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Copper Nanoparticles on Graphene Support: An Efficient Photocatalyst for Coupling of Nitroaromatics in Visible Light**

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Abstract: *Copper is a low-cost plasmonic metal. Efficient photocatalysts of copper nanoparticles on graphene support are successfully developed for controllably catalyzing the coupling reactions of aromatic nitro compounds to the corresponding azoxy or azo compounds under visible-light irradiation. The coupling of nitrobenzene produces azoxybenzene with a yield of 90% at 60°C, but azobenzene with a yield of 96% at 90°C. When irradiated with natural sunlight (mean light intensity of 0.044 W cm*$^{-2}$*) at about 35°C, 70% of the nitrobenzene is converted and 57% of the product is azobenzene. The electrons of the copper nanoparticles gain the energy of the incident light through a localized surface plasmon resonance effect and photoexcitation of the bound electrons. The excited energetic electrons at the surface of the copper nanoparticles facilitate the cleavage of the N—O bonds in the aromatic nitro compounds. Hence, the catalyzed coupling reaction can proceed under light irradiation and moderate conditions. This study provides a green photocatalytic route for the production of azo compounds and highlights a potential application for graphene.*

The localized surface plasmon resonance (LSPR) effect is a collective oscillation of conduction electrons in metallic nanoparticles, which resonate with the electromagnetic field of incident light in the visible light range.[1–4] The conduction electrons of the nanoparticles of gold (Au), silver (Ag), and copper (Cu) can gain visible light energy through the LSPR effect. Thus, one may use the major part of the sun spectrum to improve the yield of chemical synthesis at ambient temperature and pressure. Studies on light-driven reactions catalyzed by Au or Ag nanoparticles have formed the basis of a new and fast-expanding field in green photocatalysis. Recently, Sarina et al. found that the Au–Pd alloy nanoparticles can strongly absorb light and efficiently enhance the conversion of some reactions such as the Suzuki–Miyaura cross coupling.[4] However, few studies on the photocatalytic performance of Cu nanoparticles have been reported even though Cu nanoparticles exhibit strong LSPR absorption in the visible light range[1,3,5,6] and are catalytically active for many reactions such as the catalytic hydrogenation of dimethyl oxalate.[7] The primary challenge for Cu nanoparticles to be used as photocatalyst is their chemical stability under catalytic reaction conditions. Cu nanoparticles are easily oxidized to Cu_2O or CuO in air or in the presence of traces of molecular oxygen.[1,3,8] Recently we found that Cu_2O nanoparticles could exist stably when dispersed on graphene sheets.[9] The Cu_2O/graphene composite exhibits a remarkable electrocatalytic activity for the oxygen reduction reaction and the Cu_2O nanoparticles on graphene cannot be oxidized to CuO. Graphene is a two-dimensional network of sp^2-bonded carbon atoms;[10,11] and the delocalized electrons in graphene can move freely in the network with a low resistance.[12] The carbon vacancies or dangling bonds in graphene can influence the electronic structure of Cu atoms on graphene and improve their chemical stability.[13–15] Therefore, it is expected to use graphene as the support to stabilize Cu nanoparticles. Here, we prepared metallic Cu nanoparticles on graphene sheets (Cu/graphene) by reducing Cu_2O/graphene composites in a mixture of H_2 (5 vol%) and Ar at 500°C (see the Supporting Information for details). The Cu/graphene samples were used as photocatalysts for the synthesis of aromatic azoxy and azo compounds from their corresponding aromatic nitro compounds under visible-light irradiation.

Azo compounds are widely used as organic dyes, indicators, food additives, and therapeutic agents.[16–18] They are currently produced by the reduction of aromatic nitro compounds using transition metals as the reductant,[19] or by the reaction of diazonium salts with electron-rich aromatic compounds.[20] The former consumes stoichiometric transition metals, and the latter uses considerable nitrite salts. Both reactions are noncatalytic, and generate a large amount of inorganic waste.[21] Recently, Grirrane et al. reported that a catalyst of gold nanoparticles supported on titania could catalyze the production of azobenzene from nitrobenzene through a two-step and one-pot reaction at 100°C or above.[22] The aromatic nitro compounds are reduced to corresponding amines under 9 bars of H_2 first. Then, the amines are oxidized to aromatic azo compounds under 5 bars of O_2. Zhu et al. found that Au/ZrO_2 can catalyze the coupling of aromatic nitro compounds to corresponding azo compounds at 40°C with high yields when illuminated with incandescent light or ultraviolet (UV) light.[2] The goal of the present study is to develop efficient photocatalysts using copper, the low-cost plasmonic metal, for this important type of transformations.

