Assembly of three stable POM-based pillar-layer CuI coordination polymers with visible light driven photocatalytic properties

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Three new POM-based pillar-layer Cu^I coordination polymers (CPs), $Cu^I_{12}Cl(trz)_8[PW_{12}O_{40}]$ (**1**), $Cu^I_{12}Cl(trz)_8[PMo_{12}O_{40}]$ (**2**) and $Cu^I_{12}Cl(trz)_8[HSiW_{12}O_{40}]$ (**3**) (trz = 1,2,4-triazole), have been hydrothermally synthesized. Characterized by single-crystal X-ray diffraction analyses, compounds **1-3** are isostructural and copper ions coordinate with trz to form double layers with the help of Cl ions, which are supported by POMs to a 3D framework with continuous channels. The two same frameworks interwine to a 3D two-fold interpenetrating network. The compounds display high heat stability, and excellent acid and alkali resistance. The Ultraviolet-vis diffuse-reflectance spectra suggested that compounds **1-3** exhibit their nature of semi-conductivity. Thus, the reactions of photocatalytic degradation of organic dye were performed and its relevant photocatalytic mechanism was also delicately investigated. All of the title compounds show efficient visible-light-driven photocatalytic activities in the degradation of organic dyes. Also, the hydroxyl radicals (·OH) are proved to play a crucial role in visible photocatalytic degradation reaction.

Introduction

The ever-increasingly more attentions have been paid to the development and utilization of the renewable energy, in which the solar energy is being considered as the most promising clean and renewable energy to solve energy crisis we are faced with. Nowadays, the applications of POM-based CPs as visible-light driven photocatalysts are active in this field.[1-4] As an earth-abundant element, copper has been studied from the beginning of chemistry and plays a significant role in catalysis. Especially, copper salt and copper-based coordination polymers as catalysts are used to catalyze organic reactions and degrade organic pollutants.[5-7] Polyoxometalates (POMs), a large family of early transition metal oxide clusters, play a great role in various areas ranging from catalysis [8], medicine [9], electrochemistry [10], photochromism [11] to magnetism [12]. In those fields, the catalytic chemistry of polyoxometalates (POMs) grows very fast and the activity of POMs in promoting environmentally friendly photocatalytic process has attracted considerable attention. Thus, the rational design of POMs-based CPs with fascinating structures and properties has become an interesting target. Furthermore, entangled coordination networks and close-grained 3D structures always show high heat stability, excellent acid and alkali resistance.[13] These synergistic advantages contribute to the extraordinary performance of catalysis of POMs-based CPs under more severe conditions.

Based on the above considerations, we conceived an idea that POMs combined with copper to construct functional materials. In the past, our group conducted some experiments in this aspect, synthesizing a series of relevant coordination polymers, in which cooper ions connected POMs at the molecular level to exhibit some excellent performances.[14] In this work, we are prompted to construct steadily cuprous CPs by utilizing N-donor ligands 1,2,4-1H-Triazole (1H-trz) and POMs. Here, we reported three new stable 3D pillar-layer Cu^I CPs, $Cu^I_{12}Cl(trz)_8[PW_{12}O_{40}]$ (**1**), $Cu^I_{12}Cl(trz)_8[PMo_{12}O_{40}]$ (**2**) and $Cu^I_{12}Cl(trz)_8[HSiW_{12}O_{40}]$ **(3)**, in which tetra-nuclear $[Cu_4(trz)_4]$ and octa-nuclear $[Cu_8(trz)_8]$ moieties show a distinguishing feature. Through soaking crystals of compounds **1-3** into different solutions, they could retain their structures even in pH = 1 hydrochloric acid, boiling water and dilute NaOH solution, which was not very common in coordination polymers. In addition, divalent copper ions were reduced to univalent copper ions under the high temperature. In our previous study, Cu^I-based POMs CPs had been proven to be capable of extending their adsorption edge to visible light range owing to narrowed bandgap.[15] We speculated that compounds **1-3** also showed photocatalytic activity under visible light irradiation. Then, bandgap sizes of compounds **1-3** were investigated by UV-Vis diffuse-reflectance spectrometer at room temperature. Afterwards, we performed the visible photodecomposition of methylene blue (MB) under visible irradiation. The conjecture based on the theoretical level and previous work was supported with the photocatalytic results. Ultimately, the correlations

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†Electronic Supplementary Information (ESI) available: X-ray crystallographic data in CIF format, structure diagrams, UV-Vis absorption spectrum, PXRD and XPS patterns, TGA curves, tables of selected bond lengths and angles. CCDC reference numbers: 1407648 (**1**) and 1409593 (**2**). See DOI: 10.1039/x0xx00000x

between structure and properties have been attempted to revealed.

