Synthesis of Transition Metal-Modified Carbon Nitride Polymers for Selective Hydrocarbon Oxidation

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Introduction

The selective oxidation of organic molecules is of vital importance in both biological systems and chemical industry. Nature promotes oxidative catalysis in a highly selective manner by activating molecular oxygen under mild conditions. The typical oxygenase (cytochrome P-450) featuring an iron porphyrin core can catalyze a wide variety of oxidation reactions including epoxidation, hydroxylation and oxidation of amines, sulfides, alcohols, aldehydes, and even of some nonactivated hydrocarbons.[1] Thus, this class of iron-containing metalloenzymes are blueprints for the design of environmentally friendly oxidation catalysts that mimic enzyme function.

In the past decade, much effort has been focused on the development of transition-metal complexes as biomimetic catalysts containing a core structure closely resembling that of the iron porphyrin core, such as metalloporphyrins, metal-phthalocyanines, and transition metal-schiff bases. For example, iron, manganese, and ruthenium porphyrins have been examined as excellent catalysts for the selective oxidation of alkenes, alcohols, phosphines, amines, and sulfides by oxygen atom transfer of insertion reactions with terminal oxidants PhIO, NaOCl, H$_2$O$_2$, and O$_2$.[2] With similar macrocyclic structure of porphyrins (Figure 1), metallophthalocyanines catalysts have been widely used in the oxidation of hydrocarbons, phenols, and thiols.[3]

The Schiff base complexes of transition metals are also found to be efficient in loading oxygen and in mimicking the enzyme activity. As developed firstly by Jacobsen, chiral manganese salen complexes combined with oxygen donors constitute a valuable new family of homogeneous catalysts for epoxidation of olefins.[4]

These transition metal complexes are typically employed in homogeneous catalyzed reactions and are suffering from the difficulties related to separation and recycling. Heterogenization of the homogeneous catalysts is considered to be an effective method to reduce costs and also to avoid the environmental problem associated with the separation and purification of catalysts. One common strategy is to immobilize these metal complexes on various solid supports, such as resins, polymers, clays, and zeolites.[5] Nolte and co-workers have reported on effective epoxidation of alkenes by grafting a manganese meso-tetraarylporphyrin onto polysiloxanides.[6] FeTPPF2O linked to polystyrene was found to catalyze the oxidation of ethylbenzene with dioxygen to give three major products: the ketone, alcohol, and hydroperoxide.[7] Sorokin et al. have shown that metallophthalocyanines of iron, manganese, and cobalt anchored on mesoporous silica are active catalysts in the liquid phase oxidation of 2-methylnaphthalene and 2,3,6-trimethylphenol with hydrogen peroxide.[8] Unfortunately, such heterogeneous catalysts were usually limited by a lower catalytic activity relative to their homogeneous counterparts. Moreover, some of the applied synthetic approaches are very complicated and not scalable. It is thus highly desirable to explore simple, efficient, stable, and particularly cost effective bionic heterogeneous oxidation catalysts for practical applications.

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Covalent carbon nitride polymers are a rediscovered class of functional materials that have attracted great interest due to their potential applications as hard coating, lithium intercalation electrodes, metal catalyst supports, and gas storage materials. Recently, thermal polycondensation of common organic monomers was conveniently used to synthesize carbon nitride polymers close to the graphitic sheet-like structure (g-C$_3$N$_4$).[9] The idealized bulk g-C$_3$N$_4$ consists of sheets of ordered tri-s-triazine moieties, connected by planar amino groups (Figure 1). [10] The graphitic carbon nitride polymer was also found to feature semiconductor properties, exhibiting a band gap of 2.7 eV.[11] In comparison to those of other carbon nitride allotropes, such as the beta-phase C$_3$N$_4$ and cubic-phase C$_3$N$_4$, the smaller band gap of g-C$_3$N$_4$ is due to the sp$^2$ hybridization of carbon and nitrogen forming the π-conjugated graphitic planes. In addition, pure g-C$_3$N$_4$ possesses high chemical and thermal stability, can for example be heated under air to 550 °C, which enables potential catalytic and photocatalytic applications under extreme conditions. For example, it was recently proven that iron ions could be homogeneously embedded into the g-C$_3$N$_4$ framework to larger extents and thus strongly modify its electronic properties. The added functions resulted in a new bioinspired non-heme iron catalyst, capable of activating H$_2$O$_2$ under mild conditions.[16] It was a natural step to extend to other transition metals, as metal coordination chemistry could effectively alter and fine-tune the spectrochemical and catalytic properties of the organic semiconductor.

