

Efficient catalytic reduction of 4-nitrophenol by Cu_{1.96}S/NSC hybrid material derived from metal-organic framework

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Abstract. Designing carbon-based non-precious metal hybrid materials to replace precious metal catalysts to solve environmental pollution problems is a hot topic of research at this stage. In this work, a dual ligand Cu-MOF was synthesized by the solvothermal method and using Cu-MOF as a sacrificial template further vulcanized to obtain Cu_{1.96}S/NSC hybrid material. The morphology and composition of Cu_{1.96}S/NSC hybrid material were investigated by scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM), x-ray diffraction (XRD), nitrogen adsorption-desorption, and x-ray photoelectron spectroscopy (XPS) in detail. Cu_{1.96}S/NSC has excellent catalytic activity in the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) showing the reaction rate constant $k=0.0242\text{ s}^{-1}$, which can reach nearly 100% conversion rate in 3 min. Finally, the mechanism of Cu_{1.96}S/NSC hybrid material's efficient catalytic reduction of 4-NP was deeply explored.

1 Introduction

Water pollution is an environmental problem that needs to be solved urgently in today's society, among them 4-NP is one of the most difficult pollutants in industrial and agricultural wastewater.^[1,2] At present, the most beneficial way is to reduce it to 4-AP through a catalyst in the presence of the reducing agent NaBH₄, because the reduced product 4-AP is an important intermediate for the manufacture of medicines, dyes and cosmetics.^[3] Noble metal catalysts have very good catalytic activity, but their high cost and rarity limit their practical use. Therefore, cost-effective non-noble metal catalysts have attracted much attention in recent years.^[4] In particular, Cu_{1.96}S and its composite materials have received extensive attention in the fields of photoelectric catalysis, batteries, and supercapacitors.^[5] However, their application in the catalytic reduction of 4-NP is seldom due to the narrow bandgap value of Cu_{1.96}S, electrons will quickly reduce it to Cu particles instead of reducing 4-NP. Therefore, hybridizing Cu_{1.96}S with carbon materials to transfer active electrons is a feasible way to improve its catalytic performance.

Metal organic frameworks (MOFs) are a new type of crystalline materials, which have important applications in the fields of adsorption and separation, photoelectric catalysis and biomedicine.^[6,7] They are also good sacrificial templates and precursors for the preparation of carbon-based nano hybrid materials.^[8,9] As we all know, heteroatom doping is an important means to improve the catalytic performance of carbon-based materials, some of

the advantages of the parent MOF will be retained in the derived nanohybrid materials.^[10] Therefore, we choose a Cu-MOF (CCDC-2053108) with N containing ligand and S containing ligand used as a precursor to prepare hybrid material. In this study, the Cu-MOF precursor was prepared by solvothermal method, and then vulcanized to obtain Cu_{1.96}S/NSC hybrid material (Fig.1). Cu_{1.96}S/NSC has good catalytic activity for the reduction reaction of 4-NP and a series of characterizations were carried out to explore the catalytic mechanism.

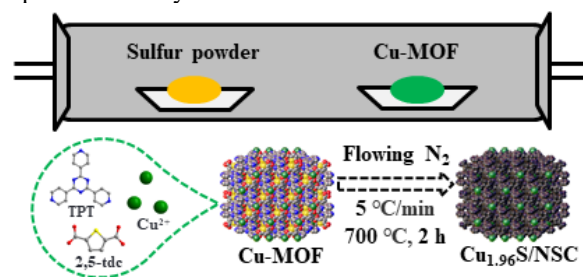


Fig. 1 Flow chart of Cu_{1.96}S/NSC hybrid material preparation.

2 Results and Discussion

2.1 Micro morphology

SEM and TEM were used to observe the microscopic morphology of Cu_{1.96}S/NSC. It can be seen from the SEM image that Cu_{1.96}S/NSC has an octahedral morphology (Fig. 2a), and many nanopores can be clearly seen on the surface of the material (Fig. 2b).

