MOF derived porous carbon supported Cu/Cu₂O composite as high performance non-noble catalyst

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ABSTRACT

Porous carbon supported copper composite (Cu/Cu₂O/C) was synthesized with a facile, low cost and novel method and used as non-noble-metal catalyst for reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH₄. In the synthetic strategy, metal organic framework Cu₃(BTC)₂ (also denoted as HKUST-1) was used as both sacrificial template and copper precursor, and phenol formaldehyde resin as carbon precursor. The catalytic Cu/Cu₂O nanoparticles (Cu/Cu₂O NPs) about 40 nm-in-diameter distributed uniformly both on the internal and external surface of the porous carbon flakes, and took up 33.38–37.56 wt% of the Cu/Cu₂O/C composite. Compared with noble metal catalysts, the prepared composite showed comparable high catalytic activity, which was mainly due to their porous structure facilitating diffusion of reactants and products, and the high dispersion of accessible catalytic Cu/Cu₂O NPs on porous carbon. Moreover, the synthesized catalyst can be reused for at least five cycles due to its good stability. These results confirmed that the as-prepared Cu/Cu₂O/C is promising candidate to replace noble metal for catalytic application.

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1. Introduction

In catalysis, noble metal catalysts (Au, Ag, etc) have been widely used due to their high selectivity and catalytic efficiency [1,2]. Despite the great progress achieved by far, the scarce and high-cost of noble metal resources make them uneconomic for practical application. With growing emphasis on economical, effective and sustainable development, increasing importance has been placed on utilizing non-noble metal materials for substitute. So far, various metal nanoparticles (NPs) such as copper, aluminum, magnesium, zinc and their oxides have been proved to be applicable in different types of reactions [3–5].

Metal NPs with nanometer scale dimensions are unstable and get self-aggregation easily because of their high surface energy and large specific surface area, which may lead to the deterioration of catalytic efficiency and influent their recycling. Therefore,

increasing efforts have been made by loading metal NPs on various supports [6–8]. The supporting matrices reported in literature generally possess low surface areas, and the NPs are usually imbedded into the supports, which results in the poor accessibility of catalysts towards targets [9]. Thereby, supporting materials, with high porous structure, may provide multiple accessible channels for diffusion and transport to take full advantage of the excellent catalytic functionalities of metal NPs.

In recent years, metal-organic frameworks (MOFs) have emerged as a particular class of multifunctional materials due to their modularity, hybrid composition, high surface area, tunable porosity, and various potential applications in different fields [10–12]. Over the past decade, research works have been mostly focused on preparing new MOFs and exploring their applications in gas adsorption and separation. So far, the research on synthesis of inorganic functional materials derived from MOFs is still in early stage [13–15].

Recently, W. Bak et al. have synthesized Cu/Cu₂O@C composite materials from MOF through vapor phase polymerization of phenolic resin inside the nanopores of the MOFs followed by thermolysis under an inert atmosphere [16]. The as-prepared composites preserved the morphology of MOF with micropores.

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Herein we present a different and facile method to obtain porous carbon supported Cu/Cu₂O composite architecture (Cu/Cu₂O/C) by using Cu₃(BTC)₂ (also denoted as HKUST-1) as sacrificial template and phenol formaldehyde resin as carbon precursor. The Cu/Cu₂O/C composites possess different pore sizes ranging from micro-to macro-pores, and the Cu/Cu₂O particles 40 nm-in-diameter distributed evenly on the internal and external surface of the porous carbon flakes, which allow the accessibility of the catalytic active sites (Cu/Cu₂O NPs). The resulted Cu/Cu₂O/C materials are employed as catalysts for the reduction of 4-nitrophenol (4-NP) with NaBH₄ and shows excellent catalytic performance. Compared with previous noble metal-based systems, copper is several orders of magnitude cheaper than noble metal. To the best of our knowledge, this is the first report on the synthesis of porous carbon supported non-noble Cu/Cu₂O hybrid material by using MOF as both sacrificial template and metal NPs precursor.

2. Experimental

2.1. Chemicals and materials

All reagents were of analytical reagent grade and used without further purification. Copper (II) nitrate trihydrate (Cu(NO₃)₂ · 3H₂O), anhydrous methanol (CH₃OH), and ammonia (NH₃ · H₂O, 25%) were purchased from J&K Chemical Ltd. (Beijing, China). Phenol, 4-nitrophenol (4-NP), benzene-1,3,5-tricarboxylic acid (C₆H₃(COOH)₃), and aqueous formaldehyde solution (37%) were obtained from Sinopharm Chemistry Reagent Co., Ltd. (Beijing, China).