We show herein that, in addition to Fe$^{3+}$, other transition metal cations (Mn$^{3+}$, Co$^{3+}$, Ni$^{3+}$, and Cu$^{2+}$) that are known to impart useful catalytic activity to porphyrins and phthalocyanines,[17] can be incorporated into the framework of graphitic carbon nitride. The physicochemical properties of this new class of complex were investigated by X-ray diffraction (XRD), FTIR, X-ray photoelectron spectroscopy (XPS), thermal analysis, elemental analysis (EA), UV/Vis, and photoluminescence (PL) spectroscopy. The catalytic/photocatalytic properties of the metal-g-C$_3$N$_4$ catalysts are also described.

**Results and Discussion**

The XRD patterns of the as-synthesized polymeric g-C$_3$N$_4$ and the transition metal-containing derivatives [M-g-C$_3$N$_4$ (M = Mn, Fe, Co, Ni, Cu)] are shown in Figure 2. All these patterns indicate a structural similarity between g-C$_3$N$_4$ and metal-containing g-C$_3$N$_4$ because all patterns are governed by the typical graphitic interlayer (002) peak at 27.4° and in-plane structural packing motif (100) peak at 12.9°. The metal-containing sam-

![Figure 1. Nitrogen-enriched π-conjugated macrocyclic scaffolds: a) Perfect g-C$_3$N$_4$ sheet, b) porphyrin, c) phthalocyanine, d) metal-HPED (HPED = N,N’-bis(o-hydroxyacetophenone) ethylenediamine) Schiff base, e) metal porphyrin, and f) metal phthalocyanine.](image)

![Figure 2. XRD patterns of pure g-C$_3$N$_4$ and M-g-C$_3$N$_4$ (M = Mn, Fe, Co, Ni, Cu) calcined at 600 °C.](image)
amples showed a slight broadening of the (002) peak and a decrease of their relative intensities, compared to pure g-C₃N₄. As X-ray scattering monitors electron density, which is mainly associated to the metal positions in such systems, we can only state that the metal positions essentially follow the structure of the host material, with a potential slight disorder of metal positions within the pores.

It had been reported[1] that the intensity of the (002) peak of Fe-g-C₃N₄ decreased with increasing Fe content, again reflecting a host–guest interaction. Inhibition of polymeric condensation by excessive metal ion species was found to occur at ever higher metal loadings. All the samples with the different transition metals behaved similarly. No peaks corresponding to the crystalline metal species such as metal oxides, metal nitrides, metal chlorides, or metal carbides were observed in the metal-containing samples, even after the samples were calcined at 500 °C. The absence of metal species peaks suggested that the metal species stayed chemically coordinated to the g-C₃N₄ host, most likely in the form of metal–N bonds, as in their low molecular weight counterparts.

The IR spectra of the metal-containing carbon nitride were compared to the pure g-C₃N₄ (Figure 3). Typical bands of aromatic CN heterocycles at 1200 to 1600 cm⁻¹ and the triazine units at 800 cm⁻¹ were observed[9]. The broad band at around 3000 cm⁻¹, corresponding to secondary and primary amines and incomplete graphitic condensation, was also present in the spectra of the M-g-C₃N₄, however with a slightly lowered intensity. Elemental analyses of all the M-g-C₃N₄ samples (see the Supporting Information, Table S1) revealed that the average C/N ratio value of about 0.74 for M-g-C₃N₄ is slightly higher than that of pure g-C₃N₄ (0.73); the expected value for perfect condensation is 0.75. Correspondingly, lower hydrogen contents (ca. 1.5%) were measured for M-g-C₃N₄. EA and FTIR were in good agreement and indicated that the addition of metal chloride even facilitated the deamination process during the self-polymerization of dicyandiamide at high temperatures.

Thermogravimetric (TG) analysis (Figure 4) of pure g-C₃N₄ showed a complete weight loss at 1000 °C, whereas the cobalt, nickel, manganese, and copper-containing samples showed a weight loss of 93.2%, 93.6%, 95.2%, and 91.7% at the same temperature, respectively. The weight loss in metal complexes at high temperature is mainly due to the decomposition of carbon nitride matrix, while the amount of inorganic residue is directly related to the metal content. The metal-containing materials exhibit similar thermal stabilities as pure g-C₃N₄ when they are heated to 700 °C, although there are small differences from one to the other. This supports the view that the metal species in the metal containing samples are chemically coordinated to the g-C₃N₄ host and do not form (amorphous) metal nitrides or metal carbides.

