



Robust photocatalytic reduction of Cr(VI) on UiO-66-NH₂(Zr/Hf) metal-organic framework membrane under sunlight irradiation

Xue-Dong Du^a, Xiao-Hong Yi^a, Peng Wang^a, Weiwei Zheng^b, Jiguang Deng^{c,*}, Chong-Chen Wang^{a,*}

^a Beijing Key Laboratory of Functional Materials for Building Structure and Environment Remediation, Beijing University of Civil Engineering and Architecture, Beijing 100044, China

^b Department of Chemistry, Syracuse University, Syracuse, NY 13244, United States

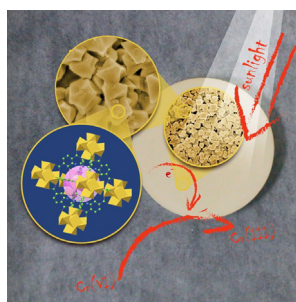
^c Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China



HIGHLIGHTS

- The UiO-66-NH₂ membranes were grown on the α -Al₂O₃ substrate.
- The membranes exhibited good photocatalytic Cr(VI) activities under sunlight.
- Foreign ions exposed no adverse effects to their photocatalytic activities.
- The UiO-66-NH₂(Zr/Hf) membranes possessed good recyclability and stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

UiO-66-NH₂(Zr/Hf)
MOF membrane
Photocatalysis
Cr(VI) reduction
Sunlight

ABSTRACT

The removal of toxic hexavalent chromium (Cr(VI)) ions from surface and ground water is highly demanded. While photocatalytic reduction of Cr(VI) to Cr(III) by traditional powder photocatalysts is a promising method, the difficult in the separation of the photocatalysts from the water hinders their wide practical applications. Herein we present the use of metal-organic framework (MOF) UiO-66-NH₂(Zr/Hf) membrane as photocatalysts to reduce Cr(VI) ions with high efficiency and easy separation from the treated waste water. The UiO-66-NH₂(Zr/Hf) MOF membrane photocatalysts were fabricated via a reactive seeding method on a α -Al₂O₃ substrate. It was found that the UiO-66-NH₂(Zr/Hf) membranes exhibited excellent photocatalytic Cr(VI) reduction performance under both simulated and real sunlight irradiation. The UiO-66-NH₂(Zr) membrane can maintain more than 94% Cr(VI) reduction efficiency after 20 cycles because of its exceptional chemical and water stability. The influences of foreign ions on Cr(VI) reduction were investigated to mimic real lake water, which revealed that no obvious adverse effects can be found with the presence of common foreign ions in surface water. The MOF membrane photocatalysts provide a new approach to carry out efficiently photocatalytic removal of pollutants in wastewater.

* Corresponding authors.

E-mail addresses: jgdeng@bjut.edu.cn (J. Deng), wangchongchen@bucea.edu.cn (C.-C. Wang).

<https://doi.org/10.1016/j.cej.2018.09.084>

Received 24 July 2018; Received in revised form 7 September 2018; Accepted 10 September 2018

Available online 11 September 2018

1385-8947/ © 2018 Elsevier B.V. All rights reserved.

1. Introduction

Among toxic heavy metal ions, hexavalent chromium (Cr(VI)) is a mutagenic and carcinogenic contaminant in surface and ground water, as it is widely utilized in electroplating, leather tanning, printing, polishing and pigment industries [1,2]. Up to now, many techniques such as adsorption [3], ion change [4], membrane filtration [5], and reduction from Cr(VI) to Cr(III) [6,7] have been developed to remove Cr(VI) from wastewater. The reduction from Cr(VI) to Cr(III) is highly desirable, considering Cr(III) has a lowly toxicity and easily forms insoluble precipitates such as Cr(OH)₃ in neutral or basic solutions [8]. Compared to traditional reduction technologies such as electrochemical reduction, chemical reduction, and micro-reduction, photocatalytic reduction of Cr(VI) to Cr(III) has the advantages of high efficiency, low-cost, and is free of any hazardous chemical formation [6]. Various nano-sized photocatalysts, such as TiO₂, ZnO, CdS, GaP, g-C₃N₄, and etc. [8–12], have been used to reduce Cr(VI) into Cr(III) under UV light or visible light. Unfortunately, these photocatalysts suffered from their quick electron-hole recombination, poor reduction efficiency and slow reduction rate [13]. As the emerging photocatalysts, metal-organic framework (MOFs) were widely utilized to efficiently reduce Cr(VI) into Cr(III) using photogenerated electrons, due to their merits of desirable topologies, high surface areas along with efficient light harvest via rational modification of organic linkers (like –NH₂) [13–18]. For instance, UiO-66-NH₂ and its derivatives have been used to accomplish outstanding photocatalytic Cr(VI) reduction [19,20]. However, both nano-sized photocatalysts and MOFs powders are very difficult to separate from treated water for recycle, which heavily hinders their practical applications [21]. Recently, the deposition of MOFs on substrates to fabricate corresponding membranes have attracted increasing attentions for use in catalysis, sensors, and especially separations [22,23]. However, up to now, only Zn₃(BTC)₂ MOF membrane was fabricated on zinc plates to conduct photocatalytic degradation of methylene blue to our best knowledge [24]. In this work, UiO-66-NH₂(Zr/Hf) membranes were fabricated on an α -Al₂O₃ support by a reactive seeding method. The MOF membranes were characterized by powder X-Ray diffraction (PXRD), Fourier Transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and UV-vis diffuse reflection spectroscopy (UV-Vis DRS). The UiO-66-NH₂(Zr/Hf) membranes demonstrated outstanding photocatalytic performance on Cr(VI) reduction under both simulated and real sunlight irradiation. The MOF membranes could be easily separated from treated solution and for further reuse, therefore exhibited great potential for the photocatalytic removal of pollutants from wastewater.

