Applied Surface Science 463 (2019) 659–667

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

# Crystal structure and photocatalytic properties of perovskite $MSn(OH)_6$ (M = Cu and Zn) composites with $d^{10}$-$d^{10}$ configuration

Shuying Dong[a,*], Lingfang Cui[a], Yinlan Zhao[a], Yawen Wu[a], Longji Xia[a], Xianfa Su[a], Chunyan Zhang[a], Dong Wang[b], Wei Guo[c], Jianhui Sun[a,*]

[a] School of Environment, Henan Normal University, Key Laboratory for Yellow River and Huai River Water Environmental and Pollution Control, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, Xinxiang, Henan 453007, PR China
[b] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, PR China
[c] Department of Chemistry, Xinxiang Medical University, East of JinSui Road, Xinxiang, Henan 453003, PR China

ARTICLE INFO

*Keywords:*
$d^{10}$-$d^{10}$
Hexahydroxy-stannates
Coprecipitation
Photocatalytic

ABSTRACT

In this study, hexahydroxy-stannates ($MSn(OH)_6$ (M = Cu, Zn)) with $d^{10}$-$d^{10}$ configuration were synthesized by using a simple coprecipitation method at room temperature to investigate the effect of cationic substitution with similar ionic radius. The obtained samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area analysis, Fourier transform-infrared spectra (FT-IR) and UV–Vis diffuse reflectance spectroscopy, etc. The photocatalytic properties of the obtained samples were evaluated by the degradation of methylene blue (MB). It is found that the difference of $M^{2+}$ in $MSn(OH)_6$ bring a change in crystal structure, morphology, chemical bond energy and photocatalytic property. The obtained $MSn(OH)_6$ nanoparticles can be used to the preparation of the different mixtures by simple calcination, but the photocatalytic performance could not be improved after the heat treatment duo to the change of crystal structure by forming the mixture of oxide. These results suggested that metal cations in A sites could induce lattice distortion of the hexahydroxy-stannates with $d^{10}$-$d^{10}$ configuration although they have the similar ionic radius, accordingly inducing the change of morphology, chemical bond energy and photocatalytic activity.

## 1. Introduction

In recent years, photocatalytic oxidation technology has great potential for development in the degradation of organic wastewater because of its high efficiency and energy saving, no secondary pollution and wide application range [1]. The most critical aspects of the photocatalytic reaction are excitation and migration of photogenic $e^-$-$h^+$, where the catalytic activity and quantum yield are determined by the mobility of photogenerated $e^-$-$h^+$ [2]. It is generally believed that this process is closely related to the crystallinity, surface area and co-catalyst, etc. In order to build a highly efficient and stable visible light catalytic system, we should not only pay attention to the electronic structure but also the type of materials, morphology, crystallinity and surface properties of the intrinsic nature. Therefore, the choice of materials is particularly important because it determines the degree of visible light response and total efficiency of the semiconductor materials [3,4].

For this reason, developing a new structural mode based on intrinsic nature as stable visible-light-driven photocatalyst are very demanding and challenging [5]. $d^{10}$ metal adopts versatile coordination numbers and tunable coordination spheres, such as Cu cation not only possesses two oxidation states but can also own distinctive coordinate modes including linear, T-type, rhombus, square-pyramidal, and octahedral [6]. This coordinative freedom is beneficial for linking other functional group, which may provide an opportunity to construct a novel material. The DFT calculations revealed that the conduction band of photocatalysts with $d^{10}$ metal ions as core elements was formed by the sp orbitals, whose electronic configuration is differed from those of the d orbitals in conventional photocatalyst with $d^0$ metal ions [7]. Such expectation led us to explore an elaborate photocatalyst with $d^{10}$-$d^{10}$ configuration on the basis of the hybridization of the sp orbitals of $d^{10}$ metal may have a significant effect on the density of states and energy dispersion in the conduction bands.

