RSC Advances

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Bio-inspired noble metal-free reduction of nitroarenes using NiS_{2+x}/g-C_3N_4†

Cite this: *RSC Adv.*, 2014, **4**, 60873

Received 10th September 2014
Accepted 31st October 2014

DOI: 10.1039/c4ra10127h

www.rsc.org/advances

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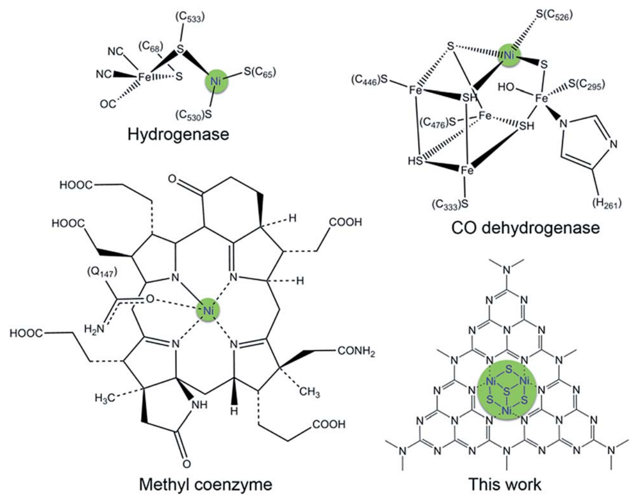
We introduce the concept of bio-inspired catalytic hydrogenation of nitroarenes by mimicking the catalytic behavior of enzymes with NiS_{2+x} nanoparticles and polymeric melon (g-C_3N_4). The g-C_3N_4-supported NiS_{2+x} nanoparticles functioned as ligand-free and noble metal-free catalysts and offered high efficiency, comparable to noble metal-based catalysts, but at a much better selectivity.

Reduction/hydrogenation of nitroarenes to corresponding substituted anilines is of great importance, due to the wide applications of aniline as one of the most important intermediates in industry for fabricating polymers and fine chemicals. Typically, the hydrogenation of nitroarenes is catalyzed by either supported noble metal nanoparticles or metal complexes with expensive ligands.[1–5] The majority of those catalysts investigated in the literature were involved with expensive noble metal components or specific ligands, limiting their applications in large scale. Moreover, only limited samples of Au or Pd nanocatalysts and Fe complexes can access the hydrogenation of nitroarenes under ambient conditions.[6–8] Recently, the M. Beller group reported that a series of iron complexes exhibit remarkable activities for catalytic or photocatalytic dehydrogenation of FA under mild conditions with very high hydrogen evolution rates.[9,10] However, practical utilization of those homogeneous catalysts for releasing H_2 from FA was obviously prevented by the cost of expensive ligands and the difficulty in reuse.

Heterogeneous catalysts are usually preferred for practical applications because of their better stability, ease of separation and recyclability as compared to homogeneous counterparts. Despite numerous developments of heterogeneous catalysts for the reduction of nitroarenes, there still exists a great interest in novel, inexpensive, active and selective catalysts. Cobalt oxide catalysts were recently introduced as an excellent heterogeneous catalyst for the hydrogenation of nitroarenes into the corresponding anilines, whilst specific ligands were still involved in the fabrication of the catalysts.[11,12] For practical applications, abundant, cheap and reusable catalysts are appreciated without the involvement of noble metal or expensive organic ligands.

In nature, enzymes composed of amino acids and [Ni–Fe–S] clusters (Scheme 1) can use binding and proximity effects to achieve an astounding rate for specific reactions (*e.g.* hydrogenation of CO) with high selectivity under mild conditions. Enzyme mimics have long been an important branch of bioinorganic chemistry, which is inspired by nature and aims to follow the general principles of natural enzymes using alternative materials. Simply mimicking the binding and proximity effects of enzymes, by using some inorganic clusters or



Scheme 1 Chemical structures of typical enzymes with [Ni–S] or [Ni–N] centers and the proposed structure of NiS_{2+x}/g-C_3N_4 nanohybrids (only one unit cell of NiS_{2+x} was depicted for simplification).

