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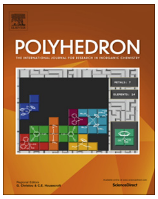

Construction of mixed-valence Cu(I)/Cu(II) 3-D framework and its photocatalytic activities

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ABSTRACT

A Cu(I)/Cu(II) 3D framework, $\{[(CuII)_3(CuI)_3(pbt)_3Cl_2]\cdot ClO_4\cdot H_2O\}_n$ (**HPU-3**) (H_2pbt = 5′-(pyridin-2-yl)–2H,4′H-3,3′-bi(1,2,4-triazole)), has been synthesized by using solvothermal method. UV–Vis absorption spectrum indicates that **HPU-3** has strong optical capability nearly in the whole range of visible light spectrum. **HPU-3** photocatalyst exhibits good photocatalytic activity toward the degradation of Methylene Blue and Methyl Orange dyes.

1. Introduction

The emission of dyes into the environment has cause serious water pollution because of their relatively high photo and chemical stability [1–3]. Many methods have been tried to ecological elimination of organic pollutants in water such as adsorption and separation, chemical treatment, and photocatalytic degradation [4–8]. By comparison, photocatalytic degradation is a more economical, convenient and recyclable method to degrade organic dyes without further contamination [9–12].

Recently Metal–organic frameworks (MOFs), a fascinating kind of porous crystalline material, have drawn increasing attention for their permanent porosity, tunable pore size, and rich surface chemistry [13–19]. In particular, mixed-valence Cu(I)/Cu(II) complex show prominent catalyst activity because they can afford high bimetallic catalyst activity through the incorporation of two different metal-based catalytic moieties into a single framework [20–22]. Considering the Cu(I)/Cu(II) motif could supply the charge transfer excited state to oxygenate water molecules to generate the ·OH radicals, mixed-valence Cu(I)/Cu(II) complex should have potential photocatalytic activity to degrade organic dyes.

In this work, a mixed-valence Cu(I)/Cu(II) complex namely, $\{[(CuII)_3(CuI)_3(pbt)_3Cl_2]\cdot ClO_4\cdot H_2O\}_n$ (**HPU-3**) (H_2pbt = 5′-(pyridin-2-yl)-2H,4′H-3,3′-bi(1,2,4-triazole)), was synthesized. UV–Vis absorption spectrum indicates that **HPU-3** has strong optical capability nearly in the whole range of visible light spectrum and displays enhanced degradation of dyes.

2. Experimental

2.1. Materials and physical measurements

All chemicals were commercially available and used as purchased. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the region of 400–4000 cm^{-1}. Analyses for C, H and N carried out on a Carlo-Erba analyzer. Powder X-ray diffraction (PXRD) patterns were recorded using Cu Kα radiation on a PANalytical X'Pert PRO diffractometer. Thermogravimetric analysis (TGA) was recorded on a Netzsch STA 449C thermal analyzer between 30 and 1000 °C and a heating rate of 10 °C min^{-1} in atmosphere. The UV–Vis spectra were recorded on a Purkinje General TU-1800 spectropho-tometer.

2.2. Synthesis of $\{[(CuII)_3(CuI)_3(pbt)_3Cl_2]\cdot ClO_4\cdot H_2O\}_n$(HPU-3)

$Cu(ClO_4)_2\cdot 6H_2O$ (0.1 mmol), H_2pbt (0.05 mmol) were dispersed in a mixture of C_2H_5OH and H_2O in the volume ratio of 5:5. And two drops of 2 M HCl were added into the solution and then heated at 160 °C for 96 h in a 25 mL Teflon-lined stainless steel vessel. After the reaction system was cooled to room temperature, black block-shaped crystals of **HPU-3** were collected. (yield, 72% based on Cu). *Anal.* Calc. for $C_{27}H_{15}Cl_3Cu_6N_{21}O_5$ (%): C: 27.10, H: 1.26, N: 24.49; Found: C: 27.11, H: 1.30, N: 24.52%. IR (KBr, cm^{-1}):

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2376 w, 1632 s, 1572 m, 1443 m, 1391 w, 1231 m, 1096 s, 994 w, 905 m, 743 w, 718 s.

2.3. Crystal data collection and refinement

The X-ray diffraction measurements for **HPU-3** were performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm) by using φ-ω scan mode. Multi-scan absorption correction was applied to the intensity data using the SADABS program [23]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-2014 program [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined isotropically. From the difference Fourier maps of **HPU-3**, a number of diffuse scattered peaks with electron density were observed, which can be attributed to the disordered solvent molecules. Attempts to model these peaks were unsuccessful because the residual electron density peaks obtained were diffused. Therefore, PLATON/SQUEEZE was used to refine the structure further [25]. The number of water molecules in HPU-3 was arrived at by combining the results of the elemental analysis, IR, and TGA studies. Crystallographic data and refinement parameters for **HPU-3** are listed in Table 1. Selected bond lengths and angles are listed in Tables S1. Crystallographic data for **HPU-3** has been deposited at the Cambridge Crystallographic Date Center with the deposition number 1506252.