Hexahydroxy-stannates ($MSn(OH)_6$, MHS) with $d^{10}$-$d^{10}$ configuration belongs to the perovskite family, which have excellent physical and chemical properties due to its special cell structure [3,8]. As is well known, it can be used in a number of areas, such as gas sensitive materials [9], optical materials [10], catalysts and lithium batteries [11]

---

* Corresponding authors.
*E-mail addresses:* dongsy@htu.edu.cn (S. Dong), sunjh@htu.edu.cn (J. Sun).

https://doi.org/10.1016/j.apsusc.2018.09.006
Received 15 June 2018; Received in revised form 7 August 2018; Accepted 1 September 2018

and so on. As the MHS semiconductor have a wide band gap with perovskite type crystal structure, M and Sn are coordinated with hydroxyl groups to form an octahedral structure and two polyhedral are linked by oxygen atoms [12]. The presence of two different $d^{10}$ metal ions in the unit cell leads to large distortion in the octahedral units of the structure. There is a large number of photo-generated carriers on the surface of MHS to form hydroxyl radicals ($^{\cdot}OH$) in the photocatalytic reactions [13,14]. The free radicals become active centers during the photocatalytic reaction, this resultant geometric and electronic effects determines the excellent photocatalytic performance of MHS.

Intrigued by the rich coordination flexibilities and potential photocatalytic behaviors of these hexahydroxy-stannates, we undertook systematic studies in exploring new hexahydroxy-stannates with $d^{10}$-$d^{10}$ configuration via comparison of two $d^{10}$ metal ions ($Cu^{2+}$ and $Zn^{2+}$) with similar ionic radius, which will afford the direct experimental understanding on the structure-dependent photocatalytic behaviors at the molecule scale. Many works have been devoted to the synthesis of MHS including the hydrothermal method, co-precipitation, mechanochemical synthesis and sonochemical methods [15–17]. In our study, a facile co-precipitation has been used to synthesize MHS nanoparticles. Subsequently, calcination of MHS nanoparticles under different temperature could obtain different mixtures. The as-synthesized products were well characterized and the photocatalytic performance was investigated by the degradation of methylene blue (MB) under natural sunlight irradiation, from which obtain the effect of ionic replacement on the microstructure and activity of $d^{10}$-$d^{10}$ configuration.

## 2. Experimental

### 2.1. Preparation of MHS (M = Cu, Zn) nanostructures

MHS (M = Cu, Zn) nanostructures were prepared by a simple co-precipitation method at room temperature. $Na_2SnO_3$, $CuSO_4{\cdot}5H_2O$, $ZnCl_4$ and concentrated ammonia solution were used as the starting materials. They are all of analytical grade purity and were used without any further purification. Distilled water was used throughout all experiments. Samples were prepared as following: The $CuSO_4{\cdot}5H_2O$ or $ZnCl_4$ was dissolved in distilled water and forming a homogeneous solution. Under magnetic stirring, 1 mL concentrated ammonia solution was dropped into the solution. Then, the reactive mixture was stirring for a few minutes. Afterwards, 16 mL 0.05 M $Na_2SnO_3$ solution was added into the above solution. Continuing magnetic stirring for 60 min at ambient temperature, the resultant products were washed with distilled water several times and then dried at 80 °C overnight.

### 2.2. Characterization

The X-ray diffraction (XRD) patterns of the as-prepared photocatalysts were collected on a Bruker-D8-AXS diffractometer system equipped with a Cu Kα radiation ($\lambda = 0.15406$ nm), the patterns were recorded in the $2\theta$ range of 16–90°. The morphologies and structures of the samples were inspected by using a JSM-6390LV scanning electron microscopy (SEM). Transmission electron microscopy (TEM) was performed on a JEM-2100 electron microscope. Fourier transform-infrared spectra (FT-IR) were inspected on a Spectrum 400 spectrometer in the range of 400–4000 $cm^{-1}$ using KBr as a reference. X-Ray photoelectron spectroscopy (XPS) data was used to determine the chemical states of elements and valence band position using a 260Xi X-ray photoelectron spectrometer with an Mg Kα radiation. The photoluminescence (PL) spectra of photocatalysts were collected at room temperature using a fluorescence spectrophotometer (FLS980) equipped with a Xenon lamp at an excitation wavelength of 325 nm. Ultraviolet-visible diffuse reflectance spectra (UV–Vis DRS) of the obtained samples were recorded at the wavelength range of 220–900 nm. Thermogravimetry and differential scanning calorimetry (TG-DSC) were carried out by using a NETZSCH STA 449F3 thermal analyzer in air at a heating rate of 10 K/min, and the testing temperature range was 22–1000 °C.

