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Langmuir, Just Accepted Manuscript • DOI: 10.1021/acs.langmuir.7b01540 • Publication Date (Web): 19 Jul 2017

Downloaded from http://pubs.acs.org on July 23, 2017

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# Decorating of Ag and CuO on Cu nanoparticles for the Enhanced High Catalytic Activity to the Degradation of Organic Pollutants

Yu Liang, Zhe Chen,\* Wen Yao, Pengyi Wang, Shujun Yu, Xiangke Wang\*

College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, PR China.

E-mail: chenz@ncepu.edu.cn; xkwang@ncepu.edu.cn

ABSTRACT: The metal/semiconductor composites are promising catalysts with superior catalytic activity. In this work, a Cu/CuO-Ag composite with structure that Ag and CuO nanoparticles (NPs) decorated on the surface of Cu were fabricated via a facile in-situ method. With the characterization by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX) and inductively coupled plasma atomic emission spectrometry (ICP-AES), the structure and structure and component of Cu/CuO-Ag composite were well-defined. The Cu/CuO-Ag composite exhibited superior catalytic activities for the reduction of 4-nitrophenol (4-NP) in the presence of NaBH<sub>4</sub> with just trace amount of Ag NPs (1.28 wt%). The reduction reaction is completed in 75 s with apparent rate constant  $k_{app}$  of  $4.60{\times}10^{-2}~{\rm s}^{-1}.$  The Cu/CuO-Ag composite also showed excellent durable catalytic stability, as no significant activity loss was detected in the consecutive five reaction runs. With the aid of Sabatier principle and volcano plot, the opportune chemical adsorption energy of the reagent 4-NP on Cu/CuO-Ag composite was inferred to be the key to their high reaction rate.

The CuO NPs as a semiconductor with narrow band gap also could help Cu/CuO-Ag composite to capture the electrons/hydride ions and increase opportunities for 4-NP to be reduced. What's more, the Cu/CuO-Ag composite exhibited outstanding activity on the oxidative degradation of methylene blue (MB). This work enriched bimetal/semiconductor catalyst system and supplied new insight on the catalysis mechanism.

# **1. INTRODUCTION**

Over the years, transition metallic nanoparticles (NPs) have attracted much research attention due to their wide range of application.<sup>1-9</sup> Among them, silver is an excellent catalyst, which has shown remarkable catalytic activity in hydrogenation,<sup>10</sup> oxygen reduction reaction,<sup>11</sup> and hydrogen production reaction,<sup>12</sup> etc. The catalytic properties of the Ag NPs are highly dependent upon size, lattice plane and shape.<sup>13-15</sup> Enormous works have been reported on the controlled synthesis of Ag nanostructures including nanosphere, nanowire, nanocube, triangular nanoplate, nanobelt, etc.<sup>16-18</sup> However, high price and harsh synthetic conditions have caused a bottleneck in industrial application. Attributing to the synergistic effects between two metals, bimetallic nanomaterials often exhibited superior physicochemical properties comparing to their individual metals, such as high activity, functionality and stability.<sup>13</sup> Cu nanomaterials are particularly attractive for the synthesis of bimetallic nanomaterials on account of copper's low cost, high natural abundance and facile production.<sup>19</sup> Many research

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have reported that Cu was coupled with noble metals to form bimetallic NPs for improving the catalytic performance, such as Cu-Au NPs promoting the reduction of carbon dioxide,<sup>20</sup> Cu–Ni NPs as the active catalyst for the synthesis of carbon nanofibers,<sup>21</sup> Cu-Pt NPs as catalyst for oxygen reduction reaction,<sup>22</sup> and Pd-Cu NPs as an excellent bimetallic catalyst for the Sonogashira reaction,<sup>23</sup> etc. Thereby, Cu-based bimetallic NPs have been regarded as the preeminent alternative metal catalyst, which could not only reduce the cost but also enhance the catalytic properties for the nanocatalysts.