Preparation section

Materials and Characterization

All reagents were commercially available and were used without further purification. $Na_9[\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$, $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 17H_2O$ and $H_3[PMo_{12}O_{40}]\cdot nH_2O$ were prepared according to the reported procedures.[16] The powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D_{max} 2000 X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation (λ = 0.15418 nm). The FT-IR spectrum was measured in KBr pellets in the range 4000-400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analysis (EA) for C, H and N was performed on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Thermal Analyzer under nitrogen atmosphere at a heating rate of 5 °C min^{-1}. The UV absorption was measured with a Cary 500 UV-Vis-NIR Spectrophotometer. XPS measurements were performed with a VG Scientific ESCALAB 250 instrument.

Synthesis of catalysts

A mixture of $Na_9[\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$ (0.150 g, 0.026 mmol) or $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 17H_2O$ ($H_3[PMo_{12}O_{40}]\cdot nH_2O$) , $CuCl_2\cdot 2H_2O$ (0.034 g, 0.3 mmol), trz (0.021 g, 0.1 mmol) was dissolved in 10 mL of distilled water at room temperature. The mixture was stirred for 30 min and then transferred into a 23 mL Teflon-lined stainless steel autoclave reactor and heated at 190-195 °C for 96 hours. After the solution slowly cooled to room temperature in 24h, dark red block crystals were obtained in 65% yield, washed with distilled water and dried at room temperature for the further characterization. The IR spectra of compounds **1-3** were shown in the Supporting Information (Fig. S7).

Experiments and Results

Structures of compounds

At high temperature 190-195°C, the reactions of $CuCl_2\cdot 2H_2O$, triazole and POMs under hydrothermal conditions generated dark-red block crystals of compound **1, 2** or **3**. Beyond our expectation, $\{PW_9\}$ became $\{PW_{12}\}$ in this case. Single crystal X-ray diffraction studies indicated that compounds **1-2** crystallized in the monoclinic space group C2/m. Compound **3** didn't obtain excellent crystals for XRD measurement, so we compared the powder X-ray diffraction (PXRD) pattern of it with simulated PXRD pattern of compound **2**. It matched well with the simulated pattern of compound **2**, indicating compounds **1-3** are all isostructural. Taking compound **1** for an example, the asymmetric unit contains a quarter of $\{PW_{12}\}^{3-}$ anion, four Cu^{I} ions (Cu2 and Cu4 site half-occupied), one fourth Cl ion and two triazole ligands. Cu ions have two kinds of coordination modes, in which Cu1, Cu3 and Cu4 are three-