XPS experiments were performed to elucidate the carbon nitride structure and the chemical state of the modified metal. Figure 5 shows the XPS spectra of C 1s and N 1s of M-g-C₃N₄ samples and pure g-C₃N₄. The C 1s binding energy shows mainly one carbon species with a binding energy of 288.2 eV, corresponding to a C–N–C coordination. In the N 1s spectrum, three binding energies can be separated. The strongest peak at 398.7 eV for the g-C₃N₄ can be assigned to the C–N+C=C groups.[17] The peak at 400.2 eV is usually attributed to the tertiary nitrogen N+C=C groups.[18] The weak additional signal at 401.3 eV can be attributed to the amino functions carrying hydrogen (C–N+H), which are related to structural defects and incomplete condensation. When the transition metals were introduced into the g-C₃N₄ body, the binding energies of N 1s slightly decreased from 398.7 eV for g-C₃N₄ to 398.6 eV for Co-g-C₃N₄, 398.5 eV for Cu-g-C₃N₄, and 398.5 eV for Mn-g-C₃N₄. This small, but systematic shift toward low binding energy is indicative of the slight increase in the electron density of the N atom. The binding energy for Ni-g-C₃N₄ remained at 398.7 eV. No additional peak was found in all the M-g-C₃N₄ complexes, suggesting that the six nitrogen atoms in the complexing cavity were chemically similar, and a coordination conjugation of six equatorial nitrogen was provided. The XPS results also showed that the intensity of the peak at 401.3 eV for M-g-C₃N₄ was weaker than that of pure g-C₃N₄, in good agreement with the results of elemental analysis and FTIR. The results of the Co 2p, Cu 2p, Ni 2p, and Mn 2p peak XPS spectra are also shown in Figure 5. The binding energies of Cu 2p₁/₂ and Cu 2p₃/₂ were 952.8 and 933 eV for the Cu-g-C₃N₄ close to the value of CuO[19] indicating Cu was in the 2+ state. The Co 2p₃/₂ peak at 782.4 eV was higher than the value of...
780.6 eV for Co\textsuperscript{II} phthalocyanine and the value of 779.8 eV for Co\textsuperscript{II} porphyrin,\textsuperscript{[20]} and was attributed to Co\textsuperscript{3+}.\textsuperscript{[21]} Furthermore, the Co 2p region did not show a satellite due to Co\textsuperscript{2+}, as in CoO. The Co 2p state was akin to Co\textsuperscript{3+} in low spin as in Co-g-C\textsubscript{3}N\textsubscript{4}.\textsuperscript{[22]}

For the Ni-g-C\textsubscript{3}N\textsubscript{4} sample, the two main Ni 2p binding energies were 856.1 eV for Ni 2p\textsubscript{3/2} and 874.1 eV for Ni 2p\textsubscript{1/2}. These values were higher than those reported for Ni\textsuperscript{II} porphyrins (855.1 eV for Ni 2p\textsubscript{3/2} and 873.0 eV for Ni 2p\textsubscript{1/2}),\textsuperscript{[20b, 21]} suggesting Ni was also in the 3+ state. The Mn 2p\textsubscript{3/2} peak was observed at 639.5 eV, and the Mn 2p\textsubscript{1/2} peak was found at 651.7 eV, indicating that Mn was in the 3+ state in Mn-g-C\textsubscript{3}N\textsubscript{4}. Furthermore, the calculated surface atomic ratios of Cl/Cu, Cl/Co, Cl/Ni, and Cl/Mn were found to be 0.03, 0.3, 0.92 and 0.5, respectively, much lower than the ratio of Cl/metal in their metal chloride precursor. These characterizations clearly indicated that the transition metals were mainly stabilized in the electron-rich g-C\textsubscript{3}N\textsubscript{4} structure by metal–N bonds, while a smaller amount of Cl was present and presumably used for the charge balance. This was especially true for the Ni\textsuperscript{3+} species.

The morphology of M-g-C\textsubscript{3}N\textsubscript{4} was investigated by transmission electron microscopy (TEM). The TEM images (Figure 6) of the metal modified samples show the layered and platelet-like structure, which is similar to that of pure g-C\textsubscript{3}N\textsubscript{4}. The results indicate that the modification with metals did not significantly change the texture of the carbon nitride polymer. No obvious particles were seen in the TEM images, indicating that there was no metal or metal oxide existing on the catalysts, which confirmed the results obtained from the X-ray diffraction. The results of the BET surface area analysis showed that the BET surface areas of the pure g-C\textsubscript{3}N\textsubscript{4} and M-g-C\textsubscript{3}N\textsubscript{4} samples were the same (ca. 8 m\textsuperscript{2}g\textsuperscript{-1}).