On the other hand, the catalytic performance of metal-based catalyst would also be affected by the decorating of semiconductor metal oxide, such as SnO<sub>2</sub>, CuO and TiO<sub>2</sub>. Zhou et al. found that mesoporous SnO<sub>2</sub> coated Ag nanostructures display interesting multifunctional activity on 4-nitrophenol (4-NP) reduction.<sup>24</sup> Oldfield et al. observed that the capacitance of Au NPs increased upon coating with SnO<sub>2</sub>, because the SnO<sub>2</sub> promoted the interactions as well as prolonged the lifetime of electrons.<sup>25</sup> Sasmai et al. reported that the catalytic activity of ternary Cu<sub>2</sub>O-Cu-CuO composite was surprisingly higher than that of the metal Cu NPs for 4-NP reduction, and they maintained that the unusual activity came from the in-situ generated ternary Cu<sub>2</sub>O-Cu-CuO nanocomposite.<sup>26</sup> Therefore, the effect of the semiconductor on the metal/semiconductor system to the catalytic activity was not fully defined and it is worth to explore its influence on catalysis. Herein, we developed a facile in-situ reduction method to build Cu/CuO-Ag composite with the structure that Ag and CuO

NPs were coexisted on the surface of metallic Cu NPs. The specific structure endowed the Cu/CuO-Ag composite much better catalytic activity for the reduction of 4-NP to 4-aminophenol (4-AP) comparing with Cu/CuO and Ag NPs. The reduction reaction could be completed in as short as 75 s with the apparent rate constant  $k_{app}$  up to  $4.60 \times 10^{-2}$  s<sup>-1</sup>. At the same time, Cu/CuO-Ag catalyst exhibited excellent durable stability, as no activity loss was detected in the consecutive five cyclic utilization. What's more, the Cu/CuO-Ag composite exhibited outstanding activity and durability on the oxidative degradation of MB. The mechanism of catalytic activity enhancement of the Cu/CuO-Ag composite was also fully discussed and put forward.

#### **2. EXPERIMENTAL SECTION**

#### 2.1 Materials

Silver nitrate (AgNO<sub>3</sub>), copper sulphate (CuSO<sub>4</sub>·5H<sub>2</sub>O), hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), sodium borohydride (NaBH<sub>4</sub>), polyvinylpyrrolidone (PVP, K30), cetyl trimethyl ammonium bromide (CTAB), ammonia (NH<sub>3</sub>·H<sub>2</sub>O), glucose, 4-NP, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and MB were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification.

# 2.2 Synthesis of Cu/CuO-Ag Composite

Cu/CuO-Ag composite was synthesized through a two-step method. In the first step, Cu NPs were synthesized according to the reference.<sup>27</sup> The 6.25 g CuSO<sub>4</sub>·5H<sub>2</sub>O was dispersed in 100 ml ultrapure water. In order to prepared  $[Cu(NH_3)_4]^{2+}$  solution, the

 $NH_3 \cdot H_2O$  solution was added by dropwise into CuSO<sub>4</sub> solution under stirring. When the mixed solution changed from cloudy to clarify, 200 mg PVP and 200 mg CTAB were added into 120 ml  $[Cu(NH_3)_4]^{2+}$  solution under stirring to form a clear solution. Then  $N_2H_4$ ·H<sub>2</sub>O (10%, 10 ml) was added by dropwise into the above solution to reduce  $[Cu(NH_3)_4]^{2+}$  to metallic Cu. After 6 h reaction, the products were collected by centrifugation and washed with ultrapure water and ethanol for several times. The samples were oxidized slightly by ambient air to form a loose CuO layer. Then the samples were freeze-dried under vacuum for further use. At second step, 200 mg Cu/CuO powders were dispersed in 50 ml ultrapure water. AgNO<sub>3</sub> (0.05 M, 10 ml) aqueous solution was added by dropwise into Cu/CuO suspension under stirring, where the Ag<sup>+</sup> was reduced in-situ by Cu and deposited on the surface of Cu NPs via the typical displacement reaction. After 6 h reaction, the final products were collected by centrifugation and washed by ultrapure water for several times, and then freeze-dried under vacuum for 24 h.

# 2.3 Synthesis of Ag NPs

The appropriate amount of ammonia, 200 mg PVP and 200mg CTAB was added in 120ml AgNO<sub>3</sub> (0.25 M) solution under stirring to form a colourless clear solution. Then 10 ml glucose (0.05M) was added into the above solution dropwise under stirring. After 4 h reaction, the suspension was harvested by centrifugation, washed with ultrapure water and ethanol for several times, and freeze-dried under vacuum for 12 h.