2.1.1. Synthesis of HKUST-1

The HKUST-1 was prepared via a method as described previously [17]. In brief, copper nitrate (1.82 g) and benzene-1,3,5-tricarboxylic acid (BTC) (0.875 g) were dissolved in 50 mL anhydrous methanol, respectively. Then, the copper nitrate solution was transferred into the tricarboxylic acid solution followed by

continuous magnetic stirring for 2 h at room temperature. The blue precipitate was retrieved by centrifugation and washed with methanol twice, and dried at 50 °C under vacuum.

2.1.2. Synthesis of carbon supported Cu/Cu₂O

Typically, 0.2 g HKUST-1 and 125 mL deionized water were added into a 250 mL three-necked round bottomed flask and ultrasonicated for 10 min. Then, 0.15 mL NH₃ · H₂O and 0.2 g resorcinol were added into the mixture under mechanical stirring for more than 1 h at 30 °C. Subsequently, 0.1 mL formaldehyde solution was added to the reaction solution and stirred for 8 h. After that, the mixture was heated at 80 °C for another 10 h under stirring. The solid product was recovered by centrifugation, dried at 50 °C under vacuum, and finally heated under a N₂ atmosphere to 600 °C (kept for 4 h) for carbonization. The obtained sample was denoted as Cu/Cu₂O/C.

2.1.3. Catalytic reduction of 4-nitrophenol

The reduction of 4-nitrophenol (4-NP) in the presence of NaBH₄ was carried out to investigate the catalytic activity and reusability of the Cu/Cu₂O/C catalyst. Typically, 2 mL of deionized water, 0.1 mL 4-nitrophenol solution (5 × 10^{−3} M), and 1.0 mL of fresh NaBH₄ (0.2 M) were added into a quartz cuvette in sequence, followed by the addition of 0.04 mg of catalyst to the mixture. The mixture was quickly subjected to UV–Vis measurements and scanned at a certain time interval. To determine the reusability, the amounts of 4-NP and catalyst were increased to 10 times of the above typical reduction. When the reduction process was completed, the catalysts were isolated by centrifugation and reused in next cycle.

2.2. Characterization

The size and morphology of the synthesized materials were investigated by using a transmission electron microscope (TEM) of

Fig. 1. SEM and TEM images of HKUST-1 (A, D), and Cu/Cu₂O/C composite (B, C, E).

Fig. 2. XRD patterns of HKUST-1 and Cu/Cu₂O/C composite.

H-7500 (Hitachi, Japan) and a Hitachi S-2400 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (FE-SEM, Tokyo, Japan). The X-ray powder diffraction patterns (XRPD) were collected by a PAN analytical X'pert Pro diffractometer (XRD, Almelo, Netherlands) by using a monochromatized X-ray beam with nickel-filtered Cu K α radiation with 0.4° min⁻¹ scan rate. The specific surface area and pore volume analysis were carried out by BET methods (ASAP2000 V3.01A; Micromeritics, Norcross, GA). X-ray photoelectron spectroscopy (XPS) measurements were conducted by using a Thermo Scientific ESCA-Lab-200i-XL spectrometer (Waltham, MA) with monochromatic Al K α radiation (1486.6 eV). A thermogravimetric analyzer (Netzsch-209, Bavaria, Germany) was used to evaluate the thermal stability.

3. Results and discussion

3.1. Structural and morphological characterization

Fig. 1 depicts the SEM and TEM images of HKUST-1 and carbon supported copper composite. Fig. 1(A and D) shows that the HKUST-1 MOF possesses homogeneous octahedral shape. During calcination of HKUST-1-phenolic polymer at high temperature in N₂, the

phenol precursor and organic ligands BTC would be decomposed and carbonized, which could lead to the reduction of Cu²⁺ to produce Cu and/or Cu₂O nanoparticles (the O atoms should come from the organic ligand BTC and/or phenolic resins). In addition, the production of various gases in the carbonization process including carbon monoxide and hydrogen, which have strong reducibility, might also lead to the reduction of Cu²⁺ [18]. The SEM images in Fig. 1B and C indicated that the prepared carbon supported Cu/Cu₂O/C composite were hierarchical structure, and their particle size is about 3–4 μ m. Fig. 1D and E displays that Cu/Cu₂O NPs with diameter of about 40 nm highly dispersed both on the internal and external surface of the porous carbon flakes.