2.4. Photocatalytic measurement

For exploring the photocatalytic behaviours of **HPU-3**, the photocatalytic decomposition of Methylene Blue (MB) and Methyl Orange (MO) were selected as the models of dye contaminants. In practice, an aqueous solution of MB or MO (0.01 mg/mL, 100 mL) was mixed with 7 mg powder of **HPU-3**, and four drops of 30% H_2O_2. Subsequently, the mixture was stirred for half an hour in a dark environment to ensure a balance of adsorption and desorption and then stirred constantly under the radiation of a 300 W high pressure Hg lamp. At regular time intervals, 5 mL of samples were taken out of the reactor and then subjected to spectroscopic measurement on the UV–Vis spectrometer to monitor the photocatalytic degradation process.

Table 1
Crystal data and structure refinement for complex **HPU-3**.

	HPU-3
Formula	$C_{27}H_{15}Cl_3Cu_6N_{21}O_4$
Fw	1185.19
T (K)	296(2)
λ (Å)	0.71073
Crystal system	cubic
Space group	*Pa3*
$a/b/c$ (Å)	19.4849(1)
$\alpha/\beta/\gamma$ (°)	90
V (Å^3)	7397.7(1)
Z	8
D_c (mg·m^{-3})	2.128
F (000)	4648
Reflections collected	8755
Unique reflections	2582
GOF on F^2	0.922
R_1[a] ($I > 2\sigma I$)	0.0383
wR_2[b] ($I > 2\sigma I$)	0.1073
R_1 (all data)	0.0460
wR_2	0.1137

[a] $R_1 = ||F_o| - |F_c||/|Fo|$.
[b] $wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. Crystal structure descriptions of HPU-3

Structure elucidation reveals that the **HPU-3** crystallizes in the cubic system with space group *Pa3*. The asymmetric unit of **HPU-3** contains two Cu ions (one Cu(I) and one Cu(II)), one pbt^{2-} ligand, one third ClO_4^-, two one-third-occupied Cl^- anions and several chemically featureless electron density peaks located in cages. This disordered distribution of electron density was modeled as variably occupied oxygen atoms of water molecules. As shown in Fig. 1a, each pbt^{2-} coordinates with three Cu1 and two Cu2 using its two bidentate chelate sites and three monodentate bridges. Cu1 ligates with five nitrogen atoms from three pbt^{2-} showing quadrangular pyramid configuration, whereas Cu2 adopts tetrahedron coordination environment completed by two nitrogen atoms from two ligands and two Cl^- anions. The oxidation states of Cu1 and Cu2 in **HPU-3** are certified by the XPS, the $\chi_m T$ values and the charge balance of the crystal structure. From the XPS spectra of HPU-3 in Fig. S1a, the peaks of 934.1 and 944.0 eV prove the existence of Cu(II) state and the peak of 930.80 eV attributes to Cu(I) state. Furthermore, the peaks of 569.8 and 574.8 eV also testify the existence of Cu(I) oxidation state (Fig. S1b). The $\chi_M T$ value of **HPU-3** at 300 K is 1.01 cm^3 K mol^{-1} which is corresponding to three magnetically isolated Cu(II) ions (theoretical value for g = 2, S = 1/2, $\chi_M T = 3 \times (N\beta^2 g^2/3k)$ S(S + 1) = 1.125 cm^3 K mol^{-1}) (Fig. S2). Moreover, the bond valence sum (BVS) values of Cu(1) and Cu2 are 2.121 and 0.973, respectively, which are consist with Cu^{2+} and Cu$^+$ oxidation state [26]. Therefore, the Cu1 and Cu2 in **HPU-3** are in the Cu(II) and Cu(I) oxidation state, respectively.

The unique characteristic of the structure of **HPU-3** is that three pbt^{2-} ligands, six Cu1 and three Cu2 ions formed nearly coplanar equilateral triangle shaped nine-nuclear secondary building unit (Fig. 1b), which connects to other six units by the six Cu1 ions thus resulting in the formation of the 3D network (Fig. 1c). More interestingly, eight triangle secondary units connect with each other to form two kinds of cubic cages. One kind of cage encapsulates two ClO_4^- anions (Fig. 1d). While the other cubic cage captures one water molecule (Fig. 1e).

3.2. PXRD and thermal stability

The PXRD patterns were recorded for **HPU-3** to confirm the phase purity (Fig. 2a). They were comparable to the corresponding simulated ones calculated from the single-crystal diffraction data, indicating a pure phase of each bulky sample.

As shown in Fig. 2b, the thermal analyses shows a slight weight loss of 2% before 325 °C, which may be contributed to the H_2O in the cages. From 325 °C on, oxidative degradation of organic liangds occurs. Complete degradation results in CuO as a final product.

3.3. Photocatalytic degradation of dyes

The optical diffuse-reflection spectra of crystalline solids **HPU-3** was measured at room temperature (Fig. S3). The energy band gaps obtained by extrapolation of the linear portion of the absorption edges (Eg) were estimated to be 1.05 eV (Fig. S4), implying their high photocatalytic efficiencies [27]. In order to better understand the intrinsic electronic properties of **HPU-3**, the cyclic voltammograms and Mott-Schottky measurements were conducted. As shown in Fig. 3, **HPU-3** shows the typical behaviour of *n*-type semiconductors where the positive slope of C^2 values versus potential is observed. Therefore, the flat-band potential of **HPU-3** determined from Mott-Schottky plots is −0.75 V versus the Hg/Hg_2Cl_2 electrode. Then, the redox potential of the conduction band (CB) of