Green Approach for Metal Oxide Deposition at an Air−Liquid−Solid Triphase Interface with Enhanced Photocatalytic Activity

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Supporting Information

ABSTRACT: Bioinspired superhydrophobic substrates have been used in many scientific and technological areas. These substrates can trap atmosphere-linked air pockets at the solid−liquid interface, offering an opportunity to address the oxygen-deficit problem in many reaction systems. Herein, we addressed the oxygen-deficit problem in metal oxide electrochemical deposition by using a triphase electrode possessing an air−liquid−solid joint interface. Oxygen in the interface is directly available from the air phase for sufficient OH− production via oxygen cathodic reaction, thereby offering us a green approach to fabricate two-dimensional mesoporous ZnO nanoarrays over a wide range of current densities. Further, because metal oxides are deposited at the triphase interface, sufficient O2, a natural electron scavenger required in photocatalytic reaction to suppress the recombination of photogenerated electron−hole pairs, can be directly supplied, and we demonstrated their enhanced photocatalytic reaction kinetics in water remediation. The present work highlights a powerful interface-engineering strategy for fabricating metal oxides with unprecedented photocatalytic ability.

1. INTRODUCTION

Inspired from the natural nonwetting surfaces, artificial superhydrophobic substrates have been fabricated and used in many scientific and technological areas, including drug release, crystal assembly, enzymatic reactions, and photocatalysis. Immersed in an aqueous solution the superhydrophobic surface traps numerous air pockets at the solid−liquid interface, linking atmospheric oxygen to the electrode surface by which sufficient oxygen can be rapidly supplied from the ambient atmosphere. This approach offers an excellent opportunity for addressing the oxygen-deficit problem in many reaction systems.

We report here a green approach for electrodeposition of ZnO, a model oxide, by using a triphasic electrode system with an air−liquid−solid (A−L−S) interface. Because of its excellent optical and electrical properties two dimensional (2D) mesoporous ZnO has received great attention in a wide variety of fields. Various methods have been reported, including electrodeposition, ionic layer epitaxy, thermal plasma, and solvothermal. Of these approaches, electrodeposition is of considerable interest because of its low cost and easy scale up. During electrodeposition, OH− is first generated by reduction of an oxygen source which, in turn, reacts with Zn2+ to form Zn(OH)2. ZnO is subsequently formed via dehydration between the OH ligands. For the electrodeposition reaction to efficiently proceed, it is necessary that a certain concentration of toxic additives, such as NO3−, H2O2 or ClO4− be available at the electrode/electrolyte interface (e.g. NO3− + H2O + 2e− → NO2− + 2OH−). While natural oxygen (O2) is an effective electron acceptor, and can easily be reduced at the electrode surface to generate OH− (O2 + 2H2O + 4e− → 4OH−), the extremely low solubility and slow mass transport rate of oxygen in aqueous solutions has limited its practical application in metal oxide deposition.

In this work, we address the O2 deficit problem in ZnO electrodeposition by developing an A−L−S triphase electrochemical reaction interface as illustrated in Figure 1a. Such a reaction system allows for the rapid transport of O2 directly from the atmosphere to the electrode surface, rather than through the liquid phase as common with conventional diphase electrodeposition systems, where it is electrochemically reduced to produce OH−. The A−L−S triphase electrochemical reaction interface enables a locally high interfacial pH value independent of the bulk phase condition. The resulting OH− will react with Cl− and Zn2+ ions to produce Zn(OH)Cl2. Crystal growth is limited along the (001) direction because of preferential adsorption of Cl− in the surface, hence, 2D Zn(OH)Cl2 nanosheets are formed. Consequently, 2D mesoporous ZnO nanosheets can be obtained via a thermal phase transformation approach as illustrated in Figure 1b.
2. RESULTS AND DISCUSSION

To fabricate the triphase electrodeposition system, a micro-porous carbon fiber substrate was first subjected to a poly(tetrafluoroethylene) (PTFE) treatment (see Experimental Section for details). Figure 2a shows a typical scanning electron microscopy (SEM) top view image of the micro-porous electrode substrate and a nearly spherical water droplet placed on the substrate with a water contact angle (CA) of 152° ± 2°, indicating a superhydrophobic surface. One side of the substrate, where the electrodeposition reactions take place, is then exposed to a brief oxygen plasma treatment to reduce the interfacial resistance and enhance the electron transfer between the substrate and the electrolyte. Partially immersed in an aqueous electrolyte, an $A^{-}L^{-}S$ triphase interface is formed because of the air pockets trapped at the electrode/electrolyte interface.