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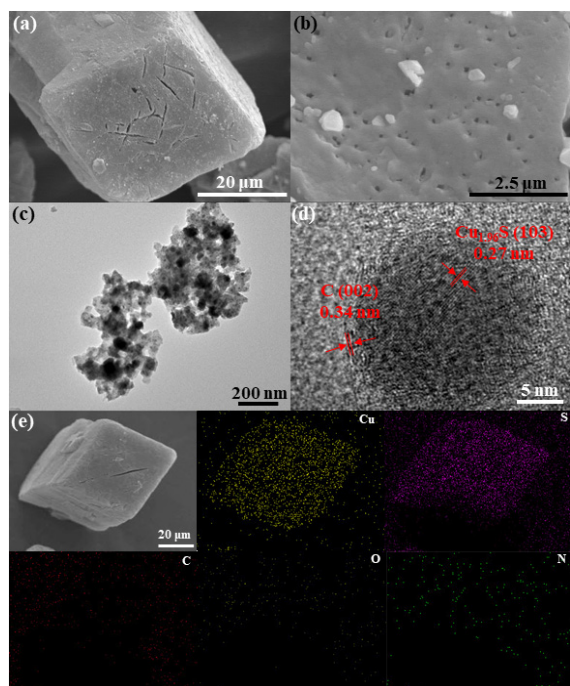


Fig. 2 SEM (a,b) images and TEM (c) image of $\text{Cu}_{1.96}\text{S}/\text{NSC}$; (d) High-resolution TEM image of $\text{Cu}_{1.96}\text{S}/\text{NSC}$; (e) Elemental mapping of $\text{Cu}_{1.96}\text{S}/\text{NSC}$.

The presence of these pores can increase the specific surface area of the hybrid material, which is very beneficial for catalytic reactions. After vulcanization in the N_2 atmosphere, copper ions form $\text{Cu}_{1.96}\text{S}$ nanoparticles, and the organic phase is transformed into a carbon skeleton doped with nitrogen and sulfur. The TEM image shows that the $\text{Cu}_{1.96}\text{S}$ particles are well dispersed and there is no obvious agglomeration (Fig. 2c). The high-resolution TEM can clearly observe the lattice fringes of $\text{Cu}_{1.96}\text{S}$ particles and graphite carbon. The lattice distances are 0.27 nm and 0.34 nm, respectively, corresponding to the Cu lattice plane (111) and the graphite carbon lattice plane (002) (Fig. 2d). The mapping of SEM shows that Cu, S, C, O and N elements are uniformly distributed in $\text{Cu}_{1.96}\text{S}/\text{NSC}$ (Fig. 2e). Cu and S elements are more densely mapped due to their high content.

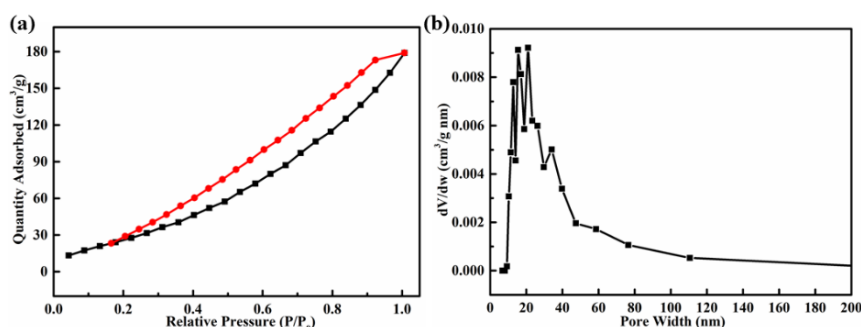


Fig. 4 N_2 adsorption-desorption isotherm (a) and BJH mesoporous size distribution (b) of $\text{Cu}_{1.96}\text{S}/\text{NSC}$.