## 2.4 Characterization and Measurements

The morphology features, crystalline state, and composition of the samples were analysed by TEM and HRTEM on JEOL JEM-2100F transmission electron microscope at 200 kV. XRD was performed on scan rate 6°min<sup>-1</sup> in the 20 range of 30°-95°. XPS measurement were conducted with a Thermo ESCALAB 250 spectroscopy. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and EDX spectroscopy mapping of Cu/CuO-Ag composite was obtained on a FEI Tecnai G2 F20 transmission electron microscope. Reduction process of 4-NP was detected by UV–vis spectrophotometer (Shimadzu UV2550) spectra with the scan range 200–500 nm. Plasma atom emission spectrometer (ICPE-9000) was employed to reveal the precise chemical composition of the Cu/CuO-Ag composite.

# 2.5 Catalytic Reduction of 4-NP

The typical catalytic reduction of 4-NP was carried as follows: At first, 0.1 ml of 4-NP (5mmol/L) aqueous solution, 0.9 ml of ultrapure water, and 1 ml of freshly prepared NaBH<sub>4</sub> (15mmol/L) aqueous solution were mixed in a quartz cell. 1 ml 1.5 mg/mL of catalyst suspension (Cu/CuO-Ag composite, Cu/CuO, and Ag NPs) was added into the mixture. The reaction of mixture was recorded by UV–vis absorption spectra at room temperature immediately. At the end of the reaction, the catalysts

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#### 2.6 Catalytic Degradation of MB

In the typical run, 10 mg catalyst (Cu/CuO-Ag, Cu/CuO or Ag) was add into 10 ml MB solution (50 mg/L). Before the reaction, the mixed suspension was sonicated for 5 min and magnetic stirred in the dark for 60 min to rule out the adsorption/desorption equilibrium. And then the degradation reaction was initiated by adding 1 mL  $H_2O_2$  (30 wt%) to the solution. Samples were taken at a given time interval in the whole reaction. The sample was separated quickly by centrifugalization, and 200 uL of sample was diluted to 3 mL for further UV-vis detection. The reactions were kept at room temperature. At the end of the reaction, the catalysts were collected from the reaction system by centrifugation, washed three times with ultrapure water for the next cycle.

#### **3. RESULTS AND DISCUSSION**

#### 3.1 Preparation and Characterization of Cu/CuO-Ag Composite

The schematic illustration for the synthesis of Cu/CuO-Ag composite was shown in Scheme 1. In the first step,  $Cu^{2+}$  was reduced to metallic Cu by N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in the presence of CTAB and PVP at room temperature. The PVP and CTAB could act as the capping agent on Cu NPs to control their size. The surface of the as-synthesized Cu NPs was oxidized slightly in the ambient air to form a non-tight oxide coating gradually. In the next step, Ag<sup>+</sup> was reduced in situ on the Cu/CuO NPs by the non-capped Cu atoms, as the displacement reaction of  $2Ag^+ + Cu \rightarrow 2Ag^0 + Cu^{2+}$ taken. As a result, both Ag and CuO NPs were decorated on the surface of metallic Cu NPs to form Cu/CuO-Ag composite.



Scheme 1. Schematic illustration for the synthesis of Cu/CuO-Ag composite.

The TEM and HRTEM images of the Cu/CuO-Ag composite was shown in Figure 1. The representative Cu NPs were irregular cuboids with the average size of 100 nm (Figure 1a). The encapsulated CuO shell was about 10 nm in thick (Figure 1d). A good deal of Ag NPs with diameter 5-10 nm were observed on the surface of Cu/CuO NPs without aggregation (Figure 1a-c). The HRTEM image showed apparent lattice fringes of the Cu, CuO and Ag with periodic spacing of 0.204, 0.244 and 0.235 nm, corresponding to standard lattice fringes of the (111) facets of the Cu, CuO and Ag phases respectively (Figure 1d, e). Both lattice fringes of Ag and CuO were observed on the outer surface of metallic Cu, indicating that metallic Cu was encapsulated with CuO and Ag NPs. The lattice fringes of Ag were also found to be mixed in the CuO crystalline region, proving that the Ag NPs were reduced in situ by the non-capped Cu atoms.



Figure 1. The TEM (a, b, c) and the HRTEM (d, e) image of Cu/CuO-Ag composite at different viewing angle and magnification.