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† Electronic supplementary information (ESI) available: Experimental details, characterizations, XPS, XRD, FTIR and PL spectra, and measurements. See DOI: 10.1039/c4ra10127h

nanoparticles as model materials, can make artificial enzyme progress for catalysis or photo-catalysis.[13,14]

Although important reports have been made recently regarding the use of metal oxide and manganese sulfide materials as robust catalysts for photo-splitting and electro-splitting of water,[15–17] few such materials exist for hydrogenation of organic compounds. Thus, we turned towards a noble metal-free heterogeneous catalyst based on transition metal sulfide nanoclusters and amine-group-rich polymeric carbon nitride (g-C_3N_4). The g-C_3N_4 materials have recently been described as an excellent support to embed and activate metallic nanoparticles for both photocatalysis and organic synthesis.[18–25] More importantly, the unique heterocyclic macrocycle structure of g-C_3N_4 with an N–C–N-bonding pattern resembling porphyry in Scheme 1 can principally act as *in situ* "solid ligands" to provide strong coordination to metal ions and thus can tune the electronic environment of the supported nanoclusters.[26–29] We here establish that highly selective reduction of nitroarenes to the corresponding anilines is efficiently catalysed by g-C_3N_4 supported NiS_{2+x} nanoclusters (NiS_{2+x}/CN) under mild conditions. A commercially available reductant, $NaBH_4$, was selected as a model hydrogen source, because $NaBH_4$ has been widely used with metallic nanoparticle-based catalysts for the reduction of nitroarenes at an ambient temperature.[8,10,30,31] The selectivity of the reduction of $-NO_2$ over NiS_{2+x}/g-C_3N_4 is very high, even in the presence of other functional groups.

The NiS_{2+x}/CN catalysts were prepared by a modified self-catalytic method previously described in our group (see the ESI† for details).[32,33] A typical TEM image revealed the stability of mesoporous g-C_3N_4 after the deposition of the NiS_{2+x} components on the surface (Fig. 1A). After the deposition of NiS_{2+x}, both the surface area and the pore size distribution of mesoporous g-C_3N_4 remained unchanged (Fig. S1†). Due to the similar contrasts of both g-C_3N_4 and NiS_{2+x} in the view range of TEM, it is difficult to distinguish NiS_{2+x} from g-C_3N_4 at a relatively low resolution. A high resolution TEM (HRTEM) image (Fig. 1B), however, ambiguously displays a fringe with lattice spacing of approximately 2.52 Å, corresponding to the (210) plate of NiS_2. The successful deposition of NiS_2 can also be confirmed by XRD (See Fig. S2†). The main peaks in the X-ray diffraction pattern can be indexed to NiS_2 (JCPDS no. 11-0099).

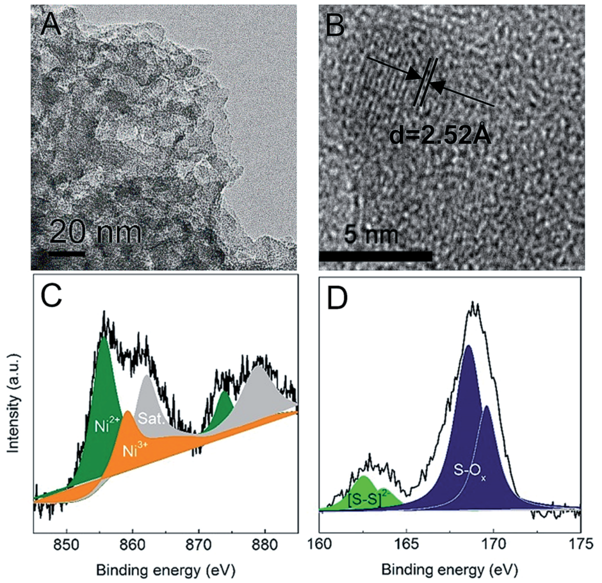


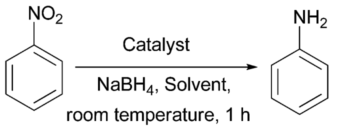
Fig. 1 TEM (A) and HRTEM (B) images of NiS_{2+x}/CN. XPS spectra of Ni 2p (C) and S 2p (D). Two shake-up satellites of Ni^{2+} (denoted as "Sat.")[34] were also observed in the Ni $2p_{3/2}$ XPS spectrum.