Figure 1A,B show the TEM images of a Cu/graphene catalyst with a Cu loading of 5 wt% (5 wt% Cu/graphene).

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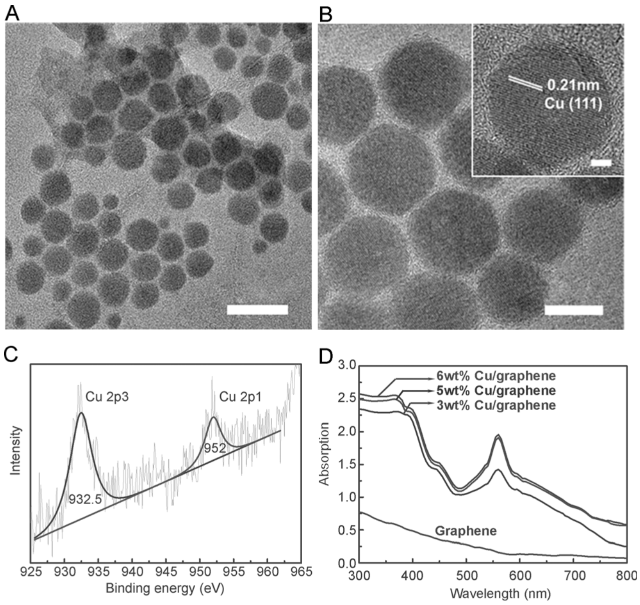
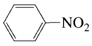
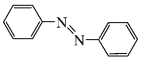
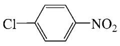
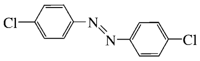
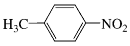
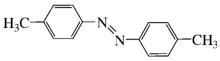
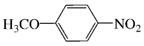
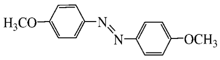
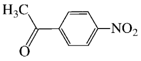
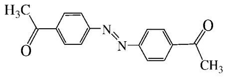


Figure 1. TEM images (A and B; the scale bars are 30 and 10 nm, respectively; the scale bar in the inset of (B) is 2 nm) and XPS profile (C) of 5wt% Cu/graphene, and UV/Vis absorption spectra of Cu/graphene photocatalysts with different Cu loadings (D).

Table 1: Photocatalytic coupling of aromatic nitro compounds over a Cu/graphene catalyst (Conv. = conversion, Select. = selectivity, and QY = quantum yield).[a]

Reactant	Main product	Conv. [%]	Select. [%]	QY [%]
		97.9	98.2	5.1
		92.6	47.4[b]	2.5
		66.3	95.8	1.8
		93.3	59.4[b]	3.7
		90.0	45.9[b]	2.3

[a] The reactions were conducted in an argon atmosphere at 90 °C using 30 mL of isopropyl alcohol mixed with 0.3 mmol KOH, 3 mmol nitrobenzene, and 100 mg of 5 wt% Cu/graphene catalyst. The irradiation intensity was 0.15 W cm^{-2}, and the reaction time was 5 h. [b] The other products are corresponding aromatic azoxy compounds.

The mean size of the Cu particles is about 15 nm, which varies with the Cu loading on graphene. It is 7 nm for 3 wt% Cu/graphene, and 40 nm for 6 wt% Cu/graphene (see Figures S1 and S2). The patterns of X-ray photoelectron spectroscopy (XPS) are similar for the Cu/graphene catalysts with different Cu loadings. In Figure 1 C, the binding energies of Cu $2p_{1/2}$ at around 952.0 eV and Cu $2p_{3/2}$ at 932.5 eV, respectively, can be attributed to the Cu^0 state, confirming that Cu exists on the graphene sheets as the metallic phase. This conclusion is also supported by the X-ray diffraction patterns (Figure S3). In the UV/Vis spectra (Figure 1 D), the absorption peak at approximately 560 nm is due to the LSPR absorption of Cu nanoparticles, since graphene only exhibits little absorption of light with wavelengths longer than 325 nm.[23] However, Cu_2O/graphene does not exhibit the LSPR absorption at 560 nm (Figure S4), and this is in agreement with the literature.[24] The above results confirm that copper in the Cu/graphene catalyst is in the metallic state rather than oxides.