The crystal phases of HKUST-1 and Cu/Cu₂O/C were investigated by XRD analysis. As shown in Fig. 2, the XRD pattern of HKUST-1 in this study was essentially identical to that of HKUST-1 powder reported in literature [19]. In the XRD pattern of carbon supported Cu/Cu₂O, the diffraction peaks and relative intensities could be readily indexed to crystalline Cu (JCPDS NO. 04-8436) and Cu₂O (JCPDS NO. 78-2076), respectively, indicating that the Cu-related nanoparticles attached to the carbon matrices were composed of two components. The weaker intensity of Cu₂O diffraction peaks than those of Cu⁰ reflected that most cupric was reduced into Cu⁰ because of the abundant reductant in the calcination process.

XPS measurement was employed to investigate the elemental composition on the surface of different composites. Curve-fitting of the Cu 2p_{3/2} and O 1s lines for both HKUST-1 and Cu/Cu₂O/C employed Gaussian (20%)–Lorentzian (80%) peak-shapes, respectively (defined in CasaXPS as GL (80)). Peak-fit for these species are shown in Fig. 3. For HKUST-1, Cu²⁺ was clearly identified according to the main 2p_{3/2} peak at 933.9 eV and the satellite peaks at 939.9, 944.1 eV (Fig. 3A) [6,20,21]. For Cu/Cu₂O/C, the main peaks at 932.7 eV and 934.7 eV were assigned to Cu₂O and/or Cu and Cu(OH)₂, respectively [21,22], whereas the shake-up peaks at 941.3 eV and 944.2 eV were ascribed to Cu(OH)₂, which is often found for atmosphere-exposed Cu₂O surfaces [22,23]. The O 1s spectrum of HKUST-1 (Fig. 3B) could be deconvoluted with two peaks at 531.8 eV (83.2%) and 533.01 eV (16.8%), which were related to the presence of Cu₂(O₂CR)₄ (where R is an aromatic ring) groups and carboxylate species of BTC ligands, respectively. For Cu/Cu₂O/C, the O 1s spectrum comprised three peaks at 530.4 eV (4.9%),

Fig. 3. High-resolution XPS spectra of Cu2p (A) and O1s (B) for HKUST-1 and Cu/Cu₂O/C composite.

Fig. 4. Nitrogen adsorption–desorption isotherms of Cu/Cu₂O/C composite (A), thermogravimetric analysis (TGA) curve of Cu/Cu₂O/C composite under air atmosphere (B).

532.2 eV (66.6%) and 533.6 eV (28.5%), respectively. The peak at the lowest binding energy was associated with the Cu₂O and Cu–OH groups [24], while those at 532.2 and 533.6 eV were related to the C–OH and C=O groups on the surface of carbon matrix. The intensity of O1s peak of Cu/Cu₂O/C composite decreased obviously compared with that of HKUST-1, which indicated the successful carbonization of phenolic polymer and BTC. This result also suggested that the content of Cu₂O nanoparticles was low in Cu/Cu₂O/C, which was consistent with the weaker intensity of Cu₂O diffraction peaks in XRD of this material.

The pore structure and specific surface area of the samples were investigated by measuring the nitrogen adsorption isotherms. As shown in Fig. 4A, a distinct increase in adsorbate volume in the low P/P_0 region indicated the presence of micropores [25], which might

be contributed by the HKUST-1 structure. The hysteresis loop at $P/P_0 = 0.4–0.6$ implied the existence of mesopores. But the N₂ uptake in this region was very small, indicating the small amount of mesopores in this material. The strong N₂ uptake at P/P_0 above 0.8 suggested the surface coverage of macropores [25], which might be the slits between carbon flakes. This result indicated that the porous structure of the obtained Cu/Cu₂O/C nanocomposites was composed of micropores, mesopores and macropores. The macropores among the carbon flakes allowed the accessibility of the Cu/Cu₂O nanoparticles dispersed both on the internal and external surface of the porous carbon flakes. The total pore volume of Cu/Cu₂O/C was determined to be 0.8 cm³ g^{−1} and the Brunauer–Emmett–Teller (BET) surface area of the obtained Cu/Cu₂O/C composite was 282 m² g^{−1}. The properties of large specific surface

Fig. 5. UV–Vis absorption spectra of the solution of 4-NP with and without NaBH₄ (A), time-dependent UV–Vis absorption spectra of the 4-NP reduced by NaBH₄ without (B) and with (C) the Cu/Cu₂O/C composites, inset (C) describes the plot of $\ln(C_t/C_0)$ versus time for Cu/Cu₂O/C catalyst, (D) plots of C_t/C_0 against reaction time under different catalytic conditions.