The X-ray photoelectron spectroscopy (XPS) spectra of the samples further demonstrated the contents and chemical status of the NiS_{2+x} nanoclusters. As revealed by the XPS analysis result (Fig. S3†), the atomic number ratio of nickel and sulphur is 1 : 2.2, which is slightly lower than the theoretical value (1 : 2) of NiS_2. Consequently, the typical sample was named as NiS_{2+x}/CN, due to the non-stoichiometric composition of our sample. The high resolution Ni 2p XPS spectrum of the typical sample (Fig. 1C) revealed that small parts of Ni^{2+} were oxidized into Ni^{3+} during the process of depositing NiS_{2+x} nanoclusters on the surface of the g-C_3N_4 support. The fact that the self-catalytic method for depositing metal sulphides was conducted at 80 °C rather suggests a photocatalytic oxidation of Ni^{2+} using g-C_3N_4 in air. Such a photocatalytic oxidation reaction has been well defined for g-C_3N_4 with a specific nanostructure for organic synthesis, where the formation of O^{2-} ions was detected.[35] The possibility of a photocatalytic oxidation reaction during the formation process of NiS_2 nanoclusters was further confirmed by the detailed S 2p XPS spectrum (Fig. 1D), with two strong peaks at 168.56 eV and 169.6 eV attributed to sulfur oxoanions (denoted as S–O_x in Fig. 1D).[36] The typical peaks at 162.55 eV and 163.68 eV suggested the presence of S–S bonds of NiS_2 in the samples, again revealing the formation of NiS_2 on the surface of the g-C_3N_4 support.[37,38] All these observations revealed a functional group-rich surface of the NiS_2 nanoparticles, well explaining the slightly lower Ni/S ratio. Obviously, these groups will benefit from the formation of a coupled interface between g-C_3N_4 and the NiS_{2+x} nanoclusters, and thus shows a potential application of NiS_{2+x}/CN as a catalyst for organic synthesis.

Aromatic amines are key intermediates in the synthesis of fine chemicals, biologically active compounds and more. As a typical aromatic amine, aniline, with a worldwide production exceeding four million tons per year, was obtained mainly (∼97%) from hydrogenation of nitrobenzene. The excess amount of H_2 gas (>100 times in moles) was usually used for the catalytic transformation of nitrobenzene to aniline at high pressure (greater than 5 atm) and high temperature (>200 °C), and the process is thus of "high-energy consumption" and unsafe in terms of H_2 handling. Thus, chemoselective hydrogenation of nitro compounds to aniline and the corresponding substituted derivates in a sustainable manner is of great importance for both industrial applications and fundamental researches. We tested the possibility of hydrogenation of nitrobenzene to aniline for the NiS_{2+x}/CN samples at room temperature by using water as the green solvent and $NaBH_4$ as the only hydrogen source.

No conversion was observed without a catalyst (entry 1, Table 1) or $NaBH_4$ (entry 2, Table 1). Bare carbon nitride offered no

Table 1 Hydrogenation of nitrobenzene[a]



Entry	Catalyst	Conv. [%]	Sel. [%]
1[b]	—	—	—
2[c]	NiS_{2+x}/CN	—	—
3	CN	—	—
4	NiS_2/N-LC	48	79[d]
5	NiS_2/C	99	77[d]
6	NiS_2	42	53[d]
7	NiS_{2+x}/CN	>99	>99
8	Pd/CN	>99	>99
9	Au/CN	>99	56[d]
10	Pt/CN	>99	54[d]

[a] Reaction conditions: 0.5 mmol nitrobenzene, 50 mL of water, 10 mg of catalyst, 0.5 mmol $NaBH_4$, room temperature, 1 h. [b] Without catalyst. [c] Without $NaBH_4$. [d] The byproduct is nitrosobenzene.

