs with high surface potential determined by the valence amount of unsaturated surface atoms and by the Fermi energy level in reducts.50−52 The catalytic activity of the Pt NPs has been reported to be highly dependent on the morphology, porosity, size distribution, and phase composition; significant enhancement could be discerned in the catalytic activity when monodispersed Pt NPs are linked into Pt nanowires.53

Mahmoud et al.54 concluded, while reducing 4-NP, that the reaction yield is a function of free surface area of the NPs. In this study, the mechanism of 4-NP reduction by Au nanocatalysts was investigated using NaBH4 in solution. The reduction process can be achieved either on the NP surface following the heterogeneous mechanisms or by the leached atoms or ions from the NPs (homogeneous mechanism) in the solution. Considering the plasmonic effect of Au NPs and measuring the dependence of the reaction yields on the surface area of the nanocatalyst by the adsorption isotherm of binding 4-NP and the changes of the plasmonic extinction band position of the NPs during the reactions, the researchers concluded that it is the surface heterogeneous-type mechanism and not the homogeneous path by the leached atoms in the solution (Figure 2) that is involved.

![Figure 2. Schematic explanation for the reduction of 4-NP by NaBH4 catalyzed by Au nanocatalysts.](image-url)

Kaur et al.55 also demonstrated this premise by reducing NA using reusable silver nanocatalysts and size-controlled copper (Cu) NPs in aqueous medium; hydrogenation proceeded on the surface of Cu NPs, and the catalytic efficiency increased as the size of particles decreased (Figure 3). It is believed that the activity of nanocatalysts would decrease once the exposed surface area is covered.56 However, a long shelf life of Cu NPs could be attained by coating polyacrylic acid without inhibiting the reduction activity.

3. BI- OR MULTIMETALLIC NANOCATALYSTS

This section describes bi-metals of the various alloys as they appear to exhibit an improved activity compared to the corresponding monometallic nanocatalysts because of synergetic effects.57 In the case of bi- or multimeatal nanocatalysts,
The extra electrons in the outer orbitals of the metallic sources having relatively higher activity are capable of transferring to the adjacent different metallic atoms with relatively lower activity, culminating in coordination between those different metallic elements. Consequently, the formed electron-rich metallic atoms facilitate the electron transfer from the adsorbed BH$_4^-$ to the 4-NP$_2$, enhancing the process efficiency. For instance, Chu et al. reported that polyelectrolyte multilayer-supported AuPt alloy NPs exhibit higher catalytic activity than Au and Pt monometallic catalysts for the reduction of 4-NP by NaBH$_4$. The uniform square nanocatalysts had an average size of 3.3 nm, while Figure 5d presents the histogram of the NPs with an average size of 3.3 nm. The catalytic activity of the Pt–Ni alloy is much higher than that of only Ni and, similarly, when compared to only Pt nanocatalysts.

3.3. Pt–Ni Nanocatalysts. Ghosh et al. synthesized the bimetallic Pt-Ni alloyed nanocatalysts by the addition of NiSO$_4$ and H$_2$PtCl$_6$ in cetyltrimethyl ammonium bromide (CTAB) micellar medium followed by injection of hydrazine (N$_2$H$_4$) and KOH solution. The catalytic activity of the Pt–Ni nanocatalysts was evaluated for the reduction of 4-NP to 4-AP using aqueous NaBH$_4$ as the reductant. The catalytic reduction was found to be equally successful for other nitroarenes such as 2-NP and 4-nitroaniline. The comparative catalytic activity between Raney Ni and Pt–Ni nanocatalysts showed that the activity of the Pt–Ni alloy is much higher than that of only Ni and, similarly, when compared to only Pt nanocatalysts.

3.4. Pt–Ni–Fe Nanocatalysts. Chen et al. synthesized Pt–Ni–Fe multimetal heterogeneous nanocatalysts wherein the as-synthesized Ni–Fe branched-dumbbell-shaped material was synthesized via electromagnetic wave assistance (Figure 8).

The morphology and structure of the Pt–Ni–Fe nanocatalysts were characterized by SEM and TEM. In addition, powder XRD was employed to characterize the phase structure of the prepared nanocatalysts. The branched-dumbbell-shaped Pt–Ni–Fe nanocatalysts presented efficient catalytic activity compared to Ni/Fe branched-dumbbells and Ni nanocatalysts for the reduction of p-NP; at least 10 successive cycles of reaction with a conversion efficiency of ~97% could be successfully achieved (Figure 9). The as-prepared Ni–Fe and Pt–Ni–Fe NPs could be easily separated from the solution and recovered using an external magnet and redispersed in solution for subsequent use.

4. SOLID-SUPPORTED NONMAGNETIC NANOCATALYSTS

Solid supports effectively inhibit the aggregation of active nanocatalysts compared with unsupported monometal and multimetal nanocatalysts. In addition, the supports generally offer vast surface area, which is crucial for the improvement of catalytic efficiency. Accordingly, significant development has been made in the field of heterogeneous catalysis by applying strong metal–support interactions to strengthen catalytic performance. The selection of supports is an important issue because of the synergetic effects between the supports and nanocatalysts, empowering catalytic processes. For example, conductive support-containing catalytic NPs may assist electron transfer between nanocatalysts and reactants/reductants. In NA reduction, the supports also facilitate the adherence of nitro moieties and reductants to the nanocatalysts, supplying more electron transport channels. This section explores various supported nanocatalysts applied
in the reduction of NAs in water. In practice, the supported nanocatalysts display enhanced recycling performance in the reduction of NAs because of their retainable mechanical properties; supports play an important role in the proficiency of the catalytic systems.

