



Photo-electrochemical and physical characterizations of a new single crystal POM-based material. Application in photocatalysis



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ABSTRACT

A new inorganic-organic hybrid material $[(\text{H}_2\text{pip})_3][\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot 4\text{H}_2\text{O}$, prepared by hydrothermal method, was structurally characterized by single-crystal X-ray diffraction. The compound based on a Keggin-type polyoxotungstate and piperazine (pip) displays a hybrid framework built from two $(\alpha\text{-Keggin})^{3-}$ polyoxoanions and three $(\text{H}_2\text{pip})^{2+}$ hydrogen-bonded fragments, forming 3-D supramolecular architecture. The diffuse reflectance spectrum shows two optical transitions directly (3.27 eV) and indirectly (3.12 eV) allowed. The electrical conductivity follows an exponential law, indicating a semi-conducting compartment with activation energy of 14 meV. The Mott-Schottky characteristic, plotted in Na_2SO_4 (0.5 M) solution indicates *n*-type conduction with a flat band potential of $-0.084 \text{ V}_{\text{SCE}}$ and electrons density of $4.24 \times 10^{18} \text{ cm}^{-3}$. As application, the photo-degradation of methylene blue (MB) upon UV irradiation was successfully achieved by OH^\bullet radicals. The improved activity is attributed to the potentials closeness of the valence and conduction bands with the radical levels.

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1. Introduction

Since the first $\text{H}_3\text{PW}_{12}\text{O}_{40}$ phosphotungstic acid discovered earlier by Keggin, polyoxometalates (POMs) species have attracted a great interest as building blocks in the design of new inorganic-organic hybrid supramolecular materials [1]. In this research field, different kinds of polyoxoanions, transition metal ions and organo-nitrogen ligands (including imidazole, pyridyl and tetrazole ligands, etc.) have been used [2–4]. The chemistry of polyoxometalates combined with small organic molecules provides knowledge about the interaction of organic molecules with the Keggin surface through hydrogen bonding [5,6]. Indeed, hydrogen bond is an important interaction in the supramolecular networks since it allows the design of materials with various architectures and enhanced functional properties, thus offering a wide range of applications in photocatalysis, materials science, catalysis, sensors and medicine [7–10]. Among the applications, the photocatalysis occupies an important place since it does not require any

sophisticated equipment and works under mild operating conditions [11].

It is well known that POMs and more especially the tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) show good photocatalytic performances in the dyes degradation [12,13]. When POMs are illuminated by incident photons ($h\nu$) with energy greater than their band gap (E_g), electrons are excited from the valence band (VB) to the conduction band (CB). The generated electron-hole (e^-/h^+) pairs allow the formation of radicals responsible of advanced oxidation process (AOP) of the organic matter [14,15]. On the other hand, there are only few works on POM-based hybrid materials with piperazine or its derivatives as organic ligands in the literature and their photoelectrochemical (PEC) properties have been little investigated.

In this work, we report the synthesis, structural characterization, physical and photoelectrochemical properties of a new inorganic–organic $[(\text{H}_2\text{pip})_3][\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot 4\text{H}_2\text{O}$ single crystal, constructed from Keggin-type $[\alpha\text{-PW}_{12}\text{O}_{40}]$ polyoxotungstate and piperazine organic units. As application, the photocatalytic degradation of methylene blue (MB) was studied under UV irradiation.

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2. Experimental

2.1. Hydrothermal synthesis

All chemicals were commercially purchased and used as received. In a typical synthesis, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (2.88 g, 1 mmol) and piperazine (0.19 g, 1 mmol) were dissolved in 10 mL of distilled water under constant agitation. The mixture was homogenised for 3 h at room temperature (pH \sim 2) and then transferred in 23 mL-Teflon-lined stainless steel autoclave. The crystallisation was then performed under autogenous pressure at 180 °C during 72 h. After cooling to ambient temperature, white transparent crystals were recovered by filtration, washed thoroughly with distilled water and dried at 60 °C overnight (50% yield based on W). The calculated composition of $[(\text{H}_2\text{pip})_3][\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot 4\text{H}_2\text{O}$ (6096.6): (wt%) P, 0.98; W, 69.9, was close to the experimental one: P, 0.82; W, 70.07.

2.2. Materials and methods

The powder X-ray diffraction (XRD) pattern was performed on a Philips X'Pert Pro MDP diffractometer with Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$). Scanning electron microscopy (SEM) images were taken using a JSM-6700F microscope, operating at 5 kV. The FTIR spectrum was recorded with a Nicolet avatar 330-FTIR spectrometer in the range (400–4000 cm^{-1}), using the KBr technique. The UV–Vis spectrum of the powder was recorded with a Jasco V-650 spectrophotometer equipped with an integrating sphere in the range (200–750 nm). The thermal analysis (TG) was performed on a Perkin Elmer STA 6000 instrument under N_2 atmosphere at a heating rate of 10 °C min^{-1} . The electrochemical measurements were carried on in a standard Pyrex cell at 25 °C using a PGZ 301 potentiostat (Radiometer analytical). A platinum foil was used as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode.