Meanwhile, Ag NPs with diameter of about 50 nm were prepared for comparison. XRD patterns of Cu/CuO, Ag and Cu/CuO-Ag composites were shown in Figure 2a. The XRD pattern of Cu/CuO NPs revealed seven diffraction peaks corresponding to the (111), (200), (220) planes of CuO and the (111), (200), (220), (311) planes of Cu, which were well consistent with the standard characteristic peaks for fcc-structure CuO and Cu. The results revealed that the samples of Cu/CuO were composed of Cu and CuO without any other impurities. For the XRD peaks of Ag NPs, five diffraction peaks at 38.1°, 44.3°, 64.4°, 77.5° and 81.5°, which could be assigned to (111), (200), (220), (311), and (222) planes of the cubic phase of pure Ag were observed. The XRD pattern of Cu/CuO-Ag composite had ten diffraction peaks, which were also found in

characteristic peeks of Cu/CuO and Ag, indicating that those peaks were belong to fcc-structure CuO and Cu, and cubic Ag respectively. The finding demonstrated that the sample of Cu/CuO-Ag composite had a good crystallinity composing with Cu, CuO and Ag phase. Figure 2b, c and d showed XPS spectra obtained from the Cu, O and Ag regions of the Cu/CuO-Ag composite. As shown in Figure 2b, the peaks at 932.38 and 952.08 eV were attributed to Cu  $p_{3/2}$  and Cu  $p_{1/2}$ , respectively, which were in good agreement with the data for Cu<sup>0</sup>. What's more, the main peaks at 932.38 and 952.08 eV had two shake-up peaks at about 943.58 and 962.15 eV, which proved the presence of Cu<sup>2+, 28</sup> In the Figure 2c, it could be figured out that the O 1s XPS was asymmetric, suggesting that two or more oxygen species were presented in the adjoining region. The peak at 529.52 eV was derived from oxygen in the CuO phase, while the peak at 530.89 was due to surface hydroxyl at CuO surface.<sup>29</sup> In the Ag 3d spectrum shown in Figure 2d, the peaks at 367.86 and 373.86 eV were assigned to Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$ , respectively, which were closed to the standard data for Ag<sup>0</sup>. The XPS data were consistent with XRD analysis, revealing the presence of Ag, Cu and CuO.



Figure 2. (a) XRD patterns of sample Cu/CuO-Ag composite, Cu/CuO and Ag NPs; (b), (c) and (d) XPS spectra of the Cu, O and Ag regions obtained from the Cu/CuO-Ag composite

HAADF-STEM was taken to further identify the nanostructure and chemical composition of Cu/CuO-Ag composite. Elemental mapping of Cu/CuO-Ag composite was shown in Figure. 3a, in which the distribution of the Ag, O and Cu elements could be observed clearly. The relatively loose distribution of O elements on the surface and the dense distribution of Cu across the whole particle illustrated that a non-tight oxide layer was deposited on the surface of Cu NPs. Meanwhile, Ag atoms had a sparse but well-proportioned distribution outside the Cu core. Furthermore, the HAADF-STEM image and the compositional line scanning profiles of a single Cu/CuO-Ag composite were shown in Figure 3b. The results revealed that the particle was composited of Cu, Ag, and O elements, and the content of Cu was much richer than O and Ag. According to the features of curve, the composite revealed a feature of

the surface decorating type nanostructures. ICP-AES was taken to further determine the elementary composition of Cu/CuO-Ag composite. The elements content of Cu, O and Ag was calculated to be 96.58 wt%, 2.14 wt% and 1.28 wt%, respectively. We could infer that 10.83 wt% CuO and 1.28 wt% Ag were decorated on Cu core with a weight percentage of 87.89 wt%.



Figure 3. (a) Elemental mapping images of Cu/CuO-Ag composite. Ag, O and Cu elements are displayed as red, green and yellow color respectively. (b) The compositional line-scanning profile of Cu/CuO-Ag composite, and the inset is the HAADF-STEM image.

