Ultrasonics - Sonochemistry 41 (2018) 67–74

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

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

Ultrasound irradiation effect on morphological properties of a 3D nano zinc (II) supramolecular coordination polymer

Hai Ning Chang, Suo Xia Hou, Zeng Chuan Hao, Guang Hua Cui*

College of Chemical Engineering, Hebei Key Laboratory for Environment Photocatalytic and Electrocatalytic Materials, North China University of Science and Technology, No. 21 Bohai Road, Caofeidian New-city, Tangshan, Hebei 063210, PR China

ARTICLE INFO

Keywords:
Coordination polymer
Nano
Photocatalytic
Sonochemical
Supramolecule

ABSTRACT

Nano-structures of $[Zn(L)(atpt)]_n$ (**1**) (L = 1,2-bis(2-methylbenzimidazol-1-ylmethyl)benzene and H_2atpt = 2-aminoterephthalic acid) were obtained by hydrothermal and sonochemical approaches, characterized by scanning electron microscopy (SEM), IR, powder X-ray diffraction (PXRD), and elemental analysis. CP **1** features a 2D (4,4) network with the point symbol $\{4^4.6^2\}$, the 3D supramolecular architecture in CP **1** is controlled through π···π stacking interactions. The influence of various concentrations of initial reagents, power of ultrasound irradiation, and ultrasound time on the morphology and size of nano-structured CP **1** were studied in detail. In addition, the luminescence and photocatalytic properties of the nanoparticles of CP **1** for the degradation of methyl blue (MB) have also been investigated.

1. Introduction

Crystal engineering of coordination polymers (CPs) is of great current interest to develop new crystalline materials for possible use in a variety of applications, such as sensing, catalysis, magnetism, gas storage and separation [1–7]. These functional materials are finely tuned by judicious combination of metal centers with predesigned bridging ligands under suitable conditions [8,9]. Zinc(II) is really a well-known metal with a variety of applications in numerous areas, they can adopt different coordination modes when they react with organic ligands, their d^{10} configuration is assigned to a flexible coordination environment to ensure that different geometries can be generated to tailor-made materials [10–13]. Organic ligands can help control the framework and topology as one-/two-/three-dimensional architectures [14,15].

Nowadays, organic dyes from the textile, dyeing and other industries are discharged into the local environment without adequate treatment [16,17]. Conventional methods have been established for wastewater treatment only make the pollutants transfer from the liquid phase to the solid phase. Hence, it is essential to search green and economical treatment to purify the pollutants, photocatalysis technology has been used to remove organic contaminants from water and air [18,19], while coordination polymer is regarded as one of the most potent photocatalyst for its low band gap, which can accelerate separation rate of photogenerated electron-hole pairs [20,21]. Further, we select 2-aminoterephthalic acid as connectors, because aminated linkers are known to enhance the absorption of light and afford photocatalysis with CPs under visible-light irradiation [22].

Assembly of CPs with diverse shape and sizes are very significant for the applications such as heterogeneous photocatalyst. In nano-sized particles, the ratio of surface area to volume is more increased than the particles with bulk sizes. The size effect plays an important role on physical and chemical properties such as catalytic behavior [23]. To prepare nano-structured CPs, utilization of ultrasound has been attracted much attention recently [24–27]. Sonochemistry is a research area of chemical reactions that are influenced by the application of powerful ultrasound radiation (20 kHz–10 MHz). Ultrasound induces chemical or physical changes during cavitation, a phenomenon involving the formation, growth, and instantaneously implosive collapse of bubbles in a liquid. This can generate local hot spots with temperatures up to 5000 °C, 500 atm pressures and a lifetime of a few microseconds. These extreme conditions can drive chemical reactions and can promote the formation of nano-structures, mostly via an increase of crystallization nuclei [28–30].

Hence, we utilize sonochemical method to synthesize nano-sized Zn^{II} coordination polymer $[Zn(L)(atpt)]_n$ (**1**) (L = 1,2-bis(2-methylbenzimidazol-1-ylmethyl)benzene and H_2atpt = 2-aminoterephthalic acid). Scanning electron microscopy (SEM) revealed that the concentration of initial reagents, ultrasound irradiation time and power exhibit significant effects on the size and shape of CP **1**. Further, the luminescence and photocatalytic properties of the CP **1** were also presented.

---

* Corresponding author.
E-mail address: tscghua@126.com (G.H. Cui).

http://dx.doi.org/10.1016/j.ultsonch.2017.09.024
Received 24 July 2017; Received in revised form 14 September 2017; Accepted 15 September 2017

2. Experimental

2.1. Materials and methods

1,2-bis(2-methylbenzimidazol-1-ylmethyl)benzene was synthesized according to the literature procedure [31]. Other reagents and solvents were purchased from Jinan Henghua Sci. and used without further purification. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku D/Max-2500 diffractometer. Ultrasound was generated by a multi-wave KQ2200DE at a frequency of 40 kHz. Elemental analyses of C, H and N were determined using a PerkinElmer 240 C elemental analyzer. IR spectra using KBr pellets were recorded on an Avatar 360 (Nicolet) spectrophotometer in the region of 4000–400 cm^{-1}. The TGA measurement was performed on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C with a heating rate of 10 °C·min^{-1} under N_2 atmosphere. The luminescence spectra were obtained by using FS5 fluorescence spectrophotometer equipped with a continuous xenon lamp at room temperature. Solid-state UV/Vis diffuse reflectance spectra were measured using a UV–Vis Puxi T9 UV–visible spectrophotometer with $BaSO_4$ as a reference. The crystallite sizes of selected samples were estimated using the Scherrer equation. The morphology of the suitable samples was investigated using a JSM-IT100 scanning electron microscope after gold coating.