4.1. Carbon Nanotube-Supported Nanocatalysts. Wang et al. synthesized carbon nanotube (CNT)-supported Au NPs for the degradation of pollutants via a multistep approach as shown in Figure 10, including (1) activation of stainless steel mesh, (2) growth of CNT arrays, (3) synthesis of Au NPs, and (4) attachment of Au NPs to CNTs. Au NP-decorated CNT-supported materials promoted the catalytic degradation of p-NP in aqueous NaBH₄ solution.

4.2. Mesoporous Silica-Supported Nanocatalysts. Han and co-workers introduced a facile one-step method for
Mesoporous silica and Ag NPs were spontaneously synthesized with the Ag NPs embedded in the channels, and their catalytic activity was examined for the reduction of 4-NP in the presence of NaBH₄. In an interesting work, Zhang et al. synthesized nanotube-shaped silica loaded with silver NPs using electrospinning technology. TEM images (Figure 11) exhibited the amorphous and extremely long nanotubes with uniform diameters (250–350 nm) independent of whether there is loading or nonloading of other active species; these nanotube catalysts exhibited excellent catalytic performances for the hydrogenation of 4-NP to 4-AP, which has been ascribed to their high specific surface area.

4.3. Graphene Oxide-Supported Nanocatalysts. Graphene oxide is one of the most widely used supports for loading of nanocatalysts such as Pd, Au, and Ag. Ye et al. designed Pt−Au NPs, which were supported on functionalized graphene oxide (Figure 12); the as-synthesized Pt−Au alloys exhibited a dendrimer-like nanostructure with a small size of ~50 nm. The size and morphology of Au NPs could affect the hydrogenation catalysis. However, the hydrogenation activity of Au is usually much lower than Pt-group metals. The introduction of engineered graphene oxide-supported Pt−Au could provide active catalytic sites, improving the electron transfer, thereby promoting the catalytic activity of the NA reduction.

Chen et al. synthesized a graphene oxide-supported CdS hybrid photosensitive catalyst via the electrostatic interaction of negatively charged graphene and positively charged CdS NPs for the light-assisted reduction of NA (Figure 13). The CdS/graphene hybrid nanocatalysts demonstrated a high reductive activity presumably via the synergistic effect emanating from CdS and graphene oxide, which provided a high transfer rate of electrons for the reduction of NA to AA. The intimate interfacial contact via an electrostatic self-assembly strategy promoted the carrier transfer at the CdS/graphene hybrid nanocatalysts upon irradiation of visible light, thus providing enhancement of the photocatalytic performance for the selective reduction of 4-NAs. The introduction of graphene increased the work function of the electrons, which were generated from CdS NPs upon irradiation of visible light. In addition, the deployment of graphene also contributes to the enhancement in the concentration of the NAs on the graphene surface, which effectively accelerates the catalytic hydrogenation.
In another effort, Zhang and colleagues introduced a facile method to decorate Pd nanocatalysts on the graphene oxide surface by a simple mixing process in aqueous Pluronic F−127 as a mild reductant at room temperature (Figure 14). TEM images confirmed the good distribution of Pd NPs on graphene oxide (Figure 15). The prepared catalyst converted NAs to AAs in aqueous NaBH₄ in a short reaction time.

4.4. Carbon Nitride-Supported Nanocatalysts. Bhowmik et al. reported the synthesis of carbon nitride-supported ultrasmall Au NPs for the reduction of 4-NP in aqueous medium, which showed an excellent catalytic activity and good stability. The nanocatalysts were characterized by TEM (Figure 16), selected area electron diffraction, energy-dispersive X-ray spectroscopy, powder X-ray diffraction, and X-ray photoelectron spectroscopy methods.

The morphology of the formed carbon nitride (Figure 16a) shows two-dimensional carbon nitride sheets. Figure 16b exhibits the uniform dispersion of Au NPs with a mean size of 1.5 nm on the carbon nitride sheets demonstrating highly loaded Au NPs. The reduction measurement of 4-NP to 4-AP was completed by employing aqueous NaBH₄ as the reductant, monitored by UV-vis spectra absorption, with the reduction time being remarkably shortened, ~15 s to complete the reduction. Li and his research group reported a similar finding for the reduction of 4-NP with mesoporous carbon nitride-supported Au NPs, showing 96% conversion using aqueous NaBH₄ in 5 min. The catalyst could be recycled by centrifugation, exhibiting at least five successive cycles with high conversion efficiency. Graphitic carbon nitrides are readily obtainable starting from urea or melamine or a mixture thereof.
4.5. Polymer-Supported Nanocatalysts. Sreedhar et al. synthesized Pt NPs supported on gum acacia, which were characterized by TEM, XRD, XPS, and Fourier transform infrared spectroscopy (FT-IR); the amount of Pt NPs in the formed heterogeneous catalyst was determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES). The strong interactions of NPs with functional molecular groups of gum acacia resulted in the formation of monodispersed NPs; catalytic activity of the catalyst was also compared with Pt/C, Pt-Al2O3, and Pt-ZrO2 in the reduction of nitrobenzene. The results (Table 1) showed an enhanced activity of gum acacia-supported Pt nanocatalysts because of the high surface area and strong hydrogen trapping property of Pt NPs. Furthermore, the nanocatalysts could be reused several times with moderate loss in catalytic activity (Table 2). Stable anchoring of Pt NPs on gum acacia was robustly maintained after recyclization measurement. The renewable gums obtained from various trees are relatively untapped resources, although they have been used as food additives for a while.

| entry | nanocatalyst       | time (min) | yield (%) |
|-------|--------------------|------------|-----------|
| 1     | gum acacia–Pt      | 6          | 91        |
| 2     | Pt/C               | 12         | 47        |
| 3     | Pt-Al2O3           | 12         | 0         |
| 4     | Pt-ZrO2            | 12         | 0         |

4.6. Polyelectrolyte Multilayer-Supported Nanocatalysts. Chu et al. synthesized Au–Pt alloy NPs supported on polyelectrolyte multilayers (PEMs) for the reduction of 4-NP using aqueous NaBH4; the ensuing nanocatalysts were analyzed by ICP-AES and were found to be well-dispersed Au–Pt alloy NPs with a narrow size distribution in the polymer matrixes. The reduction process was tracked using UV−vis absorption spectroscopy, taking ~6 min to achieve the hydrogenation of 4-NP. The optimal synergistic effect of Au/Pt was identified to be 2:1. The PEM-supported Au–Pt alloy NPs exhibited higher catalytic activity than Au and Pt monometallic NPs for the reduction of 4-nitrophenol by NaBH4, presenting synergistic effects between Au and Pt.

