

Short communication

An intercalation compound of molybdenum oxide with pyridine and water molecules. Synthesis, crystal structure and properties

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ABSTRACT

An intercalation compound of molybdenum oxide with pyridine and water ($\text{Mo}_8\text{O}_{24} \cdot (\text{py}) \cdot 2\text{H}_2\text{O}$ (**1**)) was synthesized hydrothermally and its structure and component were determined by element analysis, IR spectroscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy and single-crystal X-ray diffraction. The electrochemistry property and photocatalytic property were studied. The single-crystal structural analysis indicates that the molybdenum oxide has stair-like layer structure and the pyridine and water molecules intercalated in between the layers. Rare earth ions played an induced role to the formation of the compound. The compound exhibited a good catalytic activity to the photodegradation of methylene blue.

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MoO_3 is used as an important raw material and catalyst in chemical industry. At the same time it has been widely applied in preparing the photochromic and electrochromic materials, optical storage, optical electronic transducer due to its good light sensitivity [1–4]. MoO_3 is also n-type semiconductor with an energy gap of 2.75–3.2 eV and used as photocatalyst in treatment of pollutants [5,6]. MoO_3 has three crystal phases, thermodynamically stable orthorhombic phase (α - MoO_3), thermodynamically metastable monoclinic phase (β - MoO_3) and hexagonal phase (h - MoO_3). Orthorhombic α - MoO_3 has lamellar structure constructing from distorted MoO_6 octahedra through sharing edges in one direction and sharing corners in other direction. The layers are linked with weak Van der Waals force [7,8]. Intercalation of small molecules and ions into between the layers may change the properties of materials so that intercalation chemistry has attracted a lot of attention in materials field [9–13]. The reported organic molecules intercalated into α - MoO_3 are 4,4'-bipyridine [14], poly-(p-phenylene) [15], 2,2'-bipyridine [16], nicotinamide, hexamethylenetetramine [17], pyrrolidinedithiocarbamate [18], polyaniline [19] and pyrazine [20–22] et al. These organic molecules were hydrothermally intercalated into α - MoO_3 which was self-prepared or commercially obtained and their structures were inferred *via* XRD and Raman techniques. In this paper an intercalated compound ($\text{Mo}_8\text{O}_{24} \cdot (\text{py}) \cdot 2\text{H}_2\text{O}$ (**1**)) is reported. It was synthesized *via* one-step hydrothermal synthetic method with

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$, 4,4'-bipy as starting materials, heating at 150 °C for 3 days [23] and has a new type of lamellar structure which was confirmed by single-crystal X-ray diffraction technique [24].

As seen from the above chemical formula one of the starting materials 4,4'-bipyridine is not in compound **1**, instead its decomposed product, pyridine, is the component of **1**. The transformation of organic molecules in hydrothermal synthesis is called as *in situ* formation [25,26]. Another starting materials, lanthanides, are also not in compound **1**, and the results of many experiments show that the compound **1** could not be obtained without presence of lanthanides. That means the presence of lanthanides is a key condition of the formation of **1** due to their catalysis on cracking reaction of C—C bond [27].

Asymmetric unit of ($\text{Mo}_8\text{O}_{24} \cdot (\text{py}) \cdot 2\text{H}_2\text{O}$) consists of a $\{\text{Mo}_4\text{O}_{12}\}$ cluster, a half py molecule and a water molecule. In $\{\text{Mo}_4\text{O}_{12}\}$ cluster oxygen atoms can be divided into three types, terminal oxygen atom O_t , bridging oxygen atoms μ_2 -O and μ_3 -O. Four molybdenum atoms (Mo_1 , Mo_2 , Mo_3 , Mo_4) are in three coordination environments. Mo_1 (Mo_2) atom bonds to one O_t , two μ_2 -O and three μ_3 -O oxygen atoms, presenting a distorted octahedral geometry. Mo_1 -O bond lengths are in the range of 1.733–2.378 Å and Mo_2 -O bond lengths are in the range of 1.680–2.350 Å. Mo_3 atom bonds to two μ_2 -O, four μ_3 -O oxygen atoms with Mo_3 -O bond lengths of 1.709–2.332 Å. Mo_4 atom bonds to two O_t , two μ_2 -O and two μ_3 -O oxygen atoms with Mo_4 -O bond lengths of 1.674–2.332 Å, Mo_3 and Mo_4 atoms also have distorted octahedral geometry. Four MoO_6 octahedra combine into Mo_4O_{12} through sharing octahedral edges and corners (Fig. 1). Mo_4O_{12} links other Mo_4O_{12} through sharing octahedral edges and corners into a stair-like layer in [101] plane

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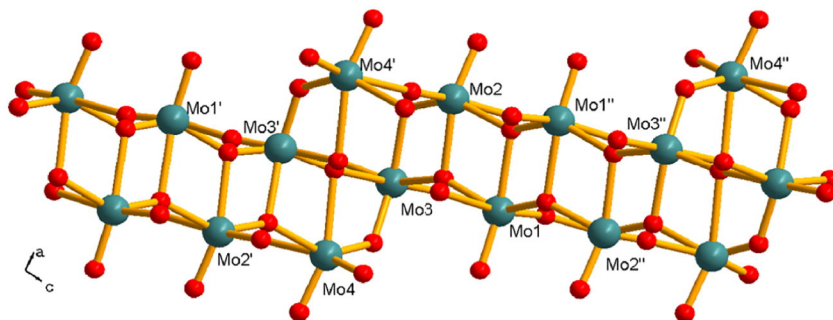


Fig. 1. Linkage of Mo atoms in **1**.