The photocatalytic performance of 5 wt% Cu/graphene catalyst for the coupling reactions of a series of aromatic nitro compounds was investigated in an isopropanol solution under the irradiation of a 300 W Xe lamp (400–800 nm; 0.15 W cm^{-2}). The results are summarized in Table 1. As can be seen, the Cu/graphene catalyst exhibits high activity and selectivity for the production of azo compounds from their corresponding aromatic nitro compounds. These results demonstrate the general applicability of the photocatalytic process for the synthesis of various azo compounds. The quantum yields of these reactions are estimated from the light absorbed by the photocatalyst (Figure S5) and the conversion rate of the photocatalytic reaction. The coupling of nitrobenzene using 5 wt% Cu/graphene achieves a yield of 5.1%. No reaction product was detected in the blank experiment using only graphene as the photocatalyst, suggesting that the active phase for this reaction is metallic Cu nanoparticles.

The catalyst of 5 wt% Cu/graphene exhibits photocatalytic activity superior to 3 and 6 wt% Cu/graphene catalysts in the nitrobenzene coupling. The nitrobenzene conversion on the 5 wt% catalyst at 90 °C is 97.9%, while it is 80.1 and 85.9% on 3 and 6 wt% catalysts, respectively. Catalysts of 5 and 6 wt% Cu/graphene exhibit similar LSPR absorption but the Cu particles in the 6 wt% catalyst are much larger than those in the 5 wt% catalyst. The larger Cu particles have smaller specific surface area and thus much less active sites where the catalytic reaction takes place. The Cu particles in 3 wt% Cu/graphene are smaller in size but show obviously weaker LSPR absorption comparing with those of the other two catalysts, as observed in Figure 1 D. This is in agreement with the literature.[25] The weaker light absorption results in a lower activity as the catalytic process is mainly driven by light. Control experiments in the dark show that the conversion of nitrobenzene over 5 wt% Cu/graphene is only 19.5% at 60 °C and 28.1% at 90 °C (Figure S6). At 90 °C, when the light intensity decreases from 0.15 to 0.1, 0.05, and 0.01 W cm^{-2}, the conversion of nitrobenzene also decreases from 97.9 to 81.6, 65.4, and 39.8%, respectively, while the selectivity of azobenzene remains almost unchanged. The dependence of the conversion on the light intensity indicates that the reaction over the Cu/graphene catalyst is driven by light, and reveals that the nitrobenzene transformation is an electron-driven chemical reaction on a metal.[26,27]

The dependence of the catalytic performance on the wavelength range of light was also investigated. The result is illustrated in Figure 2. We employed a series of optical low-pass filters to block light below specific cut-off wavelengths. Without filtration, the irradiation wavelength ranges from 400 to 800 nm and yields a nitrobenzene conversion of 97.9%. The conversion decreases to 85.4, 65.4, and 35.5% when light of 450–800, 530–800, and 600–800 nm was used, respectively. Since the conversion of nitrobenzene in the dark is 28.1% (at