5. SUPPORTED MAGNETIC NANOCATALYSTS

The magnetic nanocatalysts have a comparative advantage as they provide easier separation from the reaction media with less catalyst loss by simply using an external magnet. The nanocatalyst separation and reuse by magnetic field is an important factor for commercial manufacture and attaining cost effective reductions. However, there are also some disadvantages including the material selection for synthesizing appropriate nanocatalysts. The limited availability of model magnetic nanocatalysts for the catalytic processes restricts their practical applications. Therefore, many scientists have pursued various strategies to develop ideal magnetic nanocatalysts.

5.1. Nanocatalysts Decorated on Iron Oxide NPs. Patra et al. synthesized Ag/Fe2O3 nanocatalysts for the hydrogenation of nitroarenes; hydrothermally formed Fe2O3 NPs were obtained by admixing sodium salicylate with NaOH, followed by injection of aqueous Fe(NO3)3. Subsequently, the Ag NPs were deposited on the surface of the Fe2O3. The FESEM images (Figure 17) of the prepared magnetic nanocatalysts indicated the identical bitruncated-octahedron-shaped Fe2O3 NPs with a length of ~310 nm, a width of ~220 nm, and a height of ~150 nm and a well-dispersed coating of Ag NPs on the surface.

The catalytic activity was explored via the hydrogenation of 2 mL of aqueous 0.1 mmol/L 4-NP with 200 μL of 10 mmol/L aqueous NaBH4 at 500 μL of 1 mg/mL aqueous nanocatalysts. The reduction process required ~10 min for the complete conversion of 4-NP to 4-AP. The reusability of Ag/Fe2O3 NPs in the hydrogenation reaction was measured for 10 cycles using 4-NP as a reference, which exhibited a good catalytic activity and almost no obvious deactivation after 10 times of cyclic hydrogenation. The Ag/Fe2O3 nanocatalysts also successfully reduced other functionalized NAs such as 4-nitrobenzoic acid, which is a challenging proposition because of the presence of carboxylic acid groups (Table 3). Similarly, Pelisson et al. prepared maghemite-supported Pd NPs nanocatalysts for the reduction of nitro aromatics to amino aromatics with aqueous NaBH4.

5.2. Nanocatalysts Decorated on Carbon-Coated Magnetic NPs. An et al. synthesized Fe3O4@carbon-
supported Ag–Au nanocatalysts and studied the effect of the Ag/Au ratio on the catalytic activity in the hydrogenation of NAs (Figure 18). Remarkably, this work showed that the use of carbon can contribute to both the improvement of catalytic performance of the noble metals and in situ preparation of Ag-Au bimetallic nanocatalysts. Catalytic reduction of 4-NP by aqueous NaBH₄ using Fe₃O₄@C@Ag–Au nanocatalysts, monitored by UV–vis spectra absorption, showed significant enhancement in the catalytic activity (4.5 min).

The recycling ability of the Fe₃O₄@C@Ag–Au nanocatalysts was verified with high yields in six reaction cycles. Similarly, Zhang et al.⁹² prepared Pt–Pd nanoalloys supported on Fe₃O₄@C core–shell NPs using a facile two-step synthesis method (Figure 19) and characterized them by high-resolution TEM; Pt–Pd nanocatalyst decoration on a carbon layer coating on the surface of the Fe₃O₄ NPs was discerned. In another exploration, Du et al.⁹³ synthesized Pt–Pd NPs on super-paramagnetic core–shell nanocatalysts for the reduction of 4-NP to 4-AP using aqueous NaBH₄. The hydrogenation required 22 min to completely convert the 4-NP to 4-AP using 13.63 wt % of the prepared nanocatalysts; the yield and selectivity were obtained to be 96% and 99%, respectively.

5.3. Nanocatalysts Decorated on Polymer-Encapsulated Magnetic NPs. Various nanocatalysts can be adorned on the polymer shell containing magnetic NPs. The polymer layers can protect the magnetic NPs from dissolution and corrosion in the reaction environment. Ayad et al.⁹⁴ synthesized silver nanocatalysts decorated on a polyaniline–chitosan–magnetite (Ag@PANI-CS-Fe₃O₄) nanocomposite catalyst for the hydrogenation of 4-NP by aqueous NaBH₄ (Figure 20).

The Ag@PANI-CS-Fe₃O₄ nanocomposite catalyst successfully reduced 4-NP under aqueous NaBH₄ reaction conditions as monitored by UV–vis spectrophotometry, which confirmed rapid hydrogenation of 4-NP to 4-AP in less than 10 min; the magnetic catalytic systems reached active with an efficacy of 95% in the fourth cycle. By using a similar technique, Zeng et al.⁹⁵ synthesized Fe₃O₄@polydopamine (PDA)–Au nanocatalysts, which were characterized using TEM, indicating the presence of Au NPs on the core surface of the polymer shell. The aqueous o-nitroaniline solution could be reduced in 7 min using a small amount of Fe₃O₄@PDA–Au nanocomposite catalyst. In this work, PDA effectively protected the iron oxide and Au NPs from the aggregation in the solution. The core–shell catalyst also displayed good catalytic activity for various nitrobenzene reductions (Table 4).