The optical absorption spectra were used to investigate the effect of metal inclusion on the electronic structure of g-C\textsubscript{3}N\textsubscript{4}. As shown in Figure 7, pure g-C\textsubscript{3}N\textsubscript{4} exhibited the typical absorption pattern of a semiconductor with a band gap of 2.7 eV. The spectra of the M-g-C\textsubscript{3}N\textsubscript{4} showed obvious red shifts in the band-gap transition. The absorbance of the metal-containing samples in the visible region was in all cases higher than that of pure g-C\textsubscript{3}N\textsubscript{4}. In particular, the most pronounced effect was found for the Cu-modified g-C\textsubscript{3}N\textsubscript{4} sample, where the light absorption extended to 750 nm. Simply spoken, the color of the pure g-C\textsubscript{3}N\textsubscript{4} was pale yellow, whereas the other colors were yellow for Mn-g-C\textsubscript{3}N\textsubscript{4}, brown for Fe-g-C\textsubscript{3}N\textsubscript{4}, gray for Co-g-C\textsubscript{3}N\textsubscript{4}, brown for Ni-g-C\textsubscript{3}N\textsubscript{4}, and brown for Cu-g-C\textsubscript{3}N\textsubscript{4}.

The effect of metal inclusion on the electronic properties was also checked by PL experiments. Figure 8 depicts the PL spectra of M-g-C\textsubscript{3}N\textsubscript{4} and pure g-C\textsubscript{3}N\textsubscript{4} under 400 nm excitation at 298 K. A broad visible PL band centered at approximately 470 nm is observed for g-C\textsubscript{3}N\textsubscript{4}, which is consistent with the literature.\textsuperscript{[9]} Metal modification of g-C\textsubscript{3}N\textsubscript{4} led to significant quenching of PL. It is well known that the PL spectra are closely related to the recombination of photoinduced electron and holes, free excitons, and self-trapped excitons. The lower inten-
sity of the PL band for the M-g-C3N4 suggested that metal modification resulted in a decrease in the recombination of electron-hole pairs, which would be favorable for the photocatalytic process. Similar relations were also observed using conventional photocatalysts (e.g., TiO2) by others. [22]

Effect of different metal-containing g-C3N4 on oxidation of benzene to phenol with hydrogen peroxide

The Fe-modified g-C3N4 is efficient in the activation of H2O2 and in mimicking the enzyme activity, hence used successfully in the direct oxidation of benzene to phenol and oxidative degradation of various organic dyes, especially coupled with light irradiation. [16] The catalytic activity of the other transition metal-containing g-C3N4 samples were also evaluated by oxidation of benzene to phenol in hydrogen peroxide and visible-light irradiation. The results are shown in Table 1. Pure g-C3N4 showed no detectable activity for the oxidation of benzene to phenol, even coupled with visible light. In contrast to the pure

<table>
<thead>
<tr>
<th>Sample</th>
<th>hv Phenol yield [%]</th>
<th>Benzoquinone yield [%]</th>
<th>H2O2 conv. [%]</th>
<th>H2O2 sel [%]</th>
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<tr>
<td>g-C3N4</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>0</td>
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<tr>
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<tr>
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<td>-</td>
<td>100</td>
<td>8.3</td>
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<tr>
<td>Cu-g-C3N4/+</td>
<td>1.6</td>
<td>-</td>
<td>76.7</td>
<td>3.6</td>
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<tr>
<td>Ni-g-C3N4/+</td>
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<td>-</td>
<td>12</td>
<td>1.7</td>
</tr>
<tr>
<td>Mn-g-C3N4/+</td>
<td>0.13</td>
<td>-</td>
<td>42.9</td>
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<tr>
<td>Co-g-C3N4/+</td>
<td>0.02</td>
<td>-</td>
<td>40.2</td>
<td>0.003</td>
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<tr>
<td>g-C3N4/SBA-15/+</td>
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<td>-</td>
<td>8.2</td>
<td>-</td>
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<tr>
<td>Fe-g-C3N4/SBA-15/+</td>
<td>11.9</td>
<td>-</td>
<td>97.6</td>
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<td>Cu-g-C3N4/SBA-15/+</td>
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<tr>
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<td>-</td>
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<tr>
<td>Mn-g-C3N4/SBA-15/+</td>
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<tr>
<td>Co-g-C3N4/SBA-15/+</td>
<td>0</td>
<td>-</td>
<td>100</td>
<td>-</td>
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</table>