Table 1

Comparison of catalytic activity for 4-nitrophenol reduction with other reported catalysts based on metal NPs.

Catalyst	Moles of 4-NP (μmol)	Amount of catalyst (mg)	Required time (min)	Turnover rate ^a (mmol/mg/min)	Reference
$\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-C/Au}$	0.5	0.05	3.3	3.03	[28]
Au-Ag/GO	0.616	0.3	0.5	4.11	[29]
Ag/CLLC	2.25	10	22	0.01	[30]
SiNWAs-Cu	2.5	—	6	—	[26]
GO/Cu	3.85	22	1	0.17	[31]
Au/CuO	0.25	0.08	17.5	0.18	[21]
Cu microspheres	0.25	0.06	7.5	0.56	[32]
$\text{Cu/Cu}_2\text{O/C}$	0.5	0.04	2.67	4.68	This work

^a Turnover rate was calculated by the moles of nitrobenzene per unit mass of used catalyst per unit time.

area and high porosity could provide multiple accessible channels for $\text{Cu/Cu}_2\text{O}$ NPs contacting with targets.

TGA was carried out from room temperature to 700 °C at a heating rate of 10 °C min^{-1} to check the thermal stability of the composites (Fig. 4B). The TGA data revealed that the $\text{Cu/Cu}_2\text{O/C}$ composites showed slight weight loss below 200 °C due to the initial loss of water. After that, a slow weight increase could be observed because of the oxidation of Cu and Cu_2O NPs. When the heat temperature was above 350 °C, carbon phase in the $\text{Cu/Cu}_2\text{O/C}$ composites decomposed promptly suggesting the oxidation of carbon. The mass percent remaining after 440 °C could be regarded as absolutely CuO. According to the TGA results, the mass percentage of $\text{Cu/Cu}_2\text{O}$ NPs in the composite was estimated to be 33.38–37.56%.

3.2. Catalytic behavior and mechanism

The catalytic reduction of 4-nitrophenol to its daughter derivatives 4-aminophenol (4-AP) in the presence of NaBH_4 has often been used as a model reaction to evaluate the catalytic performance of metal NPs. The metal nanoparticles stimulate the catalytic reduction by relaying electrons from the donor BH_4^- to the acceptor 4-NP. In this study, this reaction was used to investigate the application of the $\text{Cu/Cu}_2\text{O/C}$ composites to the catalytic reduction

of nitroaromatic compounds. The 4-NP solution exhibited a strong absorption peak at 318 nm which was remarkably red-shifted to 400 nm when treated with NaBH_4 (Fig. 5A). The phenomenon was related to the formation of 4-nitrophenolate owing to an increase in solution alkalinity upon the addition of NaBH_4 [26]. In the absence of $\text{Cu/Cu}_2\text{O/C}$ catalysts, UV–Vis absorption spectra of 4-NP did not change during 10 h with the addition of NaBH_4 (Fig. 5B). After the addition of small amount of $\text{Cu/Cu}_2\text{O/C}$ catalysts, the intensity of the 4-NP characteristic absorption peak at 400 nm decreased gradually, while the characteristic absorption at 308 nm related to 4-AP appeared accordingly (Fig. 5C). The peak at 400 nm vanished absolutely within 160 s, and the color of the solution was changed from yellow to colorless, suggesting the complete reduction of 4-NP.