Table 4. Reduction of Various Nitrobenzenes Using Fe₃O₄@PDA–Au Nanocatalysts

| Entry | Compound       | Structure | Time (min) | Conversion (%) |
|-------|----------------|-----------|------------|----------------|
| 1     | o-Nitroaniline |           | 7          | 99             |
| 2     | m-Nitroaniline |           | 5          | 99             |
| 3     | p-Nitroaniline |           | 6          | 99             |
| 4     | o-Nitrotoluene |           | 67         | 93             |
| 5     | m-Nitrotoluene |           | 72         | 90             |
| 6     | p-Nitrophenol  |           | 19         | 99             |
| 7     | o-Nitrochloro-  |           | 120        | 87             |
| 8     | 2,4-Dinitrotoluene | | 108        | 99             |

Shokouhimehr and colleagues⁹⁶ prepared a magnetically retrievable nanocomposite adorned with Pd nanocatalysts, which was applied for the reduction of NAs in aqueous NaBH₄ solution. Pyrrole monomers were polymerized in the presence of Pd precursors and iron nanopowder forming Pd NPs on the polypyrrole framework without the requirement of an additional reductant (Figure 21).

TEM and FESEM images of the prepared magnetic catalytic systems showed uniform ~2 nm Pd NPs accommodated discretely on the polypyrrole layer of the prepared nanocomposite (Figure 22). The nanocomposite catalyst could be easily separated and

Figure 18. Schematic diagram for the fabrication of magnetic metal oxide@C@Ag–Au nanocatalysts.

Figure 19. Schematic procedure for the preparation of Pt–Pd NPs on magnetic core–shell nanocatalysts.

Figure 20. Synthetic strategy for the preparation of Ag@PANI-CS-Fe₃O₄ nanocomposite catalyst.

Figure 21. Synthetic strategy for the preparation of Ag@PANI-CS-Fe₃O₄ nanocomposite catalyst.

Figure 22. Synthetic strategy for the preparation of Ag@PANI-CS-Fe₃O₄ nanocomposite catalyst.

Shokouhimehr and colleagues⁹⁶ prepared a magnetically retrievable nanocomposite adorned with Pd nanocatalysts, which was applied for the reduction of NAs in aqueous NaBH₄ solution. Pyrrole monomers were polymerized in the presence of Pd precursors and iron nanopowder forming Pd NPs on the polypyrrole framework without the requirement of an additional reductant (Figure 21).

TEM and FESEM images of the prepared magnetic catalytic systems showed uniform ~2 nm Pd NPs accommodated discretely on the polypyrrole layer of the prepared nanocomposite (Figure 22). The nanocomposite catalyst could be easily separated and
recycled using a small magnet and reused for seven consecutive cycles of high-yield reduction of nitrobenzene (99−95%) in aqueous NaBH₄ solution.

5.4. Magnetic Nanocatalysts Decorated on Mesoporous Silica Nanospheres. Magnetic core−shell nanocatalysts have been utilized for hydrogenation reactions without any support. For example, a Ag@Ni nanocatalyst was prepared via a simple one-pot synthesis, which catalyzed the reduction of NAs. However, the application of mesoporous silica (mSiO₂) is an important issue for heterogeneous catalysis because of their excellent stability, high surface area, tunable pore size, and chemical inertness. Yao et al. prepared the FeₓOᵧ/Pd@mSiO₂ magnetic NPs consisting of a movable FeₓOᵧ core and mesoporous mSiO₂ (Figure 23). The FeₓOᵧ@mSiO₂ NPs were prepared by mixing glucose and FeₓOᵧ NPs in water followed by heating at 200 °C in an autoclave for 8 h. The FeₓOᵧ@mSiO₂ was prepared by adding the FeₓOᵧ@mSiO₂ in PdCl₂ ethanol solution, followed by injecting NH₂NH₂ and washing the ensuing products. Finally, the mSiO₂ on the surface was formed by using tetraethyl orthosilicate and CTAB, followed by calcination at 600 °C. The obtained product was characterized by SEM, TEM, FT-IR, and UV−vis.

The catalytic activity of the core−shell nanocomposite catalyst was verified for the reduction of NAs, which was accomplished in ~40 min; successive recycling of 4-NP reduction was achieved with the conversion of ~100% for each cycle (Figure 24).

Wang et al. designed a mesoporous silica with a dandelion-like shape, which was decorated with Ni@Pd nanocatalysts for the reduction of 4-NP and 4-chlorophenol (Figure 25). The silica spheres with a size of 200−300 nm efficiently inhibited the aggregation of Ni@Pd NPs providing an extensive accessibility for the hydrogenation of NAs. The magnetically separable catalysts can be promising candidates for important organic conversions and industrial applications.

6. CONCLUSIONS
Recent advancements in the hydrogenation of nitroaromatics to aminoaromatics, catalyzed by various nanocatalysts using aqueous NaBH₄ as a reductant, are summarized with representative examples of the mono- and multimetal supported and magnetic nanocatalysts. Promising catalytic efficiency has been attained by designing the catalysts with high specific surface area and good protection of the active nanocatalysts. However, substantial challenges still persist for the large-scale production, which requires cost efficiency and a
The capability to sustain considerable recycling operation. The synthesis of sustainable nanocatalysts needs further innovative strategies and developments to solve the current limitations such as aggregation, recyclability, stability, and durability.

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: hwjang@snu.ac.kr (H.W.J.).
*E-mail: mrsh2@snu.ac.kr (M.S.).
*E-mail: varma.rajender@epa.gov (R.S.V.).