# **3.2 Catalytic Activity Tests**

The reduction of 4-NP catalyzed by metallic nanocatalysts in the presence of NaBH<sub>4</sub> have been extensively studied recently.<sup>30-34</sup> 4-NP is a kind of notorious persistent organic pollutant, which is high toxic and difficult to be degraded under natural condition. Meanwhile, the product 4-AP is an important intermediate and applied in numerous applications such as drugs and dyes.<sup>30-32</sup> The reduction of 4-NP has emerged as one of the most widely used model reactions for assessing the catalytic activity and kinetic analysis. Hereinafter, the Cu/CuO-Ag composite was

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used as an efficient catalyst for the reduction of 4-NP to 4-AP. The equation and schematic diagram of the catalytic reaction of 4-NP to 4-AP with NaBH<sub>4</sub> were shown in Figure 4. According to the principle of thermodynamics, the reaction of 4-NP to 4-AP with NaBH<sub>4</sub> was a feasible process due to the redox potential for NaBO<sub>2</sub>/NaBH<sub>4</sub> = -1.33 V and 4-NP/4-AP = -0.76 V *versus* the normal hydrogen electrode.<sup>35</sup> But the reduction of 4-NP was hardly occurred without catalysts due to the large kinetic barrier between donor and acceptor molecules.<sup>36</sup> Generally, the process of catalytic reduction of 4-NP was mainly divided into three parts. At first, the 4-NP was adsorbed onto the surface of Ag and CuO NPs by chemical adsorption. Simultaneously, BH<sub>4</sub><sup>-</sup> was also adhered to the nanocatalyst surface and transferred electrons and hydride ions to the metal nanocatalyst surface. Then electrons were transferred to the nitro groups of 4-NP, initiating the reduction to amino groups. Finally, the product 4-AP were desorbed from catalyst surface.<sup>37-41</sup>



**Figure 4.** The equation and schematic diagram of the catalytic reaction of 4-NP to 4-AP with NaBH<sub>4</sub> and Cu/CuO-Ag composite catalysts.

The UV-Vis absorption spectra were used to monitor the reduction process of 4-NP. When the catalyst Cu/CuO-Ag composite was added into the mixture of 4-NP and NaBH<sub>4</sub>, the significant decreases of the absorption peak at 400 nm were discovered, implying the reduction of 4-NP. Simultaneously, a new absorption peak arose at 295 nm gradually, owing to the formation of 4-AP.<sup>30</sup> Two isosbestic points could be observed at 277 and 317 nm, which indicated no by-product was generated. The reduction reaction was completed 100% in 75 s, along with the color of mixed solution changing from light yellow to colorless (Figure 5a). For comparison, the catalytic activities of Cu/CuO and Ag NPs were evaluated under the identical conditions. The absorption intensity at 400 nm was used to measure the concentration of 4-NP, and the plot of absorbance vs. reaction time at 400 nm was shown in Figure 5b. The reaction completed at 75, 120, and 170 s for Cu/CuO-Ag composite, Cu/CuO, and Ag NPs, respectively, indicating that the catalytic performance of Cu/CuO-Ag was superior and significantly enhanced with only trace amount Ag (1.28 wt%) comparing with Cu/CuO and pure Ag NPs.



**Figure 5.** (a) Time-dependent UV-vis spectral changes in 4-NP catalyzed by Cu/CuO-Ag composite at room temperature; (b) The plot of  $C_t/C_0$  of 4-NP *vs.* reaction time catalysed by Cu/CuO-Ag composite, Cu/CuO and Ag NPs; (c) Linear relationship of  $-\ln(C_t/C_0)$  as a function of time for the Cu/CuO-Ag composite, Cu/CuO and Ag NPs.

In the catalytic test, the concentration of NaBH<sub>4</sub> was 30 times of that of the 4-NP. Thereby, the reductions rate constant could be calculated by the pseudo-first order reaction kinetics:  $\ln (A_t/A_0) = \ln(C_t/C_0) = -k_{app}t$ , where  $A_t$  and  $A_0$  were the absorbance values of 4-NP at time t and initial time,  $C_t$  and  $C_0$  were the 4-NP concentration at t and its initial time, and  $k_{app}$  represented the apparent rate constant. The approximately linear relationships of  $-\ln(C_t/C_0)$  vs. reaction time were displayed in Figure 5c. From the slopes of the linear relationship, the  $k_{app}$  value was calculated to be  $4.60 \times 10^{-2}$  s<sup>-1</sup> for the Cu/CuO-Ag composite, which was significant higher than Cu/CuO ( $2.00 \times 10^{-2}$ s<sup>-1</sup>) and Ag ( $2.33 \times 10^{-2}$  s<sup>-1</sup>). An important feature of the reduction of 4-NP catalyzed by Ag NPs was the induction time ( $t_0$ ). Several studies have proposed that the induction time was attributed to the substrate induced surface restructuring to