2.3. Crystal structure determination

Crystallographic data of the compound were collected at 150 K on a Bruker APEXII diffractometer with a graphite-monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). An empirical absorption correction to the intensities was carried out using SADABS [16]. The structure was resolved using sir 2002 program [17], and refined by the full-matrix least-squares technique on F^2 by using SHELX-97 software [16].

Anisotropic thermal parameters were applied to all non-hydrogen atoms. The $(\text{H}_2\text{pip})^{2+}$ molecules located in the plane (101) present a disorder which is refined with PART instruction. The hydrogen atoms were introduced as riding atoms in calculated positions and constrained with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. N–H bonds are excluded, given their theoretical value of 0.87 Å. The hydrogen atoms of water molecules could not be found from the residual peaks and were directly included in the final molecular formula. The crystal data and structural refinements are gathered in Table 1.

3. Results and discussion

3.1. Structure description

The single-crystal X-ray diffraction reveals that the synthesized compound consists of two discrete polyoxoanions $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and three diprotonated piperazine $(\text{H}_2\text{pip})^{2+}$ cations per unit cell, crystallizing in the triclinic system with the P-1 space

Table 1

Crystal data and structure refinement parameters.

Formula	$[(\text{H}_2\text{pip})_3][\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot 4\text{H}_2\text{O}$
Fw	6096.6
Temp/K	150
Crystal system	Triclinic
Space group	P-1
a/Å	10.3592
b/Å	10.5175
c/Å	19.2456
$\alpha/^\circ$	104.166
$\beta/^\circ$	92.996
$\gamma/^\circ$	91.605
V/Å ³	2028.52
Z/Z'	2/1
R_{int}	0.0397
$R_1^a [I > 2 \text{ sigma}(I)]$	0.0484
wR_2^b (all data)	0.0499
GOF	1.0070

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^2} \right]^{1/2}$$

group (Fig. S1). The $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion has a typical α -Keggin structure, consisting of a central PO_4 tetrahedron surrounded by four vertex-sharing W_3O_{13} trimers. Each W_3O_{13} group is composed of three WO_6 octahedra linked via triangular arrangement by sharing edges. There are four types of oxygen atoms with different coordination geometry in the cluster: the terminal oxygen atoms (O_t), central oxygen atoms (O_c), bridging oxygen atoms of two octahedra sharing an edge (O_b) and bridging oxygen atoms between two octahedra sharing a corner ($\text{O}_{b'}$), whose bond distances are in the ranges: W– O_t 1.681–1.717, W– O_c 2.408–2.465, W– O_b 1.897–1.944, W– $\text{O}_{b'}$ 1.875–1.941 Å (Table S1). For PO_4 groups, the O–P–O angles are in the range (109.25–109.77°) (Table S2) with P– O_c distances varying from 1.519 to 1.541 Å (O_c represents the tetrahedral oxygen atoms in distorted PO_4 tetrahedron). Hydrogen-bond interactions between Keggin anions and small organic molecules are specific and important since they help to stabilize the structure (Table S3).

As shown in Fig. S2, each α -Keggin group is surrounded by eight neighboring $(\text{H}_2\text{pip})^{2+}$ ligands and connects to them by hydrogen bonds. Each $(\text{H}_2\text{pip})^{2+}$ cation donates several typical hydrogen bonds formed by N–H \dots O and C–H \dots O interactions to terminal or bridging oxygen atoms from two $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anions. These interactions are mainly in the range (2.12–2.60 Å) (Table S3). The interactions of lattice water molecules with $(\text{H}_2\text{pip})^{2+}$ ligands are given in Fig. S3, there are four hydrogen bonds varying from 1.88 to 2.52 Å (Table S3) with the oxygen atoms of water molecules. The two disordered $(\text{H}_2\text{pip})^{2+}$ ligands are linked to O_{2w} , O_{3w} and O_{4w} atoms involving hydrogen bonds, while the six others are connected only to O_{1w} (Fig. S3). All these bonds and interactions generate a three-dimensional supramolecular lattice (Fig. 1).

3.2. Characterization

The XRD pattern is in good agreement with the simulated one, obtained from single crystal X-ray diffraction, thus confirming the phase purity of the sample (Fig. S4). The difference between the intensities of the patterns is due to preferred orientations of the powder during the data collection [18]. The crystallite size ($D \sim 34 \text{ nm}$) is calculated from the empirical Scherrer formula:

$$D = K(\beta \cos \theta)^{-1} \quad (1)$$

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