**ORCID**
Jun Min Suh: 0000-0001-8506-0739
Ho Won Jang: 0000-0002-6952-7359
Mohammadreza Shokouhimehr: 0000-0003-1416-6805
Rajender S. Varma: 0000-0001-9731-6228

**Author Contributions**
‡K.Z. and J.M.S. contributed equally to this work.

**Notes**
The research presented was not performed or funded by the U.S. Environmental Protection Agency (EPA) and was not necessarily representative of the views or the policies of the EPA. The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
The financial support of the Future Material Discovery Program (2016M3D1A1027666), and the Basic Science Research Program (2017R1A2B3009135) through the National Research Foundation of Korea is appreciated.

**REFERENCES**
(1) Varma, R. S. Journey on greener pathways: from the use of alternate energy inputs and benign reaction media to sustainable applications of nano-catalysts in synthesis and environmental remediation. *Green Chem.* 2014, 16, 2027.
(2) Goswami, A.; Rath, A. K.; Aparicio, C.; Tomanec, O.; Petr, M.; Pocklanova, R.; Gawande, M. B.; Varma, R. S.; Zboril, R. In situ generation of Pd–Pt core–shell nanoparticles on reduced graphene oxide (Pd@Pt/rGO) using microwaves: applications in dehalogenation reactions and reduction of olefins. *ACS Appl. Mater. Interfaces* 2017, 9, 2815.
(3) Shokouhimehr, M.; Lee, J. E.; Han, S. I.; Hyeon, T. Magnetically recyclable hollow nanoparticle catalysts for heterogeneous reduction of nitroarenes and Suzuki reactions. *Chem. Commun.* 2013, 49, 4779.
(4) Datta, K. J.; Rath, A. K.; Gawande, M. B.; Ranc, V.; Zoppellaro, G.; Varma, R. S.; Zboril, R. Base-free transfer hydrogenation of nitroarenes catalyzed by micro-mesoporous iron oxide. *ChemCatChem* 2016, 8, 2351.
(5) Kabalka, G. W.; Laila, G. M. H.; Varma, R. S. Selected reductions of conjugated nitroalkenes. *Tetrahedron* 1990, 46, 7443.
(6) Shokouhimehr, M.; Kim, T.; Jun, S. W.; Shin, K.; Jang, Y.; Kim, B. H.; Kim, J.; Hyeon, T. Magnetically separable carbon nano-composite catalysts for efficient nitroarene reduction and Suzuki reactions. *Appl. Catal. A-Gen.* 2014, 476, 133.
(7) Blaser, H. U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. Selective hydrogenation for fine chemicals: recent trends and new developments. *Adv. Synth. Catal.* 2003, 345, 103.
(8) Ayad, M. M.; Amer, W. A.; Kotp, M. G. Magnetic polyaniline-chitosan nanocomposite decorated with palladium nanoparticles for enhanced catalytic reduction of 4-nitrophenol. *Mol. Catal.* 2017, 439, 72.
(9) Datta, K. J.; Rath, A. K.; Kumar, P.; Kaslik, J.; Medrik, I.; Ranc, V.; Varma, R. S.; Zboril, R.; Gawande, M. B. Synthesis of flower-like maghemite nanoassembly: application in the efficient reduction of nitroarenes. *Sci. Rep.* 2017, 7, 11585.
(10) Rath, A. K.; Gawande, M. B.; Ranc, V.; Pechousek, J.; Petr, M.; Cepe, K.; Varma, R. S.; Zboril, R. Continuous flow hydrogenation of nitroarenes, azides and alkenes using maghemite–Pd nanocomposites. *Catal. Sci. Technol.* 2016, 6, 152.
(11) Vass, A.; Dudas, J.; Toth, J.; Varma, R. S. Solvent-free reduction of aromatic nitro compounds with alumina-supported hydrazine under microwave irradiation. *Tetrahedron Lett.* 2001, 42, 5347.
(12) Qin, G. W.; Wei, P.; Ma, X.; Xu, X.; Ren, Y.; Sun, W.; Zuo, L. Enhanced catalytic activity of Pt nanomaterials: from monodisperse nanoparticles to self-organized nanoparticle-linked nanowires. *J. Phys. Chem. C* 2010, 114, 6909.
(13) He, S.; Niu, H.; Zeng, T.; Wang, S.; Cai, Y. A facile and efficient method for continuous reduction of nitroaromatic compounds through the cyclic transformation between Fe (II)-complexes and nano-valent iron. *ChemistrySelect* 2016, 1, 2821.
(14) Mahmoud, A.; Tabor, C. E.; El-Sayed, M. A.; Ding, Y.; Wang, Z. L. A new catalytically active colloidal platinum nanocatalyst: the multiformed nanostar single crystal. *J. Am. Chem. Soc.* 2008, 130, 4590.
(15) Zhang, J.; Chen, G.; Chaker, M.; Rosei, F.; Ma, D. Gold nanoparticles decorated ceria nanotubes with significantly high catalytic activity for the reduction of Nitrophenol and Mechanism Study. *Appl. Catal. B* 2013, 132-133, 107.
(16) Narayanan, R.; El-Sayed, M. A. Shape-dependent catalytic activity of platinum nanoparticles in colloidal solution. *Nano Lett.* 2004, 4, 1343.
(17) Gelder, E. A.; Jackson, S. D.; Lok, C. M. The hydrogenation of nitrobenzene to aniline: a new mechanism. *Chem. Commun.* 2005, 0, 522.
(18) Shokouhimehr, M. Magnetically separable and sustainable nanostructured catalysts for heterogeneous reduction of nitroaromatics. *Catalysts* 2015, 5, 534.
(19) Ansar, S. M.; Kitchens, C. L. Impact of Gold Nanoparticle Stabilizing Ligands on the Colloidal Catalytic Reduction of 4-Nitrophenol. *ACS Catal.* 2016, 6, 5553.
(20) Zeng, H. C. Integrated Nanocatalysts. *Acc. Chem. Res.* 2013, 46, 226.
(21) Shokouhimehr, M.; Kim, J. H.; Lee, Y. S. Heterogeneous Heck reaction catalyzed by recyclable polymer-supported N-heterocyclic carbene-palladium complex. *Synlett.* 2006, 4, 0618.
(22) Shokouhimehr, M.; Shin, K. Y.; Lee, J. S.; Hackett, M. J.; Jun, S. W.; Oh, M. H.; Jang, J.; Hyeon, T. Magnetically recyclable core–shell nanocatalysts for efficient heterogeneous oxidation of alcohols. *J. Mater. Chem. A* 2014, 2, 7593.
(23) Murray, C. B.; Kagan, C. R.; Ravendri, M. G. Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies. *Annu. Rev. Mater. Sci.* 2000, 30, 545.
(24) Astruc, D.; Lu, F.; Aranzaes, J. R. Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis. Angew. Chem. Int. Ed. 2005, 44, 7852.