2. Experimental

2.1. Materials and characterization

All reagents and solvents were commercially available and used without further treatment. 2-Aminoterephthalic acid (H₂ATA, C₈H₇NO₄, 99.0%), zirconium tetrachloride (ZrCl₄, 98.0%), hafnium tetrachloride (HfCl₄, 98.0%) and 1,5-diphenylcarbazine (C₁₃H₁₄N₄O, 98%) were purchased from J&K Scientific Ltd. Potassium dichromate (K₂Cr₂O₇, guaranteed reagent), N,N-dimethylformamide (DMF, C₅H₁₃NO₂, analytical reagent), concentrated sulfuric acid (H₂SO₄, analytical reagent), phosphoric acid (H₃PO₄, analytical reagent), sodium hydroxide (NaOH, analytical reagent), anhydrous ethanol (CH₃CH₂OH), anhydrous acetone (CH₃COCH₃, analytical reagent), and acetic acid (HAc, CH₃COOH, analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd.

The PXRD patterns were recorded on a Dandonghaoyuan DX-2700B diffractometer in the range of $2\theta = 5^\circ$ – 50° with Cu K α radiation. The morphologies of membranes were studied by a field emission scanning electron microscopy (SEM) (SU8020, Hitachi Limited, Japan). The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet

6700 spectrometer in the range of 4000–400 cm^{–1} with KBr pellets. UV-visible diffuse-reflectance spectra (UV-vis DRS) of membrane were recorded from 200 to 800 nm with a Perkin Elmer Lamda 650S spectrophotometer, in which barium sulfate (BaSO₄) was used as the standard with 100% reflectance. The thickness of the membrane was measured by a SE850DUV ellipsometer with the incidence angle of 70°.

2.2. Preparation of UiO-66-NH₂(Zr) membrane

Alumina support was prepared by a solid-phase reaction [25,26] between alumina powder (particle size of ~1 μ m) and starch as a pore forming agent. Firstly, alumina powder and starch, with a mass ratio of 9:1, were mixed in the stainless-steel pot with the aid of a suitable amount of deionized water, and subsequently ground for 750 min to obtain slurry using a ball mill. Secondly, the slurry was heated and agitated at a high rate of speed until the water evaporated completely. Finally, alumina powder was pressed at 20 MPa to prepare disks with diameters of 25 mm and thicknesses of 3 mm. The disks were thermally treated at 1523 K for 12 h, and then cooled at rate of 274 K/min. One side of the α -Al₂O₃ support was polished with SiC sandpaper and washed in deionized water before being used for the growth of MOF membrane.

The UiO-66-NH₂(Zr) membrane was fabricated on an α -Al₂O₃ support by a modified reactive seeding (RS) method [27]. The synthesis includes two steps: (i) Seed growth: H₂ATA (2.0 mmol, 0.3623 g) was dispersed in deionized H₂O (25.0 mL) by sonication for 10 min. An α -Al₂O₃ support was placed horizontally in an 80 mL Teflon lined stainless steel autoclave with the H₂ATA aqueous solution. The autoclave was heated at 453 K for 12 h in an oven, and then cooled down to room temperature. After that, the seeded support was washed with deionized water and dried at 333 K for 6 h. (ii) Secondary growth: a mixture of ZrCl₄ (1.0 mmol, 0.2330 g), H₂ATA (1.0 mmol, 0.1812 g) DMF (17.0 mL) and acetic acid (7.0 mL) was sealed in an 80 mL Teflon lined stainless steel autoclave containing the seeded support. The autoclave was heated at 423 K for 48 h in the oven, and then cooled down to room temperature. Finally, the MOF membrane was washed with DMF and anhydrous ethanol, and then dried at 333 K for 6 h before further analysis. Preparation of UiO-66-NH₂(Hf) membrane followed the same procedure as the UiO-66-NH₂(Zr) membrane, except that ZrCl₄ (1.0 mmol, 0.2330 g) was replaced with HfCl₄ (1.0 mmol, 0.3203 g).

2.3. Electrochemistry measurements

The study of the electrochemical properties of UiO-66-NH₂(Zr/Hf) membranes proved difficult as the Al₂O₃ substrate provided electrical insulation. In this study, we carried out the electrochemical measurements using UiO-66-NH₂(Zr/Hf) powder samples following identical conditions to that of the membranes. To prepare the working electrodes, 5.0 mg UiO-66-NH₂(Zr) or UiO-66-NH₂(Hf) powder samples were mixed with 400.0 μ L ethanol/Nafion ($v/v = 19/1$), which was dispersed under sonication for 30 min. 10.0 μ L prepared slurry was drop-casted onto the surface of a FTO substrate (1.0 cm \times 1.0 cm), and then dried in air at 353 K for 30 min. This step was repeated five times to ensure the uniform coverage of UiO-66-NH₂(Zr) or UiO-66-NH₂(Hf) samples on the FTO substrate. The electrochemical measurements were performed via a Metrohm Autolab PGSTAT204 electrochemical station in a typical three-electrode mode with 0.2 M Na₂SO₄ solution (pH = 6.8) as the electrolyte. A saturated Ag/AgCl electrode and a platinum (Pt) electrode were used as the reference electrode and counter electrode, respectively. A 300 W Xenon lamp (Beijing Aulight Co., Ltd) was used as a light source.

2.4. Photocatalytic experiment

The photocatalytic reduction of Cr(VI) into Cr(III) was carried out at room temperature in a 300 mL quartz reactor containing an as-prepared

Download English Version:

<https://daneshyari.com/en/article/10145202>

Download Persian Version:

<https://daneshyari.com/article/10145202>

[Daneshyari.com](https://daneshyari.com)