[a] Moles of produced phenol/moles of initial benzene x 100. [b] Moles of produced benzoquinone/moles of initial benzene x 100. [c] Moles of produced phenol/moles of reacted H2O2 x 100.
g-C$_3$N$_4$ significant improvement of phenol yield could be achieved by modification of Fe and Cu. The activities of the catalysts were ordered as: Fe $>$ Cu $>$ Mn $>$ Ni $>$ Co. All of the mentioned metals modification could greatly improve the decomposition rate of hydrogen peroxide. The conversion of H$_2$O$_2$ after 4 h reaction under visible-light irradiation was 1.5% for g-C$_3$N$_4$, whereas it reached 100% for Fe-g-C$_3$N$_4$ and 76.7% for Cu-g-C$_3$N$_4$. 12% for Ni-g-C$_3$N$_4$, 42.9% for Mn-g-C$_3$N$_4$, and 40.2% for Co-g-C$_3$N$_4$, indicating that transition metals have significant influence on the activation of H$_2$O$_2$. The results implied that Mn-, Ni-, and Co-modified samples are not effective for hydroxylation of benzene to phenol with H$_2$O$_2$, but maybe suitable for other oxidative reactions.

As the surface area of the materials was considered to be one of the important factors for catalysis/photocatalysis, the bulk metal-g-C$_3$N$_4$ complex (with surface area of approximately 8 m$^2$ g$^{-1}$) was dispersed on SBA-15, a mesoporous catalyst support, to promote the direct oxidation of benzene to phenol with H$_2$O$_2$. The activity of M-g-C$_3$N$_4$/SBA-15 for the oxidation of benzene to phenol is also listed in Table 1. In the dark, the phenol yield of Fe-g-C$_3$N$_4$/SBA-15 reached 6.7%. Visible-light irradiation could further improve the yield to about 12%. Cu-g-C$_3$N$_4$/SBA-15 showed a slight decrease in phenol yield (1.4%), accompanying the formation of benzoquinone with an yield of 2.7%. The results clearly revealed that the activity of the catalyst is dependent on the exposure of the catalyst structure. The high dispersion and large surface area of the metal complex could contribute to the increased activity. Other metal-modified samples loaded in SBA-15 showed low activity in the oxidation/photo-oxidation of benzene to phenol.

Effect of different metal-containing g-C$_3$N$_4$ on oxidation of styrene with O$_2$

Many of the aerobic oxidation reactions carried out in living organisms usually make use of transition metals such as copper or iron. Iron is found in enzymes responsible for the binding and transport of oxygen in a variety of biological oxidation reactions.[21] Co complexes have also been reported as efficient catalysts for epoxidation of olefins with molecular oxygen.[22] Hence, it is necessary to examine the possibility of using the transition metal-based catalysts in O$_2$ activation. Here, the catalytic properties of transition metal- (i.e., Co, Fe, Cu, Ni, Mn) modified carbon nitride were investigated by the oxidation of styrene with O$_2$. Table 2 summarizes the catalytic performance of a series of g-C$_3$N$_4$-based catalysts in the epoxidation of styrene with O$_2$. The products of oxidation of styrene are primarily styrene oxide, benzoaldehyde, and benzoic acid. The results showed that pure g-C$_3$N$_4$ is active in the reaction and the styrene conversion is 24.1% with 46.6% styrene oxide selectivity in the dark, which can be enhanced to 37.1% with 53.0% styrene oxide selectivity under visible-light irradiation. Modification with Fe and Co ions could improve the catalytic/photocatalytic activity of the system for the oxidation of styrene. Particularly, with Co-modified g-C$_3$N$_4$ catalyst, the conversion of styrene can reach 32.6% in the dark and 55.5% in visible light, with styrene oxide selectivity of 46.4% in the dark and 58.5% in visible light. The results indicated that visible light not only improved the conversion of styrene but also enhanced the selectivity of styrene oxide. In contrast, the Cu-, Ni-, and Mn-modified g-C$_3$N$_4$ showed a poor performance in the epoxidation of styrene. The styrene conversions of Cu-g-C$_3$N$_4$ and Mn-g-C$_3$N$_4$ were even much lower than that obtained in the absence of any catalyst, suggesting that the catalysts of Cu- and Mn-modified samples in fact inhibited the styrene oxidation. Among the metal modified samples examined, Co-g-C$_3$N$_4$ catalyst exhibited the best performance in the oxidation of styrene with O$_2$, probably attributed to the fact that the redox potential of Co$^{3+}$/Co$^{2+}$ (1.808 V) is more positive than that of the other metals, as the catalytic activation of different metal complexes were influenced by the stability of different valences of the metal atoms and by the quantity of the electric potential. The result was in agreement with the earlier observation reported by Hu et al.[24]