(25) Choi, K. H.; Shokouhimir, M.; Kang, Y. S.; Chung, D. Y.; Chung, Y. H.; Ahn, M.; Sung, Y. E. Preparation and characterization of palladium nanoparticles supported on nickel hexacyanoferrate for fuel cell application. Bull. Korean Chem. Soc. 2013, 34, 1195.

(26) Han, C.; Chen, Z.; Zhang, N.; Colmenares, J. C.; Xu, Y.-J. Hierarchically CdS decorated 1D ZnO nanorods-2D graphene hybrids: low temperature synthesis and enhanced photocatalytic performance. Adv. Funct. Mater. 2015, 25, 221.

(27) Shokouhimir, M.; Shahedi Asl, M.; Mazinani, B. Modulated large-pore mesoporous silica as an efficient base catalyst for the Henry reaction. Res. Chem. Intermed. 2018, 44, 1617.

(28) Herves, P.; Perez-Lorenzo, M.; Liz-Marzan, L. M.; Drubiella, J.; Lu, Y.; Ballauff, M. Catalysis by metallic nanoparticles in aqueous solution: model reactions. Chem. Soc. Rev. 2012, 41, 5577.

(29) Ghosh, S. K.; Mandal, M.; Kundu, S.; Nath, S.; Pal, T. Bimetallic Pt−Ni nanoparticles can catalyze reduction of aromatic nitro compounds by sodium borohydride in aqueous solution. Appl. Catal. A-Gen. 2004, 268, 61.

(30) Hailes, H. C. Reaction solvent selection: the potential of water as a solvent for organic transformations. Org. Process Res. Dev. 2007, 11, 114.

(31) Tang, S.; Vongehr, S.; Meng, X. Controllable incorporation of Ag and Ag−Au nanoparticles in carbon spheres for tunable optical and catalytic properties. J. Mater. Chem. 2010, 20, 5436.

(32) Lu, Y.; Yuan, J.; Polzer, F.; Drechsler, M.; Preussner, J. In situ growth of catalytically active Au−Pt bimetallic nanorods in thermo-responsive core−shell microgels. ACS Nano 2010, 4, 7078.

(33) Layek, K.; Kantam, M. L.; Shirai, M.; Nishio-Hamane, D.; Sasaki, T.; Maheswaran, H. Gold nanoparticles stabilized on nanocrystalline magnesium oxide as an active catalyst for reduction of nitroarenes in aqueous medium at room temperature. Green Chem. 2012, 14, 3164.

(34) Liu, X.; Cheng, H.; Cui, P. Catalysis by silver nanoparticles/porous silicon for the reduction of nitroaromatics in the presence of sodium borohydride. Appl. Surf. Sci. 2014, 292, 695.

(35) Rathore, P. S.; Patid, R.; Shrivastav, T.; Thakore, S. Magnetically separable core−shell iron oxide@nickel nanoparticles as high-performance recyclable catalysts for chemoselective reduction of nitroaromatics. Catal. Sci. Technol. 2015, 5, 286.

(36) Farooqi, Z. H.; Begum, R.; Naseem, K.; Rubab, U.; Usman, M.; Khan, A.; Ijaz, A. Fabrication of silver nanoparticles in pH responsive polymer microgel dispersion for catalytic reduction of nitrobenzene in aqueous medium. Russ. J. Phys. Chem. A 2016, 90, 2600.

(37) Yanhe, H.; Mengmeng, Q.; Lei, Z.; Sang, Y.; Liu, M.; Zhao, T.; Niu, J.; Zhang, S. Degradation of nitrobenzene by synchronous oxidation and reduction in an internal circulation microelectrolysis reactor. J. Hazard. Mater. 2018, 365, 448.

(38) Saikia, H.; Borah, B. J.; Bharali, P. Room temperature reduction of nitroaromatics using Pd nanoparticles stabilized on nano-CeO2. ChemistrySelect 2017, 2, 10324.

(39) Richard, W.; Evard, D.; Busson, B.; Humbert, C.; Dalstein, L.; Tadjetdine, A.; Gros, P. The reduction of 4-nitrobenzene diazonium electrografted layer: an electrochemical study coupled to in situ sum-frequency generation spectroscopy. Electrochim. Acta 2018, 283, 1640.

(40) Iwase, K.; Fujimani, N.; Hashimoto, K.; Kамиyama, K.; Nakanishi, S. Cooperative electrocatalytic reduction of nitrobenzene to aniline in aqueous solution by copper-modified covalent triazine framework. Chem. Lett. 2017, 47, 304.

(41) Zhang, N.; Xu, Y. J. Aggregation-and leaching-resistant, reusable, and multifunctional Pd@CeO2 as a robust nanocatalyst achieved by a hollow core−shell strategy. Chem. Mater. 2013, 25, 1979.

(42) Shah, M.; Guo, Q. X.; Fu, Y. The colloidal synthesis of unsupported nickel-tin bimetallic nanoparticles with tunable composition that have high activity for the reduction of nitroarenes. Catal. Commun. 2015, 65, 85.