2.4 X-ray photoelectron spectroscopy

Study the surface element composition and chemical state of each element of $\text{Cu}_{1.96}\text{S}/\text{NSC}$ hybrid material by X-ray photoelectron spectroscopy. As shown in the Fig. 5a, the surface of $\text{Cu}_{1.96}\text{S}/\text{NSC}$ contains five main elements: Cu, S, N, C and O. In the high-resolution

2.2 X-ray diffraction

The composition and crystallinity of the hybrid material was analyzed by XRD. As shown in the Fig. 3, the hybrid material is composed of $\text{Cu}_{1.96}\text{S}$ (JCPDS No.29-0578) and graphite carbon. The characteristic peaks of $\text{Cu}_{1.96}\text{S}$ appear at 27.25° (102), 31.62° (110), 32.66° (103), 39.10° (104), 45.45° (114), 46.11° (201), 48.29° (202), 53.57° (212) 53.82° (106) and 66.71° (215). A weak and broad peak is shown near 25° , which is attributed to the C (002) diffraction peak.

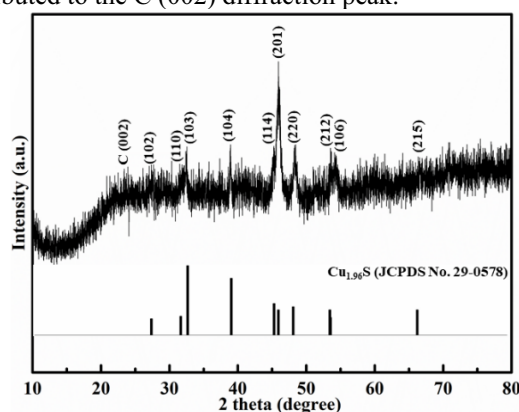


Fig. 3 XRD spectra of $\text{Cu}_{1.96}\text{S}/\text{NSC}$.

2.3 Specific surface area and porosity

The porosity and specific surface area of $\text{Cu}_{1.96}\text{S}/\text{NSC}$ were studied by N_2 adsorption-desorption isotherm. $\text{Cu}_{1.96}\text{S}/\text{NSC}$ exhibits a type IV adsorption isotherm with an H3-type hysteresis loop. From the BJH mesopore size distribution, it can be seen that the pore size of $\text{Cu}_{1.96}\text{S}/\text{NSC}$ is concentrated around 21.1 nm (Fig. 4b). Besides, the specific surface area, pore volume and pore diameter of $\text{Cu}_{1.96}\text{S}/\text{NSC}$ are $192.782 \text{ m}^2/\text{g}$, $0.32 \text{ cm}^3/\text{g}$ and 3.28 nm, respectively. The higher specific surface area has an important role in the catalytic reaction.

spectrum of Cu 2p (Fig. 5b), the peaks at 932.1 and 952.3 eV attributed to the 2p 3/2 and 2p 1/2 core levels of Cu^+ , and the peaks at 933.8 and 954.1 eV attributed to the 2p 3/2 and 2p 1/2 core levels of Cu^{2+} . In the high-resolution spectrum of S 2p (Fig. 5c), the peaks at 161.7 and 162.9 eV belong to the 2p 3/2 and 2p 1/2 core levels of Cu-S, the peaks at 163.7 and 164.8 eV belong to C-S-C covalent bonds, and the peak at 168.1 eV belongs to the

sulfur species partially oxidized on the surface of the hybrid material. The peaks at 398.4, 399.4, and 400.9 eV in the high-resolution spectrum of N 1s correspond to pyridine-N, pyrrole-N and graphite-N (Fig. 5d). The peaks at 284.5, 285.3, 286.4 and 288.8 eV in the C 1s high-resolution spectrum correspond to the bonds C-C, C-S, C-N and C-O, respectively (Fig. 5e). In the high-

resolution spectrum of O 1s, the peaks at 533.6 and 532.2 eV correspond to C=O and C-OH bonds (Fig. 5f). The XPS results show that N,S atoms are successfully doped into the carbon framework of the hybrid material, which is also an important factor to improve the catalytic activity.