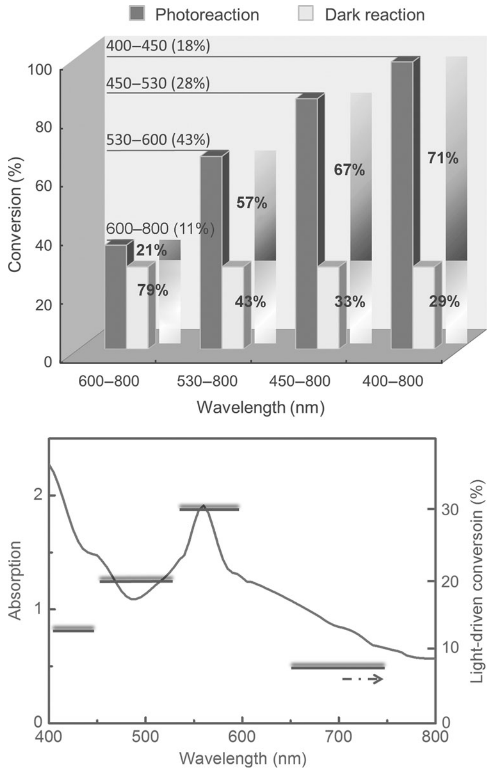


Figure 2. A) Dependence on the irradiation wavelength by the catalytic activity of 5 wt% Cu/graphene in nitrobenzene coupling. Both the light reaction and the dark reaction were conducted at 90 °C. B) The action spectrum of this photocatalytic reaction, in which the light-driven conversion is plotted against the wavelength of irradiation. The light-driven conversion was calculated as: light-driven conversion (%) = $Y_{light}-Y_{dark}$, where Y_{light} and Y_{dark} are the amounts of products formed under light irradiation and dark conditions, respectively.

90 °C), the irradiation in the wavelength range of 600–800 nm only contributes 7.4 percentage points (35.5–28.1 %) to the overall conversion. In contrast, the light in the 400–600 nm wavelength range contributes 62.4 percentage points (97.9–35.5 %), accounting for 63.7 % (62.4/97.9 × 100 %) of the total conversion and 89.4 % (62.4/(97.7-28.1) × 100 %) of the light-induced conversion—the difference between the nitrobenzene conversions of the light-irradiated reaction and the reaction in the dark. Similarly, the light in the wavelength range of 400–450, 450–530, 530–600, and 600–800 nm, respectively accounts for 18, 28, 43, and 11 % of the light-induced conversion (Figure 2 A). Figure 2 B shows one-to-one mapping between the light-induced conversion and wavelength. The highest conversion in the visible light range is observed in 530–600 nm, where the Cu nanoparticles strongly absorb the light due to the LSPR effect. Evidently, the light absorbed by Cu nanoparticles is the major driving force of the reaction. The conduction electrons of Cu nanoparticles gain the energy of the incident light through the LSPR effect and yields energetic electrons at the surface of nanoparticles. The resonance of conduction electrons with the electromagnetic field of incident light results in a significant enhancement of the local electromagnetic fields near the surface of Cu nanoparticles.[28] The light-excited electrons can activate the adsorbed reactant molecules on the surface of Cu nanoparticles.[29] The enhanced local field may also promote the reaction.

The analysis of the reaction products by GC shows the formation of acetone (0.6 mmol) and oxygen (2.4 mmol) during the reaction. Therefore, the mechanism of the photocatalytic coupling of nitrobenzene on the Cu/graphene catalyst is similar to that of the reaction on Au nanoparticles as reported previously (Figure S7).[2] In our case, isopropyl alcohol acts as a hydrogen donor and solvent in the reaction, while the presence of KOH enhances the release of hydrogen from isopropyl alcohol that is converted into acetone. The released hydrogen bonds to the surface of Cu nanoparticles, forming H-Cu species. These H-Cu species are apt to form HO-Cu by catching oxygen atoms in N−O bonds to yield azoxybenzene or azobenzene. The energetic electrons excited by the LSPR effect strongly interact with the electrophilic nitro groups in the reactant molecules, facilitating the cleavage of N−O bonds by H-Cu species. The HO-Cu species can release oxygen molecules and convert into H-Cu species, which participate in the subsequent N-O cleavage and the reaction proceeds. In such reaction process, elimination of H-Cu species will prohibit the reaction. 2,2′,6,6′-Tetramethylpiperidine N-oxyl (TEMPO) is a hydrogen-trapping agent and can abstract hydrogen atoms from the Cu surface to form hydroxylamine. When 180 mg of TEMPO was added to the reaction system, neither azoxybenzene nor azobenzene were detected after reaction. This result confirms the existence and role of H-Cu species in the system.