(43) Shang, L.; Bian, T.; Zhang, B.; Zhang, D.; Wu, L.-Z.; Tung, C.-H.; Yin, Y.; Zhang, T. Graphene-supported ultrathin metal nanoparticles encapsulated by mesoporous silica: robust catalysts for oxidation and reduction reactions. Angew. Chem. Int. Ed. 2014, 126, 254.

(44) Guo, M.; He, J.; Li, Y.; Ma, S.; Sun, X. One-step synthesis of hollow porous gold nanoparticles with tunable particle size for the reduction of 4-nitrophenol. J. Hazard. Mater. 2016, 310, 89.

(45) Gangula, A.; Podila, R.; Ramakrishna, M.; Karanam, L.; Janardhana, C.; Rao, A. M. Catalytic Reduction of 4-Nitrophenol using Biogenic Gold and Silver Nanoparticles Derived from Bryenia rhamboides. Langmuir 2011, 27, 15268.

(46) Pasricha, R.; Bala, T.; Biradar, A. V.; Umbarkar, S.; Sastry, M. Synthesis of catalytically active porous platinum nanoparticles by transmetallation reaction and proposition of the mechanism. Small 2009, 5, 1467.

(47) Pradhan, N.; Pal, A.; Pal, T. Catalytic reduction of aromatic nitro compounds by coinage metal nanoparticles. Langmuir 2001, 17, 1800.

(48) Kalekar, A. M.; Sharma, K. K. K.; Lehoux, A.; Audonnet, F.; Remita, H.; Saha, A.; Sharma, G. K. Investigation into the catalytic activity of porous platinum nanostructures. Langmuir 2013, 29, 11431.

(49) Li, A.; Luo, Q.; Park, S. J.; Cooks, R. G. Synthesis and Catalytic Reactions of Nanoparticles formed by Electrospray Ionization of Coinage Metals. Angew. Chem., Int. Ed. 2014, 53, 3147.

(50) Pradhan, N.; Pal, A.; Pal, T. Silver nanoparticle catalyzed reduction of aromatic nitro compounds. Colloids Surf. A 2002, 196, 247.

(51) Dutta, S.; Sarkar, S.; Ray, C.; Roy, A.; Sahoo, R.; Pal, T. Mesoporous gold and palladium nanoleaves from liquid−liquid interface: enhanced catalytic activity of the palladium analogue toward hydrazine-assisted room-temperature 4-nitrophenol reduction. ACS Appl. Mater. Interface 2014, 6, 9134.

(52) Zhang, W.; Tan, F.; Wang, W.; Qiu, X.; Qiao, X.; Chen, J. Facile, template-free synthesis of silver nanodendrites with high catalytic activity for the reduction of p-nitrophenol. J. Hazard. Mater. 2012, 217, 36.

(53) Imura, Y.; Tsujimoto, K.; Morita, C.; Kawai, T. Preparation and catalytic activity of Pd and bimetallic Pd−Ni nanowires. Langmuir 2014, 30, 5026.

(54) Mahmoud, M. A.; Garlyev, B.; El-Sayed, M. A. Determining the mechanism of solution metallic nanocatalysis with solid and hollow nanoparticles: homogeneous or heterogeneous. J. Phys. Chem. C 2013, 117, 21886.

(55) Kaur, R.; Giordano, C.; Gradzielski, M.; Mehta, S. K. Synthesis of highly stable, water-dispersible copper nanoparticles as catalysts for nitrobenzene reduction. Chem. - Asian J. 2014, 9, 189.

(56) Kadama, H. K.; Tilve, S. G. Advancement in methodologies for reduction of nitroarenes. RSC Adv. 2015, 5, 83391.

(57) Petkar, D. R.; Kadu, B. S.; Chikate, R. C. Highly efficient and chemoselective transfer hydrogenation of nitroarenes at room temperature over magnetically separable Fe−Ni bimetallic nanoparticles. RSC Adv. 2014, 4, 8004.

(58) Chu, C.; Su, Z. Facile synthesis of AuPt alloy nanoparticles in polyelectrolyte multilayers with enhanced catalytic activity for reduction of 4-nitrophenol. Langmuir 2014, 30, 15345.

(59) Saikia, H.; Borah, B. J.; Yamada, Y.; Bharali, P. Enhanced catalytic activity of CuPd alloy nanoparticles towards reduction of nitroaromatics and hexavalent chromium. J. Colloid Interface Sci. 2017, 486, 46.

(60) Fu, G.; Ding, L.; Chen, Y.; Lin, J.; Tang, Y.; Lu, T. Facile water-based synthesis and catalytic properties of platinum−gold alloy nanocubes. CrystEngComm 2014, 16, 1606.

(61) Ghosh, S. K.; Mandal, M.; Kundu, S.; Nath, S.; Pal, T. Bimetallic Pt−Ni nanoparticles can catalyze reduction of aromatic nitro compounds by sodium borohydride in aqueous solution. Appl. Catal., A 2004, 268, 61.
(62) Chen, H.; Zhou, L.; Wen, M.; Wu, Q.; Wang, C. A branched-dumbbell PtNiFe nanostucture and its high catalytic reduction activity for nitro-aromatic compounds. *Mater. Res. Bull.* 2014, 60, 322.

(63) Choi, K. H.; Shokouhimehr, M.; Sung, Y. E. Heterogeneous Suzuki cross-coupling reaction catalyzed by magnetically recyclable nanocatalyst. *Bull. Korean Chem. Soc.* 2013, 34, 193.

(64) Dong, Z.; Le, X.; Li, X.; Zhang, W.; Dong, C.; Ma, J. Silver nanoparticles immobilized on fibrous nano-silica as highly efficient and recyclable heterogeneous catalyst for reduction of 4-nitrophenol and 2-nitroaniline. *Appl. Catal. B-Environ.* 2014, 158, 129.