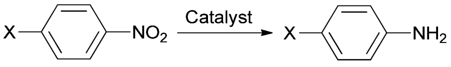
conversion at all (entry3, Table 1). Unsupported NiS_2 nanoparticles and carbon black (C, surface area: 62.5 $m^2\ g^{-1}$) or nitrogen doped layered carbon (N-LC, surface area: 190 $m^2\ g^{-1}$)[39] supported NiS_{2+x} nanoparticles could only offer moderate conversions and selectivity (entry 4–6, Table 1). Under fixed conditions, NiS_{2+x}/CN (9 wt%) offered a conversion of nearly 100% with a selectivity to aniline of up to 99% (entry 7, Table 1). Note that the content of NiS_{2+x} was calculated from the amounts of precursors used in the synthetic process for a better clarification, whilst the real content was further confirmed by XPS (Fig. S3†) analysis. Obviously, carbon nitride has played an important role in increasing both the activity and selectivity of the NiS_2 nanoparticles (Scheme S1†).

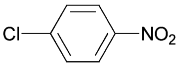
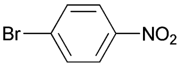
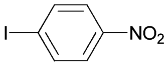
To determine the effect of the content of the NiS_{2+x} nanoparticles in the catalyst on the catalytic performance, the NiS_{2+x}/CN catalyst with weight percentages of the NiS_{2+x} species from 1 to 15% were prepared under the same conditions and used for the hydrogenation of nitrobenzene. The corresponding conversions are summarized in Table S1.† When the weight percentage of the NiS_2 nanoparticles was only 1% (1 wt%-NiS_{2+x}/CN), the catalyst gave a minor conversion (8%) and less selectivity to aniline. The conversion and selectivity have been both gradually improved to >99% as the weight percent of NiS_2 was increased to 9%. When more NiS_{2+x} species (>12 wt%) were introduced, the selectivity decreased *via* 95% to 86%. This is to say that too much NiS_2 nanoparticles deposited on the surface of the g-C_3N_4 support disturbed the synergetic effect between the two components. The synthetic temperature was optimized to be 80 °C (Table S2†). As the best catalyst here, NiS_{2+x}/CN, obtained at 80 °C with 9 wt% of the NiS_{2+x} nanoparticles, was selected for all the following hydrogenation reactions of nitrobenzene.

Some noble metal-based control catalysts (with a weight percentage of 9 wt%) were tested under standard conditions. Although full conversions (entry 8–10, Table 1) were also achieved using all these noble metal catalysts, only Pd/CN gave a selectivity of nearly 100% to aniline. Due to the same efficiency of NiS_{2+x}/CN and Pd/CN in the reduction of nitrobenzene for aniline, we further studied the reduction of halogenated nitrobenzene using the two catalysts. As shown in Table 2, the reduction of 4-chloronitrobenzene was found to have a yield of 96% for 4-chloroaniline and 4% for aniline using Pd/CN. Significant dehalogenation occurred in the reduction of 4-bromine nitrobenzene using Pd/CN with only a selectivity of 5% to the target product. Moreover, 4-iodonitrobenzene was completely reduced to aniline using Pd/CN. Such a dehalogenation reaction was normal for noble metal-based nanocatalysts, suggesting their limitation in the hydrogenation of halogenated compounds. Surprisingly, NiS_{2+x}/CN could completely transfer halogenated nitrobenzene into substituted halogenated aniline without obvious dehalogenation under standard conditions. The cheap and mild NiS_{2+x}/CN catalyst has obvious advantages for practical applications in industry.

