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Synthesis and PPy loading for enhanced visible-light photocatalytic activity of new POMOFs containing silver chains

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ABSTRACT

A new polyoxometalate based hybrid compound containing Ag-Ag chain, $[Ag_{29}(trz)_{18}][SiW^{V}_{7}W^{VI}_{5}O_{40}]$ ($Ag_{29}SiW_{12}$), was synthesized by the simple one-step hydrothermal reaction of silver nitrate, 1, 2, 3- triazole (trz), and $[SiW_{12}O_{40}]^{4-}$ polyanion. Single crystal X-ray diffraction analysis shows that the $[SiW_{12}O_{40}]^{4-}$ polyanions as coordinating guests were successfully encapsulated into the metal-organic framework host matrix. The Keggin $[SiW_{12}O_{40}]^{n-}$ polyanions as templates and trz molecules as the small and delicate ligands play the decisive factors to the formation of silver chain. In addition, to improve the photocatalytic activity of the new compound $Ag_{29}SiW_{12}$, its polypyrrole (PPy) composite (PPy@$Ag_{29}SiW_{12}$) has been prepared and exhibits excellent photocatalytic activity (93.1% for MB and 48.8% for RhB) and selectivity adsorption (16.2 mg/g for MB and 1.60 mg/g for RhB) for organic dyes under the visible light radiation.

1. Introduction

Dye effluents produced by the textile industries have caused serious environmental pollution all over the world [1–3], and photo-catalytic technology is generally considered as one of the most effective energy-saving means to solve the issue [4–6]. As one kind of green and cheap photocatalysts with a similar band gap as TiO_2, polyoxometalates (POMs) with the excellent redox property and diverse structures have been widely studied as efficient photocatalyst for various reactions [7–10]. However, the pure bulk POMs present relatively low specific surface area, high solubility in aqueous solution and low stability under catalytic conditions, which hinder their applications as solid catalysts [11,12]. Thus, many strategies have been explored to immobilize POMs on various porous solid supports [13–17], among which a promising approach is the design and synthesis of POMs-based metal-organic frameworks (POMOFs) [18–20], where the inherent drawbacks of POMs can be significantly solved with respect to the neat solid. Meanwhile, POMs as template/building blocks can also provide very negative charge to construct novel MOFs. More important, as additional catalysis site, optically active pendants, and sensing units, the new MOFs could broaden the physicochemical properties of POMs [21–23].

High-nuclearity silver clusters have been studied extensively due to not only their fascinating structures but also their good catalytic properties [24–26]. A large number of high-nuclearity silver clusters have been obtained by the utilization of the templates [27–29], especially POMs template [30–33]. Moreover, MOFs containing silver cluster as host matrix may immobilize POMs owing to the strong affinity to N/O donors of organic ligands and the argentophilicity of Ag^+ ions [34–37]. As a result, the fruitful compounds based on POMs and Ag-MOFs have been reported, whereas the sole example containing an infinite Ag chain was described in the POMOF chemistry [38], to the best of our knowledge. To resolve the problem, the 1, 2, 3- triazole (trz) molecules with smaller steric hindrance and more coordination sites are employed in the work, which is advantageous to coordinate with more Ag^+ ions to facilitate the formation of the new silver clusters.

Based on the aforementioned consideration, hydrothermal reaction of trz and $AgNO_3$ with the Keggin polyoxoanions ($[SiW_{12}O_{40}]^{4-}$) as template led to the successful isolation of a new POMOF compound $[Ag_{29}(trz)_{18}][SiW^{V}_{7}W^{VI}_{5}O_{40}]$ ($Ag_{29}SiW_{12}$), in which a new kind of infinite silver chain is observed. In addition, due to the low photocatalytic activity of POMOFs (the inactive and low quantum yields) in the visible light [38–40], polypyrrole (PPy), by virtue of their highly delocalized cyclic-electron system, have been used to improve the photocatalytic efficiency of compound $Ag_{29}SiW_{12}$. And the results of the photocatalytic degradation of rhodamine B (RhB)/methylene blue (MB) indicate that the loading of PPy on the surface of $Ag_{29}SiW_{12}$ (PPy@$Ag_{29}SiW_{12}$) can effectively enhance the photocatalytic activity. Note that PPy@$Ag_{29}SiW_{12}$ as photo-catalyst exhibits good selectivity activities (93.1% for MB and 48.8% for RhB) for organic dyes under the visible light radiation (Scheme 1).