It was reported that direct thermolysis of HKUST-1 in N_2 could obtain Cu nanoparticles and carbon composites as well. Das et al. [27] heated HKUST-1 from room temperature to 900 °C under N_2 environment, during which Cu^{2+} was reduced to Cu NPs and BTC was carbonized to graphite. The produced material had large surface areas (488 $\text{m}^2 \text{g}^{-1}$) and micropores with Cu nanoparticles embedded in the carbon matrix. In the present study, we calcined HKUST-1 under N_2 from room temperature to 600 °C, the obtained material was denoted as HKUST-1-600. Then the HKUST-1-600 was used as catalyst to reduce 4-NP. As a result, 4-NP was hardly

Fig. 6. (A) Conversion of 4-NP in five successive cycles with $\text{Cu/Cu}_2\text{O/C}$ catalyst and (B) the required time of each cycle for total conversion of 4-NP, (C) TEM images of $\text{Cu/Cu}_2\text{O/C}$ catalyst after five cycles.

reduced within 15 min (Fig. 5D). As we all know, the diffusion rate of organic molecules to microporous materials (such as MOF) is low in water solution, therefore, it would take long times for 4-NP to transport the microporous carbon coat of HKUST-1-600 to contact the catalytic Cu NPs. This result indicated that the excellent catalytic efficiencies of Cu/Cu₂O/C catalyst might result from their porous structure facilitating diffusion of reactants and products in water, and the high dispersion of accessible catalytic Cu/Cu₂O NPs on porous carbon. To verify the contribution of Cu/Cu₂O nanoparticles in reaction, the Cu/Cu₂O/C catalyst was soaked in diluted HNO₃ to remove Cu content and gain porous carbon. When the porous carbon was employed as catalyst, only slight decrease of 4-NP in reaction solution was detected within 15 min (Fig. 5D), which should result from the sorption of 4-NP to porous carbon. The comparison study suggested that the Cu/Cu₂O NPs were responsible for the rapid reduction of 4-NP. But the carbon matrixes were also important for the high catalytic activity of catalyst because they could prevent aggregation of Cu/Cu₂O NPs in water solution and provide high surface-to-volume ratio and chemical stability for the Cu/Cu₂O NPs contact with the target.

Since the concentration of NaBH₄ is high enough to be considered as a constant during the reaction period, the rate constant for the reduction of 4-NP could be evaluated by the pseudo-first-order kinetics. The ratios of C_t (the concentration of 4-NP at time t) to C_0 (the initial concentration of 4-NP) were obtained from the relative intensity ratios of the respective absorbance (A_t/A_0) at 400 nm. The inset of Fig. 5C displays the linear relationship between $\ln(C_t/C_0)$ and the reaction time for the catalytic reduction of 4-NP. The corresponding rate constant obtained from the slope of the plot was calculated to be 0.0252 s^{-1} . The ratio of the rate constant over the total weight of the catalyst was calculated by equation $k = K/m$, which was $630\text{ s}^{-1}\text{ g}^{-1}$ for Cu/Cu₂O/C. We made a comparison of the catalytic performance of our catalyst with other catalysts. From Table 1 we can conclude that the Cu/Cu₂O/C catalyst in the present work showed comparable catalytic activity with other noble metal or copper based catalysts. The smaller size (about 40 nm), larger metal loading amount (33.38–37.56 wt% evaluated by TGA analysis), and porous carbon supporting of Cu/Cu₂O NPs should be responsible for the remarkable catalytic performance.

The Cu/Cu₂O/C was used repeatedly after being separated from reaction solution by centrifugation to check the reusability. The catalyst showed high activity and excellent recyclability with a conversion over 99% even after 5 successive cycles of reactions (Fig. 6A). However, the required time to thoroughly convert 4-NP to 4-AP increased from 2 min for the first cycle to 5 min for the fifth cycle, implying a slight decrease in catalytic efficiency (Fig. 6B). The slight decrease may be related to the negligible loss of Cu/Cu₂O NPs as well as the adsorption of 4-AP emerged from the reduction reaction onto the surface of the remaining Cu/Cu₂O NPs. The TEM image of reused Cu/Cu₂O/C showed that the structure and morphology are well maintained, suggesting the good stability of the materials (Fig. 6C).

4. Conclusions

In this study, we synthesized a hybrid catalyst consisting of non-noble Cu/Cu₂O NPs supported on porous carbon by using HKUST-1 as both sacrificial template and copper precursor and phenol formaldehyde resin as carbon precursor. The obtained composite possessed porous structure (micro-, meso- and macropores) with

large amount of catalytic Cu/Cu₂O nanoparticles highly dispersed on the surface of carbon support. The Cu/Cu₂O/C composite demonstrated excellent catalytic activities for the reduction of 4-NP, which was comparable with other noble metal or copper based catalysts. In conclusion, Cu/Cu₂O/C is expected to have the potential as cost-effective, highly efficient and eco-friendly reusable catalyst to replace noble metal for certain catalytic applications.

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