After knowing the superior catalytic activity of NiS_{2+x}/CN for the hydrogenation of nitrobenzene and halogenated nitrobenzene, we further tested its compatibility with various substituted nitroarenes. The methyl substituted substrates are completely reduced to the corresponding anilines in an excellent yield of 99% (entries 1–3, Table 3). The reaction of 2,6-dimethlnitrobenzene could also reach an excellent yield of the target product of up to 99% (entry 7, Table 3). Typical halogenated nitrobenzenes were efficiently reduced with both good conversion and selectivity (entries 4–6, Table 3). Our protocol also worked well for the reduction of other typical complex nitro compounds, such as 1-nitro-naphthalene and 6-nitroquinoline (entry 8, 9, Table 3). The activity of the NiS_{2+x}/CN catalyst will not be affected by steric hindrance and conjugate phenomenon. All these results suggest that the noble metal-free NiS_{2+x}/CN catalyst can be used for the reduction of nitroarenes with an excellent conversion and selectivity in a mild process.

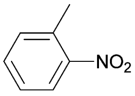
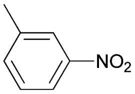
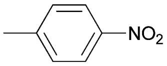
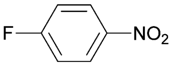
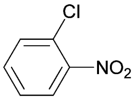
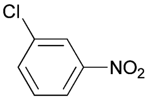
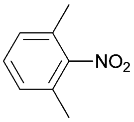
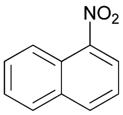
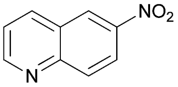
Table 2 Hydrogenation of halogenated nitrobenzene using Pd/CN and NiS_{2+x}/CN[a]



	Pd/CN		NiS_{2+x}/CN	
Substrate	Conv. [%]	Sel. [%]	Conv. [%]	Sel. [%]
	>99	96[b]	>99	>99
	>99	5[b]	>99	>99
	>99	0[b]	>99	>99

[a] Standard conditions described in Table 1. [b] The byproduct is aniline.

Table 3 Hydrogenation of nitro compounds using NiS_{2+x}/CN[a]

Entry	Substrate	Conv. [%]	Sel. [%]
1		99	>99
2		99	>99
3		>99	>99
4		>99	99
5		>99	>99
6		>99	98
7		>99	99
8		>99	94
9		>99	>99

[a] Standard conditions described in Table 1.

The catalytic reduction of 4-nitrophenol was studied as a model reaction to investigate the stability and reusability of the catalyst. NiS_{2+x}/CN is successfully recycled and reused 2 times, almost without any significant loss of catalytic activity (Fig. S7†). The conversion of 4-nitrophenol decreased by 20% until the third round of reaction. This deactivation might be mainly attributed to the decomposition of the NiS_{2+x} nanoparticles, which was confirmed by the XRD analysis (Fig. S5†). This phenomenon is normal for metal sulfide based catalysts.[15,17] As the g-C_3N_4 support remained stable after multiple cycles of catalytic reactions (Fig. S6†), the regeneration of the used catalyst was facilely conducted *via* depositing additional NiS_{2+x} species. The regenerated catalyst offered a full conversion of 4-nitrophenol again (Fig. S7†). Further efforts will be focused on developing more stable noble metal-free heterogeneous catalysts by improving the stability of the metal sulfide nanoclusters or using other stable transition metal-based nanoparticles as active centers.

Conclusions

In summary, we developed an efficient g-C_3N_4 supported NiS_{2+x} nanoparticle (NiS_{2+x}/CN) catalyst system for the hydrogenation of nitroarenes under mild conditions. Our noble metal-free NiS_{2+x}/CN catalyst offered excellent catalytic activity, which was comparable to that of Pd nanocatalysts and much better than those of Au and Pt nanocatalysts. More importantly, the chemoselective hydrogenation of halogenated nitrobenzene to corresponding anilines using the NiS_{2+x}/CN catalyst is rather speaking for the advantages of the NiS_{2+x}/CN catalyst as a mild catalyst against noble metal counterparts. The strategy reported here may supply new possibilities for developing sustainable nanocatalysts for practical applications.

Acknowledgements

This work was supported by the National Basic Research Program of China (2013CB934102 and 2011CB808703) and the National Natural Science Foundation of China (21331004 and 21301116).

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