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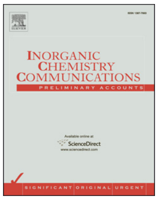

Short communication

Assembly of a high stable POM-based Cu(I) coordination polymer with visible-light-driven photocatalytic properties

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ABSTRACT

A new coordination polymer (CP), $[(PW_{12}O_{40})_2Cu^I_6(trz)_6]\cdot H_2O$ (**1**), has been prepared by hydrothermal method. Six Cu(I) ions are bridged by six *trz* molecules and six surface oxygen atoms of PW_{12} to generate a wheel-type Cu^I_6 cluster, and each Cu^I_6 cluster was capped with two PW_{12} anions to form a dumbbell-like second building block (SBB). **1** can remain intact in solution with pH range from 1 to 10, boiling water and boiling organic solvents, which shows the high heat stability, acid and alkali resistance. It also shows efficient visible-light-driven photocatalytic activities in the degradation of organic dyes.

Polyoxometalates (POMs), a class of nanosized transition-metal oxide clusters with both red-ox activities and acid-base properties, have attracted considerable attentions due to their wildly applications [1]. The combination of POM clusters with metal-organic moieties to prepare stable functional materials, which combine the advantages of both POMs and CPs, is promising in POM chemistry. In this field, POMs not only can provide functional units, but also can perform as anionic templates and/or stabilizing agents. Up to now, some of POM-supported CPs and their derivatives, such as the serials of NENU-x [2a] and Z-POMOFs [2b], have been reported with laudable properties and high stabilities [2]. It is predicted that further exploration of novel POM-based CPs will expand and deepen the study of the applications of CPs. Our group has also used N-donor ligands to assembly series of interesting POM-based CPs for catalytic purposes [3]. These materials can be easily prepared by adopting simple hydrothermal techniques, which is easy to be handled and environmental friendly.

Copper(I) materials are attracting more and more interests because of their wildly applications in the field of catalyst, chemical sensors, luminescence, et al. [4] Specifically, some modified cuprous oxide materials show high catalytic efficiency for water splitting, and copper diimine compounds can substitute the ruthenium polypyridyl compounds as light sensitizer in solar energy conversion processes [5]. Although the excellent properties of Cu(I) materials attract the interest of chemists, the weak chemical stability of these reagents severely restricted their applications [6]. Some strategies have been carried out to prevent the deterioration of the Cu(I) compounds but these always bring out adverse side effects [7]. Thus, it is a challenge but urgent task to construct functional Cu(I) compounds with high chemical stability.

In this work, we are prompted to construct stable functional CPs by utilizing N-donor ligands 1,2,4-1H-Triazole (1H-*trz*) and Keggin-type $H_3PW_{12}O_{40}\cdot xH_2O$ (PW_{12}), where the Keggin-type POMs are considered as the most stable structures in POM chemistry [8]. Herein we report a POM-based CPs, namely $[(PW_{12}O_{40})_2Cu^I_6(trz)_6]\cdot H_2O$ (**1**). It is interesting that **1**, which is constructed by wheel-type hexacopper (Cu^I_6) clusters and Keggin-type PW_{12}, exhibits high chemical stability and efficient photocatalytic activities in the degradation of organic dyes.

In-situ reduction of Cu(II) with *trz* in the presence of PW_{12} under hydrothermal condition generates brownish red block crystals of **1**. Single crystal X-ray diffraction study shows that the crystal of **1** crystallizes in the hexagonal space group *R*-3 (Table S1). The asymmetric unit of **1** contains one independent Cu(I) ion, one *trz* ligands, one-third PW_{12} anion and one-sixth solvent water molecule. All of the copper atoms in **1** are in +1 oxidation state, which was confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. S16), coordination environment and bond valence sums (BVS) calculations [9] (Table S2). So compound **1** can be formulated as $[(PW_{12}O_{40})_2Cu^I_6(trz)_6]\cdot H_2O$. As shown in Fig. S1, Cu(I) ion is five-coordinated by two nitrogen atoms from two *trz* molecules and three oxygen atoms from three PW_{12} anions. The coordination geometry around the Cu(I) ion is a distorted trigonal biyramid. The Cu1-N1 and Cu1-N2 bond lengths are 1.893(9) and 1.890(9) Å, respectively.