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initialize the reaction.<sup>42, 43</sup> No obvious induction time was found on Cu/CuO-Ag composite and Cu/CuO, indicating that the exposed surface of 5-10 nm Ag NPs on Cu/CuO-Ag composite was highly active. These results remarkably suggested the improved catalytic property of Cu/CuO-Ag composite. Comparing with other reported materials, the  $k_{app}$  value of Cu/CuO-Ag composite was still preferable. From Table 1, it could be clearly found that the rate constant of Cu/CuO-Ag composite was much larger than Cu-DENs (2.43×10<sup>-2</sup> s<sup>-2</sup>),<sup>44</sup> Ag-DENs (1.18×10-2 s<sup>-1</sup>),<sup>45</sup> Ag/CNFs  $(6.2 \times 10^{-3} \text{ s}^{-1})$ , <sup>36</sup> SiO<sub>2</sub>(a)Ag NPs  $(1.24 \times 10^{-3} \text{ s}^{-1})$ , <sup>46</sup> Ag/HLaNb<sub>2</sub>O<sub>7</sub>  $(3.01 \times 10^{-3} \text{ s}^{-1})$ , <sup>47</sup> rGO/Fe<sub>3</sub>O<sub>4</sub>/Au (1.14×10<sup>-2</sup> s<sup>-1</sup>)<sup>48</sup> and so on. What's more, the ratio of rate constant  $k_{app}$ for the total weight of the catalyst (K= $k_{app}/m$ ) was used as the comparison with reports in the literature. The active factor K of the Cu/CuO-Ag composite was 30.67  $s^{-1}g^{-1}$ , which was about 15 times more than that previously reported K for bimetallic Cu/Ag (1.975 s<sup>-1</sup>g<sup>-1</sup>).<sup>49</sup> Both of the outstanding efficiency and low cost (1.28 % Ag loading) endowed the Cu/CuO-Ag composite with great application prospect.

**Table 1.** The comparison of catalytic activities for the reduction of 4-NP with catalysts reported in literatures.

Catalysts	$k_{app} \left( s^{\text{-1}} \right)^{[a]}$	$k_{app}/m \; (g^{-1}s^{-1})^{[b]}$	Concentration of 4-NP (mmol L <sup>-1</sup> )	Ref.
CNFs/Ag NPs	6.2×10 <sup>-3</sup>	6.2	0.12	36
	1 2 4 4 2 3	a <b>a</b> 1a	0.12	

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Ag/HLaNb <sub>2</sub> O <sub>7</sub>	3.01×10 <sup>-3</sup>	1.0	0.10	47
rGO/Fe <sub>3</sub> O <sub>4</sub> /Au	1.14×10 <sup>-2</sup>	2.858	5	48
Cu/Ag	3.95×10 <sup>-3</sup>	1.975	0.10	49
Pd/RGO/Fe <sub>3</sub> O <sub>4</sub>	5.1×10 <sup>-2</sup>	10.2	2.50	50
Cu/CuO-Ag	4.60×10 <sup>-2</sup>	30.67	0.17	This
				work

[a] The reaction rate constant. [b] The ratio of rate constant for the total weight of the catalyst.

Reusability is very important for practical applications of heterogeneous catalytic systems. The reusability of Cu/CuO-Ag composites, Cu/CuO and Ag NPs for the reduction of 4-NP were shown in Figure 6a, b and c, respectively. It can be seen that Cu/CuO-Ag catalyst exhibited excellent durable stability. The plots of absorption intensity at 400 nm *vs.* reaction time almost overlapped with every cycle in the consecutive five cyclic utilization. After 5 runs, no significant activity loss was detected (Figure 6a). However, the catalytic activity of Cu/CuO NPs was decreased significantly with the increase of cycling times, as shown in Figure 6b. The conversion of 4-NP was 85.0% in 75 s at the 1st run, but it was decreased to 26.2% at the 5th run (Figure 6d). Ag NPs also presented an outstanding reusability in the reduction of 4-NP as shown in Figure 6c. The results indicated that loading of silver NPs could effectively improve the stability of the Cu/CuO-Ag catalyst.