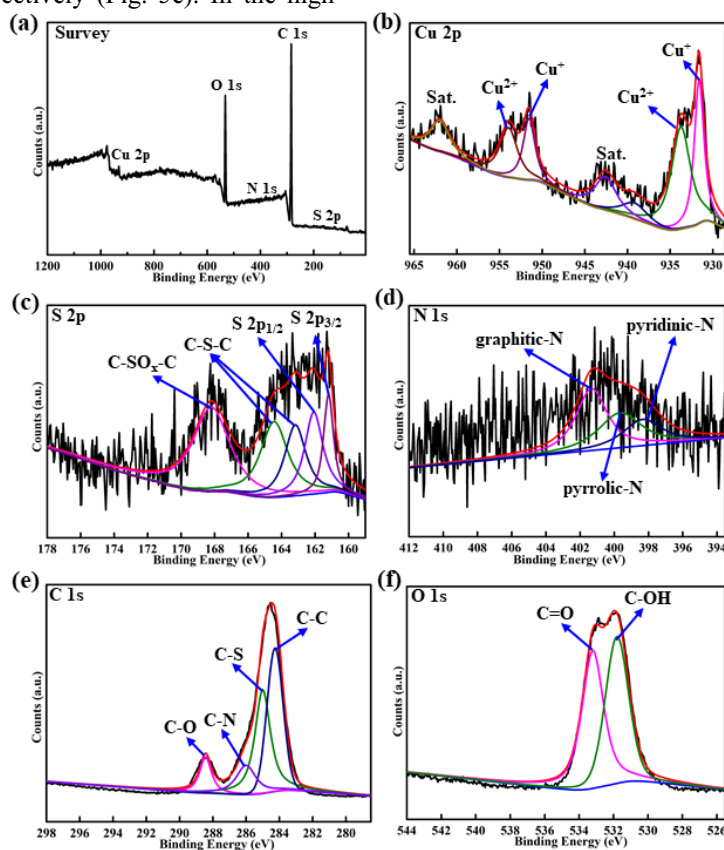


Fig. 5 XPS analysis of $\text{Cu}_{1.96}\text{S}/\text{NSC}$: (a) full spectra, (b) Cu 2p spectra, (c) S 2p spectra, (d) N 1s spectra, (e) C 1s spectra and (f) O 1s spectra.

2.5 Reduction of 4-NP

In this work, at the presence of NaBH_4 , the catalytic performance of $\text{Cu}_{1.96}\text{S}/\text{NSC}$ hybrid materials for the reduction of 4-NP to 4-AP was explored to evaluate its potential application in the field of environmental remediation. As shown in Fig. 6a, the characteristic absorption peak of the pure 4-NP (2.7 mL 0.185 mM) solution appear at 317 nm. After the addition of NaBH_4 (0.2 mL 0.2 M), the peak shifted significantly to 400 nm, due to the formation of 4-nitrophenolate ion. After the catalytic reduction starts, the generated 4-AP will have a new characteristic absorption peak at 300 nm (Fig. 6b). As shown in the Fig. 6c, when only 4AP and NaBH_4 were present without adding catalyst, no reduction

reaction was observed for 30 minutes. When 0.1 mL $\text{Cu}_{1.96}\text{S}/\text{NSC}$ (1 mg/mL dispersed in water) catalyst was added, the reduction reaction started quickly (Fig. 6d) and completed 100 % conversion in 3 minutes (Fig. 6e). Since the concentration of NaBH_4 in the experiment is much higher than that of 4-NP, pseudo first-order kinetics can be used to evaluate the rate constant of catalytic reduction. The kinetic equation can be expressed as equation $\ln(A_t/A_0) = \ln(C_t/C_0) = -kt$. Among them, the concentration ratio C_t/C_0 can be obtained from the corresponding absorbance ratio A_t/A_0 at 400nm. The first-order kinetic constant of $\text{Cu}_{1.96}\text{S}/\text{NSC}$ hybrid material was 0.0242 s^{-1} (Fig. 6f), which exceeds that of many precious metal catalysts.

