



A nonanuclear nickel cluster-based coordination polymer for solar hydrogen production from water in open atmosphere



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ARTICLE INFO

Article history:

Received 21 April 2016

Received in revised form 26 May 2016

Accepted 28 May 2016

Available online 31 May 2016

Keywords:

Cluster-based CP

Solar-driven H₂ production

Aerotolerance

ABSTRACT

In this work, a novel 2D double-layered metal-organic coordination polymer, [Ni₉(Hmna)₂(mna)₈(H₂O)₁₀](H₂O)₁₁ (**1**) (H₂mna = 2-mercaptionic acid), based on a nonanuclear nickel cluster was synthesized to function as an efficient heterogeneous catalyst with an optimized TON of 685.4 for solar-driven H₂ production from water. Both the solar conversion and water utilization were achieved simultaneously in this photocatalytic system. Without the protection of inert atmosphere, the catalyst was still able to produce hydrogen with a TON of 93.5 in air. The influence of oxygen was studied by virtue of cyclic voltammograms (CVs) and UV–vis adsorption spectrum. The active radicals generated in the photocatalytic process were examined by *in-situ* electron paramagnetic resonance (EPR) experiments which provided solid evidence to support the reductive mechanism.

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1. Introduction

The production of fuels from sunlight represents one of the major challenges to the development of a sustainable energy system [1–5]. Molecular hydrogen is the simplest fuel to produce which is considered to be an ideal “green” energy carrier and potential transportation fuel for the future. Platinum and other noble metals are efficient catalysts for photo-hydrogen evolution. However, for large scale use, it is urgent to explore new cost-effective materials with high efficiencies to replace these noble-metal catalysts.

Metal-organic coordination polymers (CPs) are a new class of hybrid inorganic-organic materials constructed by nodes of metal ions/clusters and multitopic organic linkers. Benefiting from their diverse structures and tailorable chemistry, CPs have become competitive candidates in some areas, such as chemical sensor, gas storage/separation and catalysis [6–15]. For solar hydrogen production, they have unique advantages as compared to other photocatalytic systems. Firstly, some of them, *e.g.* MIL-125, UiO-66 and their amino derivatives can act as semiconductors due to their

appropriate valence and conduction bands that are suitable for use in photocatalytic H₂ evolving systems [16–20]. In addition, they can be designed as photosensitizers or catalysts by modifying the linkers or nodes with some specialized chromophores, such as Ru- and Ir-based complexes and phthalocyanine derivatives, or by incorporating photocatalytic active complexes like [FeFe]-hydrogenase mimics into the polymers [17,21–29].

Although photo-evolution of H₂ based on CPs has recently made some progress, the activity is still expected to be improved. In addition, the poor stability of CPs during the catalytic process greatly restricts their application in this area. Therefore, it is necessary and urgent to explore novel CP material with both excellent stability and high activity for photo-H₂ production.

The superior robustness of cluster-based CPs endows them with natural advantages in heterogeneous catalysis [30]. Some of the well-known cluster-based CPs and their derivatives, for example, have been successfully applied in the photocatalytic H₂ production systems that function in aqueous media owing to their high stability in water [16,18,19,24,25]. However, all these systems are operated under inert atmosphere and their ability to tolerate oxygen, which is a crucial issue to practical application, has not yet been explored. Herein, we report a 2D double-layered coordination polymer, namely [Ni₉(Hmna)₂(mna)₈(H₂O)₁₀](H₂O)₁₁ (**1**) (H₂mna = 2-mercaptionic acid), in which a nonanuclear Ni-S cluster serve not only as a connecting node of the polymer, but also as the photocatalytic center. With the help of the highly active

Abbreviations: CP, coordination polymer; CV, cyclic voltammetry; Fl, fluorescein; EPR, electron paramagnetic resonance; TEA, triethylamine; QE, quantum efficiency; TON, turnover number.

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Ni-S site [31–35], compound **1** exhibits excellent performance in the photo-H₂ production with activity slightly higher than some noble-metal based CPs. Moreover, hydrogen was still able to be produced when **1** was suspended in the aqueous fluorescein (Fl) and triethylamine (TEA) just under the direct sunlight outdoors in open atmosphere, which is, as far as we know, firstly reported for the solar-driven system based on CPs.

2. Experimental

2.1. Materials and characterization

All chemicals were purchased and without further purification before use. The XML2 white light diode (LED) light was purchased from Cree Company and the light power was set to 2.02 W, which was measured by Yuanfang PMS-80_V1 system. The average light intensity of the white LED was measured to be 0.64 W/cm² by Yuanfang SPIC-200 spectral irradiance colorimeter. A Rigaku MiniFlex diffractometer was used to record the powder X-ray diffraction (PXRD) patterns of crushed single crystals in the 2θ range of 5–50°. The Bruker Vetex 70 was used to record the FT-IR spectrum and the Sartorius PB-10 pH meter was used to measure the pH value of the solution. The HRTEM diagrams were recorded on the field emission transmission electron microscope (FETEM) Tecnai F20 with the accelerating voltage of 200 kV.