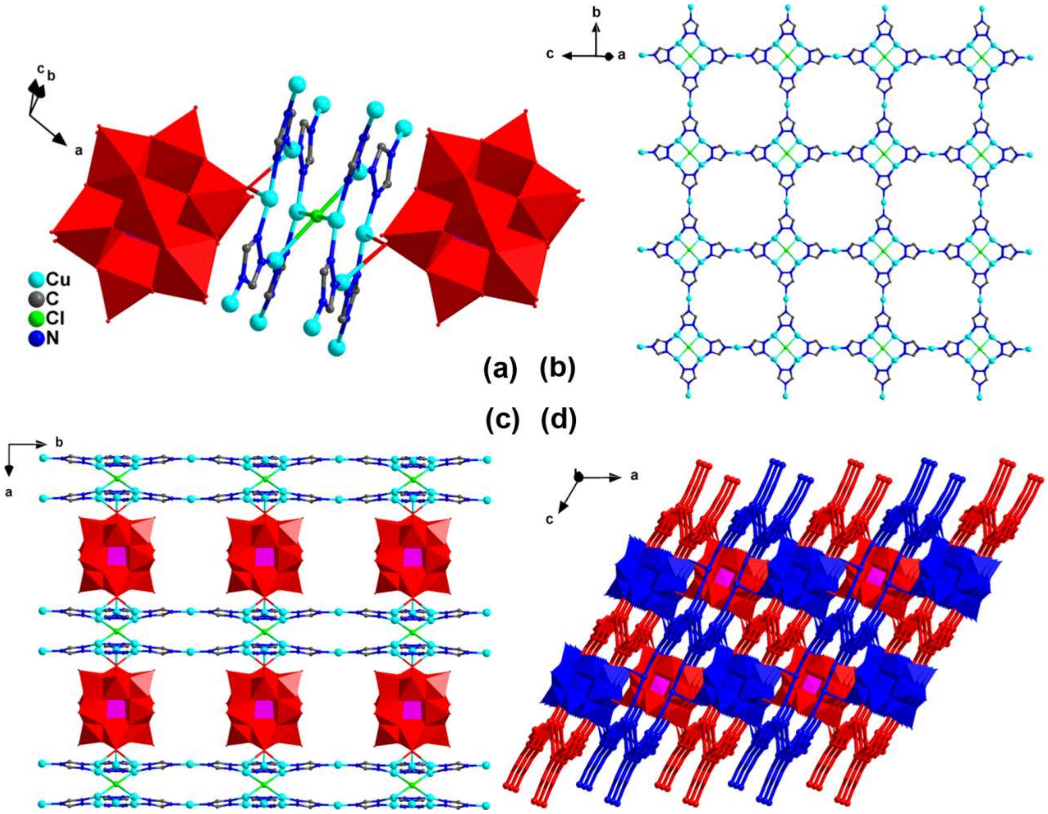

Fig.1 (a) Two layers tetra-nuclear copper rings locates in between two $\{PW_{12}\}$ anions. (b) Metal-organic 2D layer with tetra-nuclear $[Cu_4(trz)_4]$ and octa-nuclear $[Cu_8(trz)_8]$ moieties. (c) {PW12} connected 2D bilayers into a 3D framework with channels. (d) Two same 3D networks form a 3D two-fold interpenetrating structure.

coordinated by two nitrogen atoms and one oxygen atom or chlorine atom in approximate "T" shaped coordination environments, while Cu2 is two-coordinated linear type by two nitrogen atoms (Fig. S1 and relevant bond lengths and angles are showed in Table S4-S5). As shown in Fig. 1a and 1b, Cu ions link triazole ligands into 2D double layers with the help of Cl ions, in which tetra-nuclear $[Cu_4(trz)_4]$ and octa-nuclear $[Cu_8(trz)_8]$ moieties show a distinguishing feature. The whole 2D sheet can be regarded as an alternative arrangement of four- and eight-segment Cu-trz circles. Then, $\{PW_{12}\}$ anions support those 2D bilayers to a 3D network I through weak Cu-O bonds (Cu3-O9 2.636 Å, Cu4-O4 2.569 Å), which possesses continuous channels (Fig. 1c). Network I interpenetrates another same 3D network II to form a 3D two-fold interpenetrating structure. POM anions located in network I just inlay the channels of network II, so the whole framework is close-grained (Fig. 1d).

Stability of compounds

All copper atoms are in +1 oxidation state in the compounds **1-3**, which were confirmed by charge neutrality, coordination environments and valence sum calculations (Table S2-S3 in the supporting information). The powder X-ray diffraction (PXRD) patterns of the as-synthesized compounds match well with the simulated patterns, indicating their crystalline phase purity (Fig. S2-4). The TGA curves illustrate the structures of three compounds can keep stable under 300 °C (Fig. S6), which is mainly ascribed to coordination strength of metal-organic framework. Afterwards, we performed acid and alkali stability tests for three compounds.

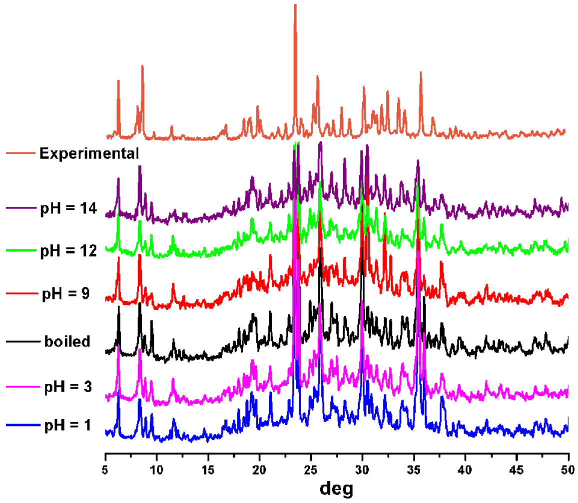

Fig. 2 PXRD patterns for as-synthesized compound **1** and crystals of compound **1** after soaking in different concentrations of HCl, boiling water, or base solution.