(65) Tang, J.; Shi, Z.; Berry, R. M.; Tam, K. C. Mussel-inspired green metalization of silver nanoparticles on cellulose nanocrystals and their enhanced catalytic reduction of 4-nitrophenol in the presence of β-cycloextrin. *Ind. Eng. Chem. Res.* 2015, 54, 3299.

(66) Wu, Y.; Wen, M.; Wu, Q.; Fang, H. Ni/graphene nanomaterial and its electron-encatalyzed action for hydrogenation reaction of nitrophenol. *J. Phys. Chem. C* 2014, 118, 6307.

(67) Polskhettivar, V.; Varma, R. S. Green chemistry by nanocatalysis. *Green Chem.* 2010, 12, 743.

(68) Mirzaiheri, B.; Shokouhimehr, M.; Beitollahi, A. Synthesis of mesoporous tungsten oxide by template-assisted sol–gel method and its photocatalytic degradation activity. *J. Sol-Gel Sci. Technol.* 2017, 82, 148.

(69) Kim, A.; Rafiei, S. M.; Abolhosseini, S.; Shokouhimehr, M. Palladium nanocatalysts confined in mesoporous silica for heterogeneous reduction of nitroaromatics. *Energy Environ. Focus* 2015, 4, 18.

(70) Shoohouhimehr, M.; Piao, Y.; Kim, J.; Jang, Y.; Hyeon, T. A magnetically recyclable nanocomposite catalyst for olefin epoxidation. *Angew. Chem. Int. Ed.* 2007, 46, 7039.

(71) Matsu, J. C.; Zhang, S.; DeRita, L.; Marinovic, N. S.; Chen, J. G.; Graham, G. W.; Pan, X.; Christopher, P. Adsorbate-mediated strong metal–support interactions in oxide-supported Rh catalysts. *Nat. Chem.* 2017, 9, 120.

(72) Ye, W.; Yu, J.; Zhou, Y.; Gao, D.; Wang, D.; Wang, C.; Xue, D. Green synthesis of Pt–Au dendrimer-like nanoparticles supported on polydopamine-functionalized graphene and their high performance toward 4-nitrophenol reduction. *Appl. Catal. B* 2016, 181, 371.

(73) Wang, H.; Dong, Z.; Na, C. Hierarchical carbon nanotube membrane-supported gold nanoparticles for rapid catalytic reduction of p-nitrophenol. *ACS Sustain. Chem. Eng.* 2013, 1, 746.

(74) Han, J.; Fang, P.; Jiang, W.; Li, L.; Guo, R. Ag-nanoparticle-loaded mesoporous silica: spontaneous formation of Ag nanoparticles and mesoporous silica SBA-15 by a one-pot strategy and their catalytic applications. *Langmuir* 2012, 28, 4768.

(75) Zhang, Z.; Shao, C.; Sun, Y.; Mu, J.; Zhang, M.; Zhang, P.; Guo, Z.; Liang, P.; Wang, C.; Liu, Y. Tubular nanocomposite catalysts based on size-controlled and highly dispersed silver nanoparticles assembled on electrospun silica nanotubes for catalytic reduction of 4-nitrophenol. *J. Mater. Chem.* 2012, 22, 1387.

(76) Yang, M. Q.; Pan, X.; Zhang, N.; Xu, Y.-J. A facile one-step way to anchor noble metal (Au, Ag, Pd) nanoparticles on a reduced graphene oxide mat with catalytic activity for selective reduction of nitroaromatic compounds. *CrystEngComm* 2013, 15, 6819.

(77) Zeng, J.; Zhang, Q.; Chen, J.; Xia, Y. A comparison study of the catalytic properties of Au-based nanocages, nanoboxes, and nanoparticles. *Nanotechnology* 2010, 10, 30.

(78) Li, X. H.; Wang, X.; Antonietti, M. Mesoporous g-C3N4 nanorods as multifunctional supports of ultrafine metal nanoparticles: hydrogen generation from water and reduction of nitrophenol with tandem catalysis in one step. *Chem. Sci.* 2012, 3, 2170.

(79) Chen, Z.; Liu, S.; Yang, M. Q.; Xu, Y. J. Synthesis of uniform CdS nanoparticles/graphene hybrid nanocomposites and their application as visible light photocatalyst for selective reduction of nitro organic in water. *ACS Appl. Mater. Interfaces* 2013, 5, 4309.

(80) Zhang, K.; Hong, K.; Suh, J. M.; Lee, T. H.; Kwon, O.; Shokouhimehr, M.; Jang, H. W. Facile synthesis of monodispersed Pd nanocatalysts decorated on graphene oxide for reduction of nitroaromatics in aqueous solution. *Res. Chem. Intermed.* 2018, 1–13.
stability and their application in catalytic reduction of 4-nitrophenol. 
*Nanoscale* **2013**, *5*, 5896.

(100) Wang, Y.; Biradar, A. V.; Duncan, C. T.; Asefa, T. Silica nanosphere-supported shaped Pd nanoparticles encapsulated with nanoporous silica shell: efficient and recyclable nanocatalysts. *J. Mater. Chem.* **2010**, *20*, 7834.

(101) Dong, Z.; Le, X.; Dong, C.; Zhang, W.; Li, X.; Ma, J. Ni@Pd core–shell nanoparticles modified fibrous silica nanospheres as highly efficient and recoverable catalyst for reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol. *Appl. Catal. B* **2015**, *162*, 372.

(102) Sharma, R. K.; Dutta, S.; Sharma, S.; Zboril, R.; Varma, R. S.; Gawande, M. B. Fe₃O₄ (iron oxide)-supported nanocatalysts: synthesis, characterization and applications in coupling reactions. *Green Chem.* **2016**, *18*, 3184.