**Figure 6.** Cycling performance of Cu/CuO-Ag, Cu/CuO and Ag NPs for the reduction of 4-NP. (a-c) the absorption intensity of 4-NP at 400 nm *vs.* reaction time for Cu/CuO-Ag, Cu/CuO and Ag NPs in 5 consecutive reaction cycles respectively. (d) The conversion of 4-NP for 5 consecutive reaction cycles catalysed by Cu/CuO-Ag, Cu/CuO and Ag NPs at 75 s.

The superior activity and reusability could be attributed to three aspects. Firstly, the chemisorption of 4-NP molecule to the catalyst surface correlates with the reaction rate constant. According to the Sabatier principle,<sup>51</sup> the adsorption interaction between the reactants and the surface of catalytic should not be too weak, nor too strong, but

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rather be appropriate affinitive to achieve ideal catalytic properties. The binding geometry for 4-NP chemisorption on atom of Cu, Ag, and Cu-Ag NPs were shown in Figure 7a, the adsorption energy of 4-NP on Ag and Cu surface is ~-0.78 eV and -1.45 eV respectively.<sup>52</sup> Thus, Ag NPs are inactive due to weakly binding the reactants ( $E_{Ads} = -0.78 \text{ eV}$ ,  $k_{app} = 2.33 \times 10^{-2} \text{ s}^{-1}$ ), while Cu NPs are inactive due to too strongly binding ( $E_{Ads} = -1.45 \text{ eV}$ ,  $k_{app} = 2.00 \times 10^{-2} \text{ s}^{-1}$ ). In the typically volcano plot,<sup>52</sup> the points of the Ag and Cu located on the side of the plot. After alloying as Cu-Ag bimetal, the calculated adsorption energy of 4-NP on Cu-Ag would have an average adsorption energy that sits near to the volcano peak, which means that overly strong and weakly binding are balanced as proved by Henkelman.<sup>52</sup> As a result, the opportune chemical adsorption of reagent 4-NP on Cu/CuO-Ag composite would facilitate a faster catalytic reaction (Figure 7b). That's why the much higher  $k_{app}$  (4.60×10<sup>-2</sup> s<sup>-1</sup>) was observed on the Cu/CuO-Ag composite.

Secondly, the CuO NPs on the surface of Cu played important role in catalysis. Zhou et al. claimed that when metal oxide closely contacted with metal, Fermi level alignment would lead to charge redistribution: electrons would escape from the metal and transfer into the semiconductor.<sup>24</sup> Zhang et al. used Ag/CNF as the catalyst for the reduction of 4-NP. <sup>36</sup> They reported that electrons could be injected into the CNF from Ag/CNF interface, and the enhanced reaction sites on CNF endowed Ag/CNF high catalytic activity. In our work, CuO was known as a p-type semiconductor with low band gap (1.4 eV).<sup>53</sup> Both of Ag/Cu interface, Ag/CuO interface and Cu/CuO

interface existed in the composite. When the Cu/CuO-Ag composite was used as catalyst, part of the electrons and hydride ion that injected from BH<sub>4</sub><sup>-</sup> to Ag or Cu NPs could transfer to the neighboring CuO surface (Figure. 7c), resulting in charge redistribution and the formation of a depletion layer surrounding the Ag/CuO and Cu/CuO interface. The existence of the surplus electrons on CuO provided larger surface area and increased opportunities for reduction reaction, facilitating the capture of electrons by 4-NP molecules. Plenty of surplus electrons exist at a large amount of Ag/CuO and Cu/CuO interfaces in the Cu/CuO-Ag composite, thus the catalytic activity was increased accordingly.

Thirdly, Cu/CuO-Ag composite exhibited enhanced recycling performance. Several works reported that the rate constant of 4-NP reduction rapidly decreased from the first cycle and remained fairly stable in the after successive cycles.<sup>54-56</sup> They speculated the rate decrease might be associated with the production of 4-AP, as 4-AP could directly adsorb onto the catalyst surface and block the diffusion of reactant 4-NP. We observed similar phenomenon on the recycling reaction catalyzed by Cu/CuO. The opportune adsorption energy of 4-AP on Cu/CuO-Ag was supposed to be the key of enhanced recycling performance. For the Cu/CuO-Ag composite catalyst, the introduction of Ag NPs accelerated desorption of product 4-AP due to Cu-Ag alloy NPs had a suitable chemisorption for the 4-AP. Moreover, Ag NPs could prevent the oxidation of the internal Cu core, which also played an important role regards to its outstanding cycling performance.