The crystals of 100mg compound **1** (**2** or **3**) were soaked in boiling water for 12h and aqueous solutions with pH=1, 3, 9, 12, 14 for 24 hours, respectively. Then the crystals were filtered, washed and dried under ambient condition. The crystals of compound **1** still kept dark-red block as before handling, while the crystal surface of compound **2** and **3** became somber when pH = 12 and became powder when pH = 14. PXRD analyses showed that **1** remained stable in pH = 1 hydrochloric acid, pH =14 NaOH solution and boiling water (Fig. 2), and compounds **2** and **3** kept frameworks unchangeable in the range of pH = 1 to pH = 12 (Fig. S7). The stability of the catalyst has been a difficult problem in industrial application, such catalysts with good stability have more application spaces.

Bandgap sizes and Photocatalysis

Through the previous investigation, we inferred that those compounds would play a significant role in visible light photocatalysis. Hence, we measured the bandgap sizes of compounds **1-3** by a UV-Vis diffuse-reflectance spectrometer at room temperature. The results presented the Eg (bandgap energy) values of 2.42 eV, 2.10 eV and 2.24 eV for compounds **1-3**, respectively (Fig. 3 and Fig. S8). All compounds could be excited under visible light range. Subsequently, we first carried out the experiments on the photocatalytic degradation of MB through a typical process: 100mg of catalyst finely ground were mixed together with 250 mL of 3×10^{-5} mol L^{-1} MB solution. The mixture was stirred for 1 h to arrive at the surface-adsorption equilibrium of compound under the darkness. The first group was no H_2O_2, while 1ml H_2O_2 was added to the second to fourth group. At 0, 15, 30, 45, 60 min, 4 ml of the sample was taken out from the beaker respectively, followed by several minutes centrifugation to remove the title compound

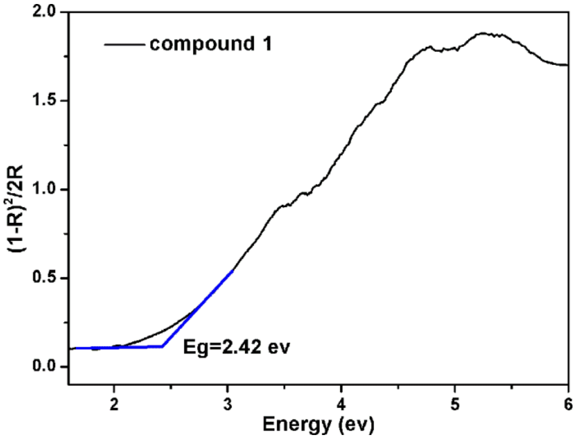

Fig. 3 The $(1-R)^2/2R$ *vs. hv* curve of compound **1**.

and a clear solution was obtained for monitoring the photodecomposition of dye with the UV-vis spectrophotometer. As shown in Fig. 4, after irradiation for 60 min in the presence of H_2O_2, the photocatalytic decomposition rate was 92.7% for compound **1**, 89.66% for compound **2** and 84.16% for compound **3**, respectively. Only compound **1** existed in the system, degradation rate was 56.7% (Fig. S9). The PXRD patterns of compounds **1-3** at the end of three experiments were almost identical with that of the as-prepared samples (Fig. S2-4).

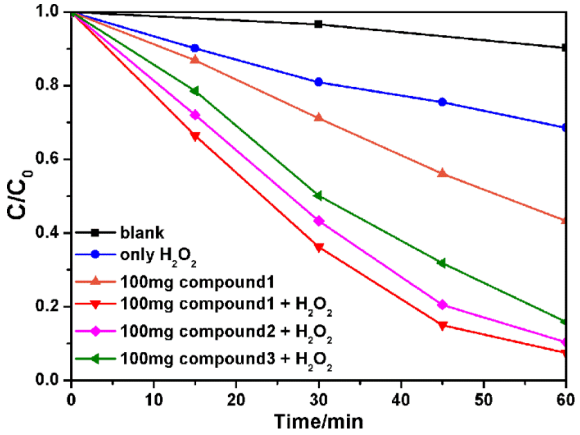

Fig. 4 Photodegradation of MB under visible light irradiation.