### Conclusions

In this paper, we showed that transition metals including Fe, Co, Ni, Mn, and Cu can be successfully included into a g-C$_3$N$_4$ matrix by a simple soft-chemical method without destroying the graphic structure of the host. The structure of those complexes were analyzed by a variety of techniques and turned out to be solid solutions of metal ions within the nitrogen pores of the matrix. Among the analyzed species, Fe and Cu modified carbon nitrides were shown to be efficient catalysts for the hydroxylation of benzene to phenol with H$_2$O$_2$, and Co and Fe modified samples were proven to be active for the epoxidation of styrene with O$_2$. By taking advantage of the photocatalytic functions of g-C$_3$N$_4$, the activity could be greatly improved by simultaneous illumination. The results demonstrated that the metal ion strongly modifies the electronic, optical, and...
catalytic properties of g-C$_3$N$_4$. We expect that direct functionalization of carbon nitride by various transition metals in general will result in hybrid materials which will have a broader potential for heterogeneous catalysis.

Experimental Section

Catalyst preparation

M-g-C$_3$N$_4$: Dicyandiamide (3 g, 36 mmol) mixed with deionized water (15 mL) was heated and stirred at 100 °C with 2 mmol of metal chloride (FeCl$_3$, CoCl$_2$, MnCl$_2$·4H$_2$O, NiCl$_2$·6H$_2$O, CuCl$_2$·2H$_2$O) added. The mixed solution was continuously heated at 100 °C to remove water. The resulting mixtures were then heated at 500–600 °C for 4 h under flowing nitrogen atmosphere. The sample was then cooled to room temperature under nitrogen gas. The sample was denoted as M-g-C$_3$N$_4$ (M = metal).

M-g-C$_3$N$_4$/SBA-15: Dicyandiamide dissolved in deionized water (15 mL) was mixed with metal chloride (e.g., 2.4 mmol dicyandiamide and 0.13 mmol metal chloride) and stirred at 100 °C for 30 min. Then SBA-15 (1.0 g) was added into the mixture. The resultant mixture was continually stirred at 100 °C to remove water. Finally, the mixture was calcined at 600 °C for 4 h under flowing nitrogen gas and then cooled to room temperature under nitrogen gas. The sample was denoted as M-g-C$_3$N$_4$/SBA-15.

Characterization

XRD measurements were performed on a Bruker D8 Advance diffractometer with CuKα1 radiation (λ = 1.5406 Å). TG analysis was carried out using a NETZSCH TG 209 at a heating rate of 10 °C min$^{-1}$ under air. Elemental analysis was performed with a varioMICRO cube form Elementar Analyserysysteme GmbH. FTIR spectra were recorded on a BioRad FTS 6000 spectrometer. XPS data were recorded on a Bruker D8 Advance diffractometer. All the measurements were performed in a glovebox filled with argon gas to prevent oxidation of the samples.

Catalysis experiments

Oxidation of benzene with H$_2$O$_2$: A sample of metal modified g-C$_3$N$_4$ (50 mg) was suspended in a mixture of acetonitrile (4 mL), benzene (0.8 mL, 9 mmol), water (4 mL), and hydrogen peroxide (30 wt%, 0.51 mL, 6 mmol). The resulting biphasic system was stirred at 60 °C for 4 h in the dark. At the end of the reaction, ethanal (5 mL) was poured into the mixture at 4 °C for quenching the reaction and then the biphasic system into a single-phase one. A 500 W Xenon lamp together with a 420 nm cut-off filter was used as a visible-light source for the irradiation of the reaction system. The products of the reactions were analyzed by a gas chromatograph (HP6890) and GC–MS with toluene as an internal standard. To carry out the photocatalytic reaction, a 300 W xenon lamp together with a 420 nm cut-off filter was used as a visible-light source for the irradiation of the reaction system, with otherwise the same experimental conditions as those in the dark.

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