Figure 2b is a typical SEM image of the hexagonal structured Zn$_5$(OH)$_8$Cl$_2$ 2D nanoarrays electrodeposited at a current density of $-2$ mA/cm$^2$ using the triphase electrode; the nanosheets are about 1.2 μm in diameter and 30–50 nm in thickness. The X-ray diffraction (XRD) pattern of the as-prepared samples (red curve of Figure 2c) can be respectively indexed to (021), (202), and (205) of the standard Zn$_5$(OH)$_8$Cl$_2$ (JCPDS card no. 07-0155). In marked contrast, no materials are obtained (data not shown here) when the deposition is attempted using a traditional diphasic electrode (e.g. hydrophilic carbon fiber, fluorine-doped tin oxide substrate), where oxygen at the reaction interface has to diffuse through the liquid phase.

To help understand the formation process of hexagonal Zn$_5$(OH)$_8$Cl$_2$ nanosheet arrays, using a triphase electrode synthesis experiments were carried out at different current densities ranging from $-0.3$ to $-10$ mA/cm$^2$. At a relatively low current density, $-0.3$ mA/cm$^2$, see Figure 2d and the black curve of Figure 2c, only a small amount of hexagonal Zn$_5$(OH)$_8$Cl$_2$ nanosheets were obtained, with most of the material having no regular microstructure. At low current densities, OH$^{-}$ is produced at low concentration, and hence, Cl$^{-}$ plays a major role in determining the resultant morphology. At higher current densities, $-0.5$ to $-7$ mA/cm$^2$, a higher local interfacial pH value is obtained, leading to the formation of a higher density of regular hexagonal Zn$_5$(OH)$_8$Cl$_2$ nanosheets (Figure 2e and blue curve of Figure 2c). When the current density was further increased beyond $-8$ mA/cm$^2$ ZnO nanoparticles, rather than nanosheets, were obtained. In this case the high interfacial pH value favors the direct reaction between OH$^{-}$ and Zn$^{2+}$ with the subsequent formation of Zn(OH)$_2$. ZnO nanoparticles are formed because of dehydration between the OH ligands. Figures 2f and S1 show that ZnO nanoparticles, approximately 70 nm in diameter, are obtained at a current density of $-10$ mA/cm$^2$.

Figure 1. (a) Schematic illustration of Zn$_5$(OH)$_8$Cl$_2$ synthesis by electrodeposition using an $A^{-}L^{-}S$ triphase reaction interface. Oxygen is directly transported from the ambient atmosphere to the electrode surface. OH$^{-}$ is in situ generated through the oxygen reduction reaction ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^{-}$), which enables a locally high interface pH. (b) Evolution process of the 2D mesoporous ZnO nanosheets.

Figure 2. (a) FE-SEM image of the nanoporous electrically conducting carbon fiber substrate used in this work; the inset is a photograph of a spherical water droplet placed on the substrate with a water CA of 152 ± 2°, indicating a superhydrophobic surface. (b,d−f) are FE-SEM images of the samples fabricated at current densities of $-2$, $-0.3$, $-7$, $-10$ mA/cm$^2$, respectively, with insets showing magnified images. (c) XRD patterns of samples deposited at current densities of $-0.3$ mA/cm$^2$ (black curve), $-2$ mA/cm$^2$ (red curve), and $-7$ mA/cm$^2$ (blue curve) using the triphase electrode.
For organic pollutant remediation in water. Despite great efforts to optimize photocatalytic activity of ZnO, the reaction interface architecture, a crucial factor to the performance of metal oxides. The triphase reaction system enables the rapid transport of oxygen, a natural electron acceptor, from air phase to the reaction interface for efficient production of reactive oxygen species such as O$_2^*$ and OH$^*$ for efficient oxidation reactions.