### 2.3. Photocatalytic activity measurements

The photocatalytic activities of the prepared photocatalysts were examined through the photocatalytic degradation of methylene blue (MB) under natural sunlight irradiation. Moreover, the illumination intensity of the natural sunlight was measured by using a digital Lux meter (UA1010B, Shenzhen UYIGAO E&T Co., China), where the average time-dependent illuminations of the natural sunlight were about 60,000–80,000 Lux. In each experimental run, the samples (0.1 g) were dispersed into 200 mL MB (5 mg/L) aqueous solution. All photocatalytic processes were carried out in a 250 mL capacity bottle and maintained constant magnetic stirring under sunlight irradiation. Prior to sunlight irradiation, the suspension was stirred for 60 min in the dark to insure the adsorption/desorption equilibrium between the MB and the samples. The MB solution was collected 5 mL away at the predetermined time intervals for analysis. Finally, the concentrations were determined by the absorption intensity at its maximum absorbance wavelength ($\lambda_{max}$) at 664 nm.

## 3. Results and discussion

### 3.1. Detailed characterizations of the as-synthesized MHS

X-ray diffraction (XRD) was employed to probe the crystal phases of as-prepared MHS. The red[1] and blue curves in Fig. 1a show the XRD patterns of MHS, which is readily in accordance with the structure of $CuSn(OH)_6$ (CuHS) (JCPDS No. 70-0117, a = b = 7.586, c = 8.103) and $ZnSn(OH)_6$ (ZnHS) (JCPDS No.73-2384, a = b = c = 7.8), respectively. This result is consistent with previous reports [14,17]. No impurity peaks were observed. As shown in Fig. 1a, the diffraction peaks of the both samples at around $2\theta = 19.9°$, 22°, 33°, 40°, 47°, 53° and 59° corresponding to the (1 1 1), (2 0 0), (2 2 0), (2 2 2), (4 0 0), (4 2 0) and (4 2 2) planes, respectively. Both the main reflection peaks are similar except that the main peak of CuHS broadens slightly compared with ZnHS. These results suggested that metal cations in A sites could induce lattice distortion of the hexahydroxy-stannates with $d^{10}$-$d^{10}$ configuration although they have the similar ionic radius.

FT-IR spectra of MHS nanoparticle is shown in Fig. 1b, from which several characteristic bands can be observed. The band at 3100–3300 $cm^{-1}$ is assigned to the hydroxyl (—OH) group in the structure of MHS. The sharp peak observed at 1176.29 $cm^{-1}$ and 1158.22 $cm^{-1}$ are due to the Sn—OH bending vibration, while the peak at 780.51 $cm^{-1}$ and 765.23 $cm^{-1}$ relates to water-water hydrogen bonding. Moreover, the peak at 538.97 $cm^{-1}$ and 543.89 $cm^{-1}$ are due to the Sn—O stretching type. Therefore, the FT-IR results provide additional proofs for the formation of MHS. Compared with that of ZnHS, the characteristic bands in CuHS apparently red shift, which may be related to the change of chemical bond in MHS and in accordance with the XRD results.

In order to investigate the effect of heat treatment on the photocatalytic activities, we accomplished TG-DSC of the prepared MHS photocatalysts. Fig. 1c and d display the DSC and TG were simultaneously performed over a 22–1000 °C range at a heating rate of 10 K/min. As shown in the figures, the DSC curves of the two samples display an intense endothermic peak centered at ~220 °C and a smaller exothermic peak centered at ~700 °C. The TG curves involve a weak weight loss from 22 °C to 120 °C with a total weight loss of about 3.6% (ZnHS) and 2.2% (CuHS), respectively, which corresponding to the

---

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.