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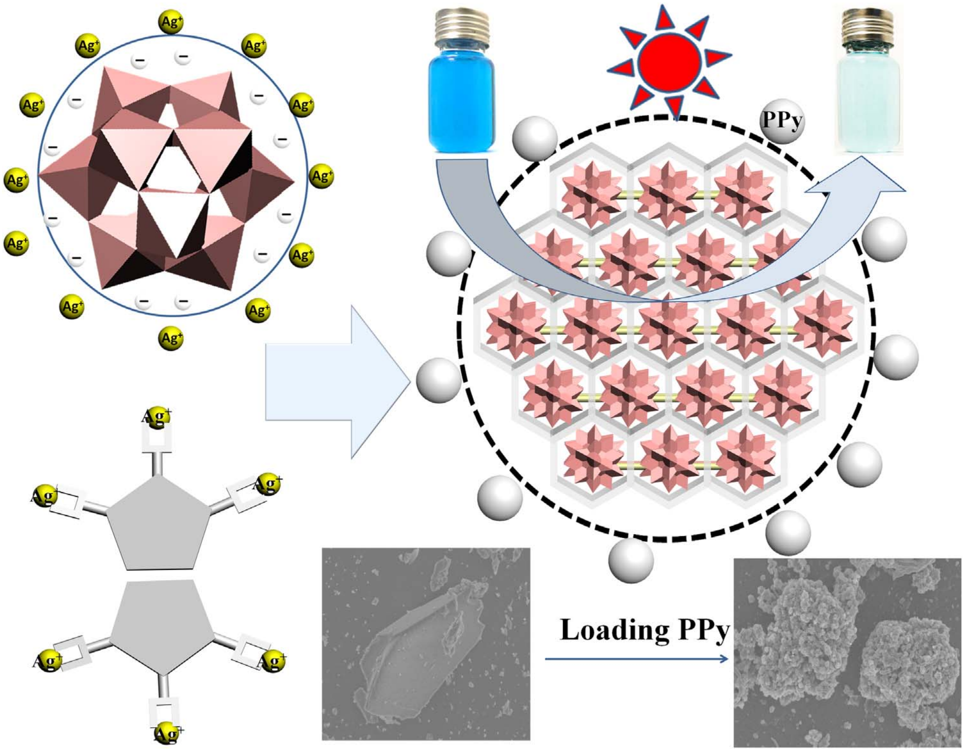

Scheme 1. Schematic representation of assembly process and its photochemical catalysis under the visible light irradiation by loading PPy.

2. Experimental section

2.1. Materials and methods

All reagents are purchased commercially and used without further purification. Elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer for C, H, N and a inductively coupled plasma mass spectrometry agilent 7700× for Ag. The IR spectrum was obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellet in the 400–4000 cm^{-1} region. The XRPD patterns were obtained with a Rigaku D/max 2500 V PC diffractometer with Cu-Kα radiation, the scanning rate is 4°/s, 2θ ranging from 5° to 40°. The diffuse reflectance spectra were scanned on T9 spectrometer, and the UV–vis spectra were recorded on a 756 CRT spectrophotometer. XPS analyses were performed on thermo ESCALAB 250 spectrometer with an Mg–Ka achromatic X-ray source. The thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer-7 thermal analyzer at a heating rate of 10 °C min^{-1}.

2.2. Synthesis of $[Ag_{29}(trz)_{18}][SiW^{V}_{7}W^{VI}_{5}O_{40}]$ ($Ag_{29}SiW_{12}$)

The mixture of $H_4SiW_{12}O_{40}$ (300 mg, 0.10 mmol), $AgNO_3$ (150 mg, 0.89 mmol), trz (30 mg, 0.43 mmol) was dissolved in distilled water (10 mL) with stirring for 0.5 h at room temperature, and pH value was adjusted to *ca.* 4.3 by 1 mol L^{-1} NaOH. The resulting solution was transferred into the 20 mL Teflon lined stainless steel container under autogenous pressure and heated at 170 °C for 4 days. After the autoclave was cooled to room temperature at 10 °C h^{-1}, the dull yellow block crystals suitable for X-ray crystallography were obtained, and then washed with distilled water and air-dried (yield: 36% based on Ag). Elemental analysis: Anal. calcd for $C_{36}N_{54}H_{36}Ag_{29}SiW_{12}O_{40}$ (7227.5): Calcd. C 5.98, H 0.50, N 10.46, Ag 43.33%; Found C 5.95, H 0.77, N 10.45, Ag 43.42%.

2.3. Synthesis of PPy@$Ag_{29}SiW_{12}$ hybrid material

Py (8.5 µL, 1.25×10^{-4} mol) was dissolved in 10 mL H_2O in a beaker. $Ag_{29}SiW_{12}$ (3.0 g, 4.1 $\times 10^{-5}$ mol) was also placed in the above solution and supersonically dispersed for 30 min. Finally, 10 mL ammonium persulfate (57 mg, 2.5×10^{-4} mol) solution was slowly added to the above mixture as oxidant. The mixture was stirred for 12 h, and then left undisturbed for 12 h. The resulting PPy@$Ag_{29}SiW_{12}$ hybrid material was separated, subsequently rinsed with water, alcohol and finally dried at 60 °C for 24 h in an oven.

2.4. Photocatalytic activity measurements

The photocatalytic activities of the as-prepared samples were evaluated by the degradation of RhB or MB as model dye under visible light irradiation. In a photocatalytic process, each 25 mg sample was mixed together with 50 mL of about 1.0×10^{-5} mol/L (C_0) RhB or MB solution in a beaker by ultrasonic dispersion for 10 min. The mixture was stirred over period of time till reached the surface-adsorption equilibrium. Then, the mixture was stirred continuously under visible light irradiation from a 300 W Xe lamp. At 1, 2, 3, 4, 5, and 6 h, about 3 mL of the sample was taken out from the reaction cell respectively, and the catalyst was separated from the suspension by high-speed centrifugation. The resulting solution was obtained for UV–vis analysis by examining the intensity of the maximal absorption peak. After the photocatalysis experiment, the catalyst was separated by filtration and soaked in the ethanol for removing the adsorbed organic dyes.

2.5. X-ray crystallographic study

Crystallographic data for compound $Ag_{29}SiW_{12}$ was collected on the Bruker SMART-CCD diffractometer with Mo-Kα radiation (λ = 0.71069 Å). The structure was solved by the direct method and refined full-matrix last squares on F^2 through the SHELXTL and OLEX2 software package [41]. All non-hydrogen atoms were refined anisotropically and the 'ISOR' command was used to refine some ADP