3. CONCLUSIONS

In summary, by development and use of an A−L−S triphase electrochemical reaction system we have addressed the long-standing O$_2$ deficit problem inherent to electrodeposition of metal oxides. The triphase reaction system enables the rapid transport of oxygen, a natural electron acceptor, from air phase to the reaction interface for sufficient production OH$^−$ concentrations. We have demonstrated the system with synthesis of 2D mesoporous ZnO nanosheets, and applied these in application to photocatalytic degradation of RhB, an efficient natural electron scavenger needed to suppress recombination of photogenerated electron−hole pairs during photocatalytic reaction systems, with correlation coefficients higher than 0.99. The k value of A−L−S reaction was calculated to be 0.02366 min$^{−1}$, a value approximately 7-fold higher than that of the N−L−S system (0.00331 min$^{−1}$). These results indicate that the solid−liquid−air triphase photocatalytic reaction interface is very advantageous for promoting photodegradation kinetics. In the A−L−S photocatalytic system, sufficient O$_2$ at the interface can be supplied directly from the air phase, which can efficiently remove photogenerated electrons from the surface of the photocatalysts, thereby suppressing the electron−hole pairs recombination and generating larger amounts of oxidative reactive oxygen species such as O$_2^*$ and OH$^*$ for efficient oxidation reactions.

Figure 3. (a) Powder XRD patterns of the as-prepared ZnO nanosheets. (b,c) are, respectively, FE-SEM images of mesoporous nanosheets at low and high magnifications. (d) High resolution TEM images of a mesoporous ZnO nanosheet.

Figure 4. Degradation of RhB under UV light illumination. (a,b) are, respectively, illustrations of photocatalytic reaction interface based on the A−L−S triphase system and nitrogen−liquid−solid (N−L−S) system. (c) Degradation of RhB by mesoporous ZnO nanosheets based on the A−L−S triphase system (red curve) and N−L−S triphase system (blue curve). (d) Photocatalytic kinetic of mesoporous ZnO nanosheets based on the A−L−S triphase system (red curve) and N−L−S triphase system (blue curve).
organic pollutant. The triphase reaction system reported here can be readily extended to electrodeposition of other metal oxides, and thus represents a novel opportunity for obtaining high-performance photocatalysts.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Zinc chloride (ZnCl₂, ≥98%) was purchased from Sigma (USA). Potassium chloride (KCl, ≥99.8%), and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). RhB was used as probe pollutant. All chemicals were directly used without further purification. All solutions were prepared with Milli-Q water (18.2 MΩ-cm, Hitech laboratory water purification system).

4.2. Preparation of ZnO Nanostructures. A carbon fiber substrate filled with carbon powder (~20 nm) was cleaned by sonication in water and ethanol (15 min each) and then immersed in a PTFE suspension (2 wt %) for 10 min. It was removed from the suspension, dried in air, and then annealed at 350 °C for 30 min. At this point the carbon fiber substrate showed superhydrophobic properties. The superhydrophobic carbon fiber substrates were then cleaned by using a mixture of ethanol and water (for 3 min) in an ultrasonic bath and dried in air. One side of the substrate was then exposed to a short-term oxygen plasma (100 mW, 3 min) treatment. Mesoporous ZnO nanosheets were prepared on the substrates by cathodic electrodeposition from an aqueous solution composed of 50 mM ZnCl₂ and 2.0 M KCl kept at room temperature for 3 min, followed by thermal decomposition removing HCl(g) and H₂O(g) at 400 °C. Electrodepositions were carried out on a CHI 660E workstation (CHI Instruments Inc., Austin, USA) with a platinum wire as the counter electrode and a saturated calomel electrode as a reference electrode.

4.3. Photocatalytic Measurements. The photocatalytic performance was evaluated by the photodegradation of RhB in water. The photodegradation reactions were conducted in a quartz cell (1.0 cm × 1.0 cm × 4.5 cm) containing 2 mL of RhB (15 mg/L). The portion of substrate covered by ZnO was immersed in RhB solution, while another part of substrate (free of ZnO) was exposed to air. 2D mesoporous ZnO nanosheets obtained at ~2 mA/cm² were chosen as photocatalysts. The mass of the photocatalyst deposited on the substrate was 0.5 mg. Before testing, an absorption step was carried out in the dark to reach the absorption–desorption equilibrium. The photocatalytic system was then illuminated with a UV lamp