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The Cu-O distances range from 2.528 to 2.720 Å. Six Cu(I) ions are bridged by six *trz* molecules and six surface oxygen atoms of PW_{12} to generate a wheel-type Cu^{I}_{6} cluster (Fig. 1a). Each Cu^{I}_{6} cluster was capped with two PW_{12} anions to form a dumbbell-like second building block (SBB) (Fig. 1b and Fig. S2). Thereafter, the SBBs were connected by weak Cu-O interactions (Cu1-O12 2.865(8) Å) to generate a 3D framework (Fig. 1c). From topological view, the SBB can be considered as a six-connected node. Then, the 3D framework of **1** can be reduced into the **pcu** network (Fig. 1d) [10].

The powder X-ray diffraction (PXRD) patterns of the as-synthesized **1** matched well with the simulated patterns indicating its crystalline phase purity (Fig. S4). The TGA analysis of **1** reveals that the first weight loss occurs at about 320 °C, and then the organic groups start to decompose gradually in the range of 320 to about 500 °C (Fig. S5). Variable temperature powder X-ray diffraction (VTPXRD) experiments have also been carried out under air to examine the thermal stability of **1**. As shown in Fig. S6, the framework of **1** retains up to 300 °C. Afterward, the framework undergoes irreversible phase transformation. The result of VTPXRD is well consistent with the TGA data.

Furthermore, it is noteworthy that the framework of **1** exhibits very high chemical stability. Typical experiments were carried out as follows: 100 mg fresh prepared crystals of **1** were soaked in a 20 ml solution for 48 h. Then the crystals were filtered and dried under ambient condition. PXRD analyses show that **1** remains intact in pH = 1 hydrochloric acid, pH = 10 NaOH solution, boiling water and even in 80 °C organic solvents, such as methanol, ethanol, dichloromethane, chloroform, carbon tetrachloride, tetrahydrofuran, acetone, cyclohexane and dimethylformamide (Fig. 2 and Fig. 3). In addition, the crystals of **1** can also stable under air atmosphere over six months, and no efflorescence was observed. From Fig. S7, we can see that the surface of the crystals after treated under different conditions is also as smooth as the as-synthesized ones. These further confirm the high chemical stability of compound **1**.

The band-gap size (Eg) of compound **1** was investigated by a UV-Vis diffuse-reflectance measurement at room temperature. The Tauc plots exhibit an Eg value of 1.91 eV for compound **1**, which is consistent with the brownish red color of the crystals (Fig. S8). The electronic structure of **1** was investigated by means of density functional calculations at BP86/TZP level in gas phase with ADF program [11]. As seen from Fig. 4, the lowest unoccupied molecular orbital (LUMO, −4.83 eV) of **1** was found to mainly contribute by the empty W 5d orbitals delocalized within the PW_{12} anions and little contributions from the O 2p orbitals via $d(\pi) - p(\pi)$ antibonding interactions (Fig. 2a). However, the highest occupied molecular orbital (HOMO, −6.53 eV) of **1** is found to consist of the Cu 3d orbitals with little mixed compositions on the N 2p orbitals. Thus, when the crystals of **1** were excited by visible light, the electronic excitation between the valence and conduction band edges is considered as charge transfer primarily from a filled $3d^{10}$ Cu(I) to empty $5d^{0}$ W(VI) orbital [12]. This result is consistent with that in copper(I)–octamolybdate compounds which also owns filled d [10] Cu(I) in the structure 12a. It should be not that the energy gap between the HOMO and LUMO is only a little underestimated (1.70 eV) respect to the experiments ($E_g = 1.95$ eV) for compound **1**. In fact, the bandgap in compound **1** ($E_g = 1.95$ eV) is significantly decreased because of the Cu(I) in the structure compared to that in compound **2** (2.78 eV), which will extend their light adsorption range in solar energy applications.