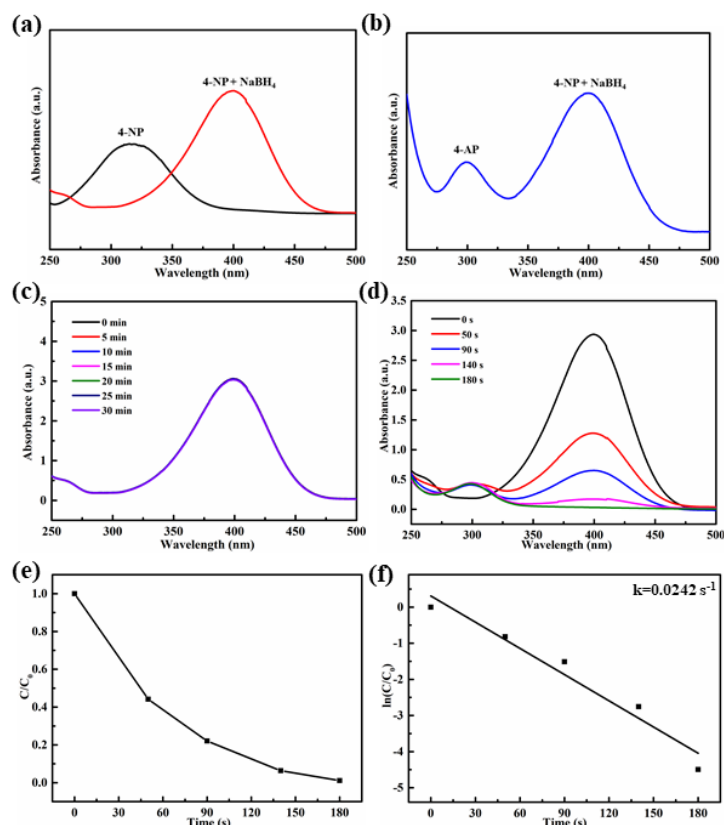
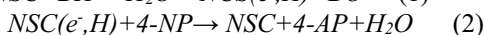
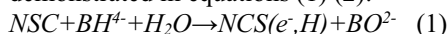


Fig. 6 (a) The characteristic peak of 4-NP and 4-NP+NaBH₄; (b) The characteristic peak of 4-AP; UV-vis spectrum before (c) and after (d) adding Cu_{1.96}S/NSC (e) The relationship between time and C/C₀; (f) The relationship between ln(C/C₀) versus time.

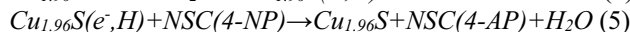
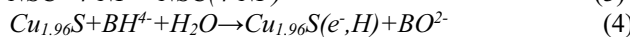
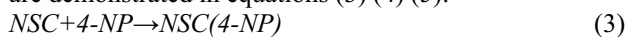
Cu_{1.96}S/NSC hybrid material has broad application prospects in the field of environmental restoration.

2.6 Catalytic mechanism

There are two possible catalytic processes for Cu_{1.96}S/NSC hybrid materials. When the catalytic reaction progresses, one catalytic processes is that NSC adsorbs BH⁴⁻ ions in the solution, electrons and active hydrogen atoms migrate to the surface of the NSC, and then these electrons and active hydrogen atoms attack 4-NP to generate 4-AP. The reduction process are demonstrated in equations (1) (2):



The pores of NSC can quickly adsorb 4-NP, another catalytic processes is that the electrons produced by the adsorption of BH⁴⁻ by Cu_{1.96}S are quickly transferred from Cu_{1.96}S to 4-NP which adsorbed by NSC, completing the reduction reaction. The reduction process are demonstrated in equations (3) (4) (5):



3 Conclusion

In short, the Cu_{1.96}S/NSC hybrid material was successfully vulcanized using the synthesized Cu-MOF as the sacrificial template. Cu_{1.96}S particles are uniformly dispersed in the N, S-doped porous carbon framework. In the presence of NaBH₄, only 0.1 mg of catalyst is needed to catalyze the reduction of 4-NP to 4-AP in 3 minutes. Then two possible mechanism processes were analyzed to explain the reasons for its efficient catalysis.

Acknowledgments

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