An important feature of the photocatalytic process on plasmonic metal nanoparticle catalysts is that the photocatalytic activity of nanoparticles can be increased by elevating the reaction temperature.[26] We conducted the reaction at different reaction temperatures under a constant light intensity. The conversion of nitrobenzene increases with increasing the reaction temperature, as shown in Figure 3. When the temperature is higher than 80 °C, over 97 % of nitrobenzene is converted. More importantly, it is found that the product selectivity changes significantly when the reaction temperature is elevated. Below 60 °C, the main product is azoxybenzene (about 98 %). As the reaction temperature continues to increase, the selectivity of azoxybenzene drops substantially while the selectivity of azobenzene increases remarkably. At 90 °C, the selectivity of azobenzene reaches a maximum of 97 %, and then declines while the further reduced product (aniline) emerges.

When the reaction temperature is raised, the relative population of reactant molecules in excited states increases according to the Bose–Einstein distribution, which means that the reactant molecules will require less energy to overcome the activation barrier and this energy could be easily provided by light irradiation. On the other hand, the number of conduction electrons of Cu nanoparticles at high energy levels increases. These thermally excited electrons can still gain further energy through the LSPR effect.[27] The conduction electrons with higher energy levels have a stronger ability to activate the reactant molecules on the surface of the Cu nanoparticles. This means that the electrons of Cu nanoparticles on graphene can effectively couple thermal

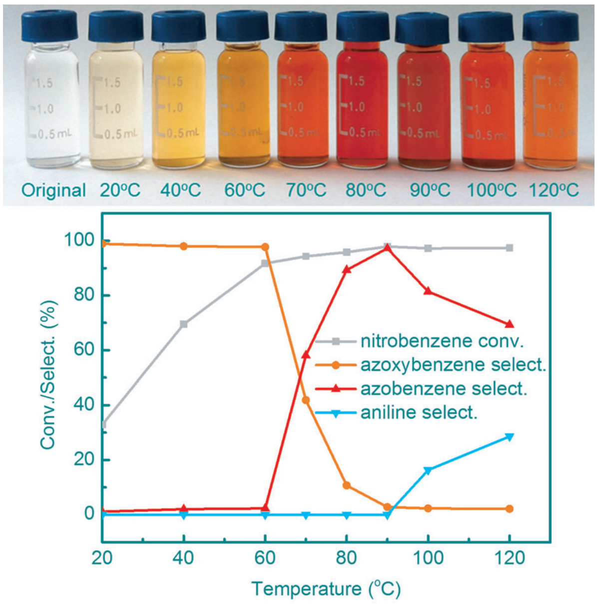


Figure 3. Top: A photograph of the products obtained at different reaction temperatures. Bottom: The photocatalytic performance of 5 wt% Cu/graphene at an irradiation intensity of 0.15 $W\,cm^{-2}$.

and photonic energies to drive the chemical reactions. This property provides us with an opportunity to select the reaction products. The activation energy required to convert nitrobenzene to azoxybenzene is lower than that to convert azoxybenzene to azobenzene.[30] Therefore, at lower temperatures the excited electrons of Cu nanoparticles can activate the conversion of nitrobenzene to azoxybenzene but not the further reaction of azoxybenzene to azobenzene. Therefore, one can select the products simply by controlling the reaction temperature. This demonstrates the potential of the Cu nanoparticle catalyst to use the infrared irradiation of sunlight, which accounts for a large fraction of the solar energy.

An experiment under the irradiation of natural sunlight was also conducted. The mean intensity of the sunlight was 0.044 $W\,cm^{-2}$ with the ground temperature on the day being about 35 °C. Conversion of 70% of nitrobenzene is achieved with a 57% selectivity for azobenzene (Figure S8). Given the relatively low reaction temperature, the high azobenzene selectivity is attributed to the UV irradiation from sunlight. The UV absorption of Cu nanoparticles (Figure 1D) can induce the interband electron transition (the bound electrons in the energy band below the conduction band are excited to energy levels above those occupied by the conduction electrons in the conduction band). Thus, these UV-excited electrons have high energy and are capable of overcoming the energy barrier for the conversion from azoxybenzene to azobenzene.[31,32] Under UV irradiation of 0.05 $W\,cm^{-2}$ at 40 °C, the nitrobenzene conversion is 81% with a 69% selectivity for azobenzene. The results under UV irradiation also demonstrate that one can select the reaction products by selectively using different irradiation wavelengths, and that it is viable to drive the synthesis of aromatic azo compounds on the Cu nanoparticle photocatalyst with sunlight at ambient temperatures.