2.2. Synthesis of $[Zn(L)(atpt)]_n$ as single crystal

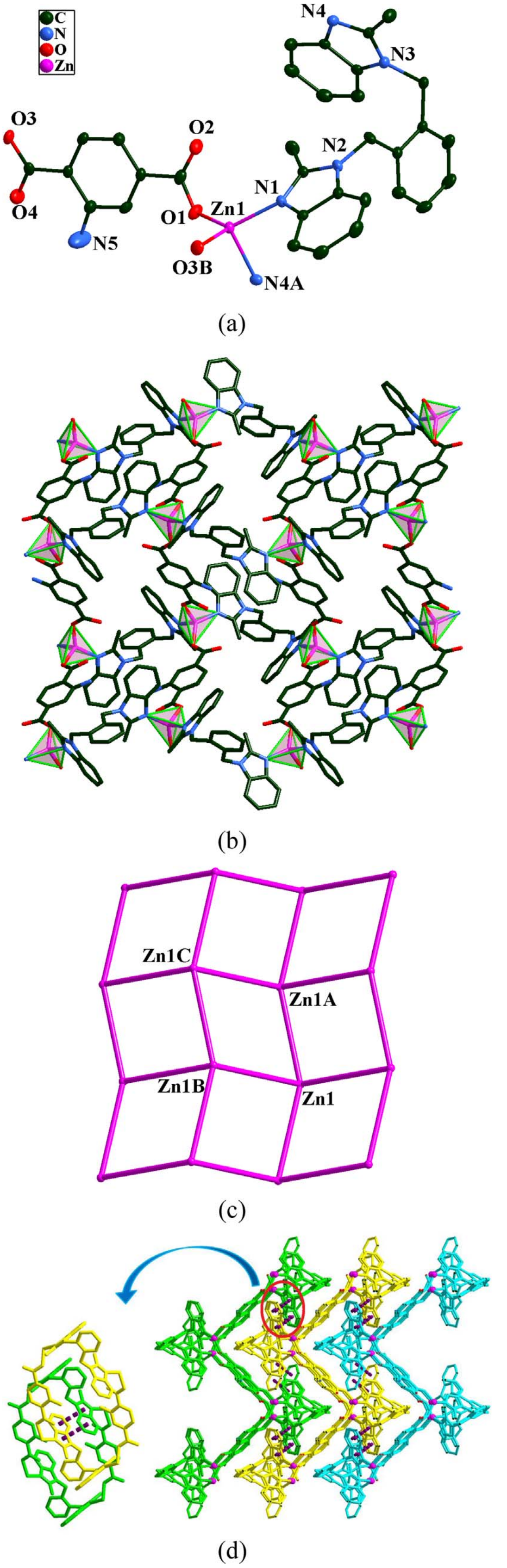
A mixture of $Zn(OAc)_2·2H_2O$ (0.2 mmol, 43.9 mg), L ligand (0.2 mmol, 73.2 mg), H_2atpt (0.2 mmol, 36.2 mg), and H_2O (10 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 140 °C for 3 days under autogenous pressure. Afterwards, the autoclave was cooled to room temperature at a rate of 5 °C·h^{-1}. Colorless block-like crystals of CP **1** were obtained. Yield: 42.4% based on Zn. Calc. for $C_{32}H_{27}ZnN_5O_4$ (610.98): C, 62.91; H, 4.45; N, 11.46%. Found: C, 62.45; H, 4.16; N, 11.75%. IR (KBr, cm^{-1}): 3331 w, 3142 w, 2914 w, 1570 s, 1370 s, 1260 m, 1132 m, 1067 m, 840 w, 537 w.

2.3. Synthesis of $[Zn(L)(atpt)]_n$ via a sonochemical process

Ultrasonic syntheses of CP **1** were carried out in an ultrasonic bath at room temperature and atmospheric pressure. To prepare the nanoparticle, a solution of zinc(II) acetate two hydrate with certain concentration in water was placed in an ultrasonic bath. Into this solution, we added a mix-ligand solution of L ligand and H_2atpt in water dropwise. For further studies, these series of experiments were performed in the concentration of all reagents of 0.005 M, times of 60 min, and power of 70 W. After that, the resulting precipitates were isolated by centrifugation, washed with some quantities of distilled cold water and drying in air. 64.1% of sample **1** was obtained referred to Zn. Calc. for $C_{32}H_{27}ZnN_5O_4$ (610.98): C, 62.91; H, 4.45; N, 11.46%. Found: C, 62.57; H, 4.21; N, 11.45%. IR (KBr, cm^{-1}): 3331 w, 3134 w, 2925 w, 1551 s, 1370 s, 1251 m, 1128 m, 1069 m, 830 w, 529 w. These processes were also done with other two various concentrations of all reagents (0.005, 0.01 and 0.05 M), different times (30 and 90 min), and different powers (40 and 100 W) to study its effects on the size and morphology of nanostructured CP **1**.

2.4. X-ray crystallography

Diffraction data for CP **1** was collected at 296(2) K with a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) and ω scan mode. Absorption corrections were applied using the SADABS program [32]. The structure was solved by direct methods and refined with full-matrix least-squares technique based on F^2 using the SHELXL-2016 program [33]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were placed in geometrically calculated positions and refined with isotropic thermal



(a)

(b)

(c)

(d)

(caption on next page)