2.2. Synthesis and characterization

A suspension of NiCl₂·6H₂O, KOH and 2-mercaptopicnic acid (1:2:1) in water (10 mL) was stirred in a Teflon pot before sealed in a stainless steel autoclave and heated at 453 K for one day. Pure yellow brown square crystals were obtained by filtration and repeatedly washed by water (yield 42% based on Ni). Anal. Found (%) for [Ni₉(mna)₁₀(H₂O)₁₀](H₂O)₁₁: C 28.53 H 3.29 N 5.62 S 13.10. Calcd (%): C 29.01 H 3.06 N 5.74 S 13.14. FT-IR (KBr pellet, cm⁻¹): 3434.5 (s), 1586.7 (s), 1544.1 (m), 1443.8 (w), 1395.7 (s), 1263.0 (w), 1225.8 (w), 1151.4 (w), 1130.2 (w), 1093.1 (w), 1061.6 (w), 987.3 (w), 875.7 (m), 769.3 (m), 673.7 (w), 647.5 (w), 567.3 (w). UV-vis (BaSO₄, nm, Fig. S1): 306.6 (s), 363.7 (s), 675.0 (w).

Crystallographic data: [Ni₉(Hmna)₂(mna)₈(H₂O)₁₀](H₂O)₁₁, *M*_r = 2440.28, monoclinic, *P*2(1)/*c*, *a* = 19.414(5) Å, *b* = 22.268(5) Å, *c* = 20.521(4) Å, α = 90°, β = 94.887(4)°, γ = 90°, *V* = 8840(3) Å³, *Z* = 4, θ_{max} = 27.49°, θ_{min} = 2.08°, ρ_{calcd} = 1.834 g cm⁻³, μ = 2.204 mm⁻¹, 20126 total reflections, 15869 observed (*I* > 2σ(*I*)), *R*₁ = 0.0617, *wR*₂ = 0.2430, GOF = 1.151. Other crystallographic data of **1** can be freely obtained from CCDC 1421257 in the Cambridge Crystallographic Data Centre.

2.3. Photocatalysis

Fluorescein and the ground catalyst **1** was added to an aqueous triethylamine (TEA) solution with the adjusted pH value in a Schlenk tube and the volume of the solution was kept at 10 mL. Before the illuminated by the white LED, the above mixture was freeze-pump-thaw treated for three times to keep the system under the specific atmosphere. If the photocatalytic test was conducted in the presence of air, no degassing treatment was carried out for the mixture before illumination. The hydrogen was monitored by gas chromatograph (Fuli 9790II) equipped with a thermal conductivity detector in negative polarity and a 5 Å molecular column (Φ3 mm × 3 m) heated at 353 K under argon atmosphere.

2.4. Quantum efficiency test

The Cree XTE sapphire blue LED (λ = 455 nm) and Cree XPE green LED (λ = 525 nm) were respectively used to replace the white LED

in the quantum efficiency test in the presence of catalyst (5 mg), fluorescein (4 mM) and triethylamine (15%) with the pH value of 10. The average intensity of the light (*I*) was measured by Yuanfang SPIC-200 spectral irradiance colorimeter and the irradiation area (*A*) was 3.14 cm². The amount of produced hydrogen (*n*_{H₂}) after the illumination for 1 h was determined by the GC and recorded in Table S1. The number of passed photons (*F*) was calculated based on the Eq. (1) and the quantum efficiency was calculated according to the Eq. (2).

$$F = \frac{E\lambda}{hc} = \frac{IA\lambda t}{hc} \quad (1)$$

$$QE = \frac{2n_{H_2}N}{F} \quad (2)$$

In the Eq. (1), *t* is the irradiation time, *h* is the Planck constant, and *c* is the speed of light. In the Eq. (2), *N* is the Avogadro constant.

2.5. Isotope experiments

An identical amount of deuterium oxide and aqueous deuterium chloride were used to replace water and hydrochloric acid in typical photocatalytic experiments. After illumination for 48 h, 5 mL gas above the solution was syringed out and injected into the gas chromatograph (Fuli 9790II) equipped with a thermal conductivity detector in positive polarity and a TDX-01 molecular column (Φ3 mm × 2 m) heated at 353 K under helium. The identical amount of gas produced during the photocatalytic reaction was also used for mass spectrometry (MS) analysis on Hiden-qic-20 mass spectrometer.

2.6. Electrochemistry

Electrochemical experiments were carried out on a CHI 600D electrochemical potentiostat. Cyclic voltammograms were recorded in a three-electrode cell under specific atmosphere with a glassy carbon disc (diameter 3 mm) as working electrode, a Ag|AgCl electrode as reference electrode and a platinum wire as auxiliary electrode. A 0.1 M sodium perchlorate solution was used as electrolyte. Compound **1** (5 mg) was dispersed in a mixture of water (1 mL) and Nafion (5%, 50 μL) before ultrasonicated for 30 min. Afterwards, 5 μL of the resultant mixture was applied to the surface of glassy carbon. After drying under illumination of infrared lamp, Nafion (0.05%, 10 μL) in ethanol was coated on the surface of the catalyst and dried again before the electrochemical test.

2.7. UV-vis spectrum

Liquid samples (0.02 mL) were syringed out during the photolysis at different time and then diluted by 100 times with the same aqueous TEA solution to record the UV-vis spectrum on PerkinElmer Lambda35 UV/vis spectrometer. For solid state UV-vis spectrum of **1**, the solid sample was mixed with BaSO₄ and grinded prior to the measurement.

2.8. Fluorescence quenching experiments

The emission spectra of Fl (0.01 mM) was detected by R928 photomultiplier detector on a Cary Eclipse fluorescence spectrometer with the excitation wavelength of 460 nm from a flash xenon lamp when increasing amount of **1** and TEA were added as quenchers, respectively.

2.9. Zeta potential measurement

The catalyst (5 mg) was suspended in aqueous sodium hydroxide (10 mL) containing fluorescein (4 mM) at pH = 10 and sonicated

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