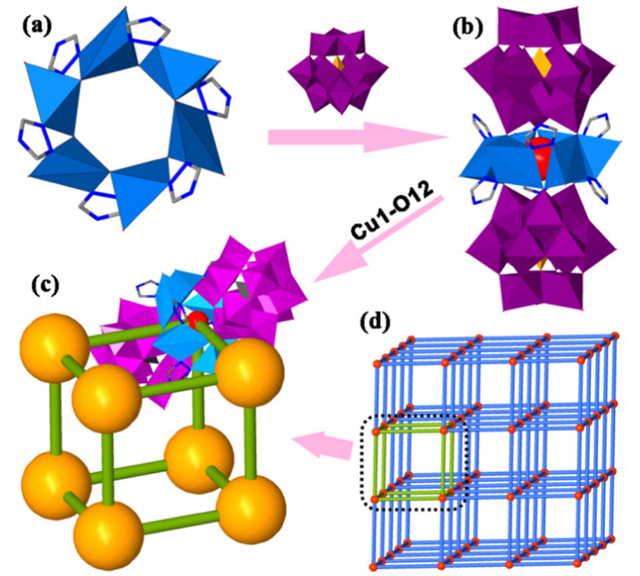

Fig. 1. (a) Polyhedron representation of Cu_6 cluster. (b) The dumbbell-like second building block. The position of guest water molecule in the middle of the cage was highlighted in big red ball. (c) Schematic view of single cubic unit constructed from SBB. Some of SBBs are replaced by yellow balls for clarity. (d) View of the **pcu** net of **1**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

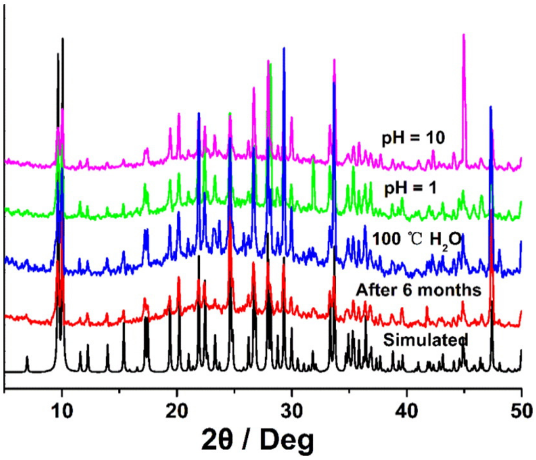

Fig. 2. PXRD patterns for simulated **1** and crystals of **1** after treating under different conditions.

The band gap size of **1** reveals its nature of semiconductor. The photocatalytic properties of **1** were investigated with photodegradation reactions of methylene blue (MB) and rhodamine B (RhB) under visible light irradiation. In typical processes, 300 ml dye solutions (12 mg L^{-1}) were used. Then, the mixture were magnetically stirred in the dark for 40 min and then exposed to visible light irradiation (A 300 W Xe lamp with 420 nm filter) under stirring continuously, and 2.5 ml of solution was taken out every 10 min for analysis by UV-Vis

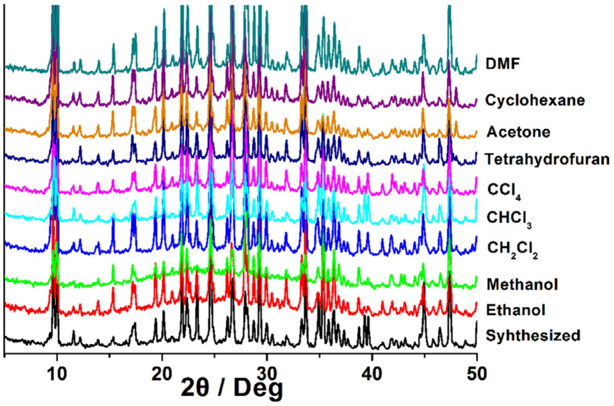

Fig. 3. PXRD patterns for simulated **1** and crystals of **1** after soaking in different organic solvents at 80 °C for 48 h. From top to bottom: dimethylformamide, cyclohexane, acetone, tetrahydrofuran, carbon tetrachloride, chloroform, methanol, dichloromethane, ethanol and simulated pattern.