Asymmetric azo compounds can also be synthesized using the Cu/graphene catalyst. For instance, the selectivity of 4-methoxyazobenzene over the 5 wt% catalyst at 90 °C was found to be 47% when 4-nitroanisole and nitrobenzene were employed as reactants (Figure S9). Light irradiation can enhance the conversion of the Suzuki–Miyaura cross-coupling with the Cu/graphene catalyst. These results suggest that the copper nanoparticles on graphene are a potential efficient photocatalyst for various organic reactions under moderate conditions.

The operational life is an important property of photocatalysts. The activity of the 5% Cu/graphene catalyst was monitored for five successive rounds. A slight activity decrease was detected (Figure 4). The TEM images (Figure S10) of the catalyst used for 5 rounds at 60 and 90 °C show no obvious change in morphology and aggregation of the Cu nanoparticles. The X-ray diffraction results of the used catalyst also did not show observable changes in the Cu phase (Figure S3). However, when the used catalyst was heated in hydrogen atmosphere at 500 °C, its activity was restored to the level of the fresh Cu/graphene catalyst. This indicates that a slight oxidation of Cu nanoparticles occured, most possibly at the surface of the nanoparticles during the photocatalytic reaction which led to a decline in their photocatalytic activity.

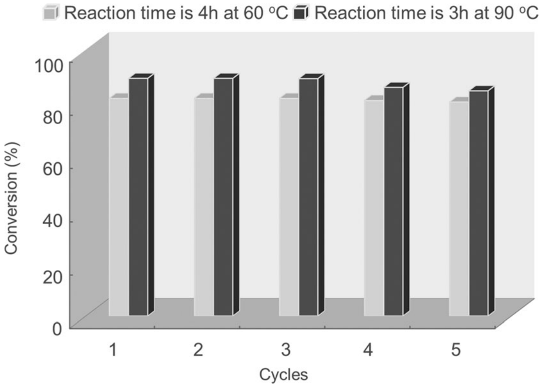


Figure 4. The photocatalytic stability of 5 wt% Cu/graphene in five cycles at 60 and 90 °C.

The findings of the present study demonstrate a new class of photocatalysts, graphene-supported copper nanoparticles, which are feasible for igniting and promoting the coupling reactions of aromatic nitro compounds to corresponding azoxy or azo compounds under visible-light irradiation. Meanwhile, one can select the product simply by tuning the reaction temperature or the irradiation wavelength. Therefore, the reaction processes using the new photocatalysts have the potential to use solar energy and are greener than conventional processes which are driven by heating. Given that graphene can be used as support to stabilize nanoparticles susceptible to oxidation, the present work also highlights a new application for graphene beyond electronic applications.

Experimental Section

Preparation of Cu/graphene catalysts: Graphene oxide and copper acetate were first dispersed into absolute ethanol under sonication, and then the suspension was magnetically stirred to form a homogeneous mixture of copper acetate and graphite oxide. In the subsequent step, the mixture was reduced using diethylene glycol for 2 h at 180°C to yield Cu_2O/graphene composites. Finally, metallic Cu nanoparticles supported on graphene (Cu/graphene) were obtained by reducing the Cu_2O/graphene composites in a mixture of H_2 (5 vol%) and Ar at 500°C.

Coupling reactions of aromatic nitro compounds: The photocatalytic reactions were conducted in a 1 atm Ar atmosphere (Figure S11). The reactant mixture consists of 30 mL isopropyl alcohol, 0.3 mmol KOH, 3 mmol aromatic nitro compounds, and 100 mg Cu/graphene catalyst. The irradiation intensity was $0.15\,W\,cm^{-2}$ and the reaction time was 5 h unless otherwise specified. The dependence of the catalytic performance on the wavelength range of light was investigated by employing various low pass optical filters to block light below specific cut-off wavelengths while maintaining the light intensity to the reaction system unchanged.

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