Figure 7. (a) the binding geometry for 4-NP chemisorption on atom of Cu, Ag, and Cu-Ag NPs, (b) the volcano plot diagram for the Cu, Ag, and Cu-Ag NPs for reduction of 4-NP (c) the electrons distribution diagram on Cu/CuO-Ag NPs surface, as the electrons transfer from metal to the CuO semiconductor.

#### 3.3 The Degradation of Organic Dyes

To further evaluate the catalytic performance of Cu/CuO-Ag composite, the activity for the degradation of MB was investigated. MB, an organic dye, was degraded with assistance of  $H_2O_2$  at room temperature. Figure 8a showed the plot of  $C_t/C_0$  of MB *vs*. reaction time catalyzed by Cu/CuO-Ag composite, Cu/CuO and Ag NPs. In Fig. 8a, more than 96.0 % of MB was decolored in 36 min catalyzed by the Cu/CuO-Ag composite. For comparison, the catalytic activities of Cu/CuO and Ag

NPs were evaluated under identical conditions. They showed relatively lower activity. About 95 % of MB was decolored in 65 min and 125 min for Cu/CuO and Ag NPs, respectively. The rate constant *k* was calculated to be 5.09 h<sup>-1</sup> for Cu/CuO-Ag composite, which was much higher than that of Au-Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> (1.99 h<sup>-1</sup>),<sup>57</sup> GT-Fe NPs (1.26 h<sup>-1</sup>)<sup>58</sup> and FePt NPs (1.38 h<sup>-1</sup>)<sup>59</sup>. The enhanced activity of Cu/CuO-Ag composite comparing with Cu/CuO and Ag NPs agreed well with the 4-NP reduction degradation. In addition, the Cu/CuO-Ag composite could be easily recovered by centrifugation and reused for the next run of reaction. No obvious decrease in activity was observed in five consecutive reaction runs (Fig. 8b). The results suggested that the Cu/CuO-Ag composite was a promising catalyst for the degradation of organic pollutants.



Figure 8 (a) The plot of  $C_t/C_0$  of MB vs. reaction time catalysed by Cu/CuO-Ag composite, Cu/CuO and Ag NPs, (b) The degradation of MB for 5 consecutive reaction cycles catalysed by Cu/CuO-Ag composite at 35 min.

#### **4 CONCLUSIONS**

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In summary, we developed a facile two-step process for the preparation of Cu/CuO-Ag composite with fine crystallinity. XRD pattern, XPS spectra, ICP-AES, TEM image and elemental mapping of the product demonstrated that in the Cu/CuO-Ag composite the metallic Cu was decorated with CuO and Ag NPs. The specific structure endowed the Cu/CuO-Ag composite high catalytic activity with trace loading amount of Ag NPs (1.28 wt%). In the reduction of 4-NP to 4-AP, the reaction could be completed in 75 s with an apparent rate constant  $k_{app}$  as high as  $4.60 \times 10^{-2}$  s<sup>-1</sup>. The functions and synergistic effect mechanism of Ag, Cu and CuO was fully discussed. What's more, the Cu/CuO-Ag composite exhibited outstanding oxidative degradation of activity on the MB. The work enriched bimetal/semiconductor catalyst system and supplied new insight on the catalysis mechanism. The fabrication route of Cu/CuO-Ag composite provided a low-cost approach to build high-efficient nanocatalysts for the application in degradation of organic pollutants.

#### ACKNOWLEDGEMENTS

We appreciate the financial support from National Natural Science Foundation of China (NSFC 51502089), National Key Research and Development Program of China (2017YFA0207000) and the Fundamental Research Funds for the Central Universities (2016MS03).

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Entry for the Table of Content



A Cu/CuO-Ag composite with the structure that Ag and CuO nanoparticles (NPs) decorated on the surface of Cu NPs was developed. The bimetal/semiconductor composite showed enhanced high catalytic activity and durability for the degradation of organic pollutants.