(Fig. 2). This layer is very different from the reported MoO_3 layer [7] in which every MoO_6 octahedron has a terminal oxygen atom.

The layers arrange in such a way of staggered and parallel each other so that there are two O–O distances between two layers, 3.8373 Å and 6.1789 Å. Lattice water molecules locate in between two layers with small distance, and pyridine molecules situate in between two layers with big distance (Fig. 3). Plane of pyridine molecule angles 45° to the plane of the MoO_3 layer and the distances between C atoms of pyridine molecule and O atoms of the MoO_3 layer are in the range of 2.933–3.228 Å and that between O atoms of free water molecules and O atoms of the MoO_3 layer are O1W–H1WA...O11 2.682 Å, O1W–H1WA...O6 3.024 Å (Fig. 4). That is, it is the $\text{CH}\cdots\text{O}$ and $\text{OH}\cdots\text{O}$ hydrogen bonds that combine these MoO_3 layers, water molecules and pyridine molecules into a three dimensional architecture.

In the infrared spectrum of **1** (Fig. S1) the bands at 936, 910, 839, 786, 743, 707, 642 cm^{-1} come from vibration absorption of Mo–O_a, Mo–O_b, Mo–O_c–Mo bonds. The bands at 1650–1110 cm^{-1} belong to vibration absorption of H–O–H, C–C, C–N, C=C, C=N bonds of pyridine molecule. The broad band in 3000–3500 cm^{-1} results from vibration absorption of C–H bonds and water molecules. TG curve (Fig. S2) of **1** shows the deintercalation of pyridine and water molecules below 400 °C. The weight loss is consistent with its chemical formula.

In XPS (Fig. S3) the peaks at 234, 286, 400, 418, 534 eV are attributed to Mo^{VI} ($3d_{5/2}$), C(1 s), N(1 s), Mo^{VI} ($3p_{3/2}$) and O(1 s) electron binding energy [21], confirming the chemical components of **1**. The PXRD data of **1** were recorded and are displayed in Fig. S4. The diffraction peaks of the simulated and the experimental structures match well, indicating the phase purity of the compound.

The electrochemical behavior of compound **1** in carbon paste electrode (**1**-CPE) has been investigated. The cyclic voltammograms of **1**-CPE in 0.5 mol/L Na_2SO_4 - H_2SO_4 (pH = 2.35) aqueous solution in different scan rates are presented in Fig. 5. In the potential range of -0.10 ~ $+0.90$ V, there are three pairs of reversible redox peaks (I–I', II–II', III–III') (Fig. 5 left), with the mean peak potentials $E_{1/2} = (E_{\text{pc}} - E_{\text{pa}})/2$ at 22,166, 304 mV at scan rate of $70 \text{ mV}\cdot\text{s}^{-1}$, respectively. The redox peaks correspond to three one-electron processes of Mo [28], showing a medium oxidative property of **1**. With the increasing of scan rates from $10 \text{ mV}\cdot\text{s}^{-1}$ to $70 \text{ mV}\cdot\text{s}^{-1}$, the anodic peak potentials shifted slightly toward the positive direction, and the corresponding cathodic peak potentials shifted slightly toward the negative direction. The peak currents were proportional to the scan rate (Fig. 5, right inset), which indicates the redox process of **1**-CPE is surface- controlled [29].

Organic dyes discharged from textile industry and dye manufacture factories cause fearful pollution of water system. Treatment of industrial

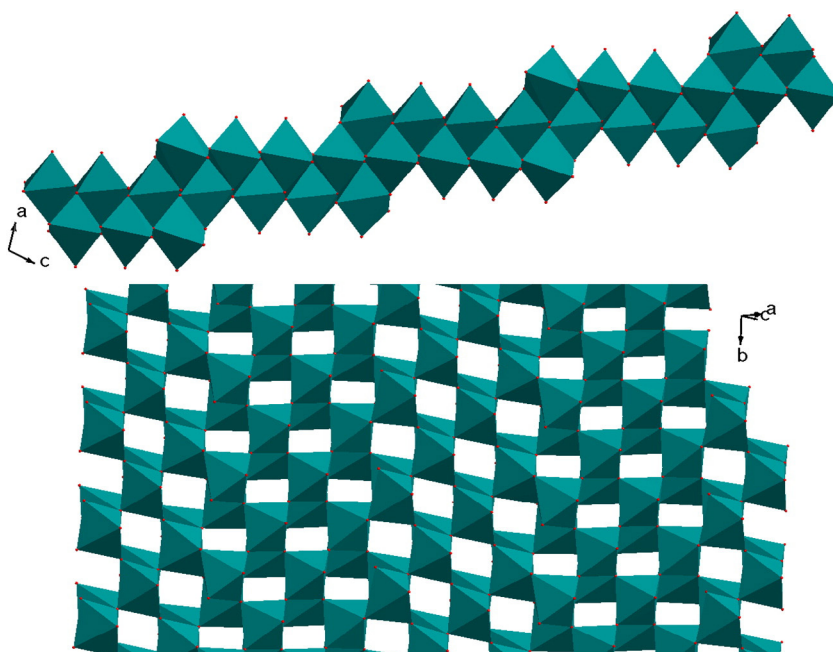


Fig. 2. MoO_3 layers viewed from two directions.

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