In order to further clarify the visible light photocatalytic reaction of the compounds with H_2O_2 system, we performed active species trapping experiments to get significant evidence on the role of active species during photocatalysis. The addition of CCl_4 (an electron scavenger), the isopropyl alcohol (IPA, a ·OH scavenger) could induce a depression effect on the photodegradation of MB.[17] Furthermore, we carefully compared the photocatalytic depression efficiencies. As shown in Fig. S10, about 43.73% and 23.35% inhibition were observed when CCl_4 and IPA were added to no H_2O_2 system respectively, while 36.44% and 33.61% inhibition were shown in H_2O_2 system. Compared inhibitory effect of CCl_4 and IPA in two systems, obviously, e^- was strongly trapped in no H_2O_2 system than in the counterpart, while ·OH was quenched more severely in H_2O_2 system. It could be inferred that photogenerated electron and ·OH was the main contributor to the photocatalytic process.[18] When CCl_4 and H_2O_2 existed in the system, both of them competed to capture photoinduced electrons in the excited state ($H_2O_2 + e^- \rightarrow \cdot OH + OH^-$). Thus, inhibition effect of CCl_4 was wakened in the present of H_2O_2.

After photocatalyitic degradation, Cu^I ions in compound **1** became divalent copper ions partly, but Cu^I still constituted the main part (Fig. 5). According to Chemical States Tables, the peaks at 932.58 eV and 952.18 eV corresponded to the binding energy of Cu $2p^{3/2}$ and Cu $2p^{1/2}$, which originated from Cu^+ (CuCl and Cu_2O). The peaks at 934.68 eV, 942.68 eV and 954.58 eV corresponded to the binding energy of Cu $2p^{3/2}$ and Cu $2p^{1/2}$, which originated from Cu^{2+} ($CuCl_2$ and CuO or $Cu(OH)_2$).[19] We also measured the compounds **2** and **3** after the photocatalytic experiments, and it displayed the same situation (Fig. S12). We ascribed the generation of divalent copper ions to two parts: (1) Grinding process; (2) Photocatalytic process. Both of this two processes had a possibility to oxidize the univalent copper ions on the surface of compounds to divalent ones.

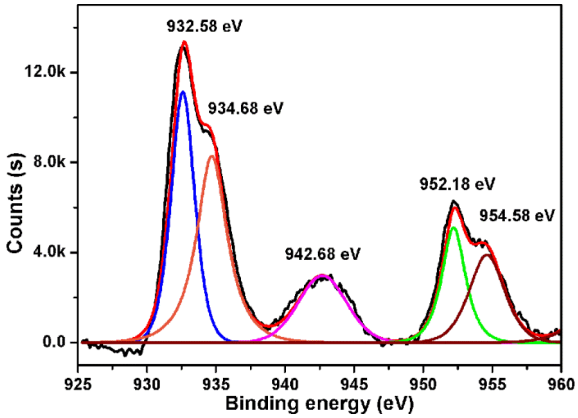

Fig. 5 XPS of Cu in compound **1**.

Conclusions

In conclusion, three new 3D POM-based Cu^I CPs have been successfully prepared by hydrothermal reaction. Compounds **1-3** are isostructural and exhibit a 3D two-fold interpenetrating network. Moreover, the structures of compounds **1-3** exhibit remarkably chemical and thermal stability and effective ability towards photocatalytic degradation of MB, and these properties have a great correlation with structures of compounds. Rigid and close-grained framework leads to higher stability because it is hard to occur dynamic distortion and breakdown.[20] Apart from stability, all Cu^I ions in network can efficiently narrow bandgap of compound to make them work under visible light irradiation.[21] Through simple design and experiments, we further confirm that H_2O_2 works in this system by capturing electrons to form hydroxyl radicals. This work not only shows a simple and easy way for preparing Cu^I catalysts, but also provides a clue that cuprous compounds use solar energy in oxidation system.

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Graphical abstract

Three new 3D POM-based Cu^I coordination polymers have been successfully prepared by hydrothermal reaction. Compounds ***1-3*** *show remarkably high heat stability, acid and alkali resistance, and effectively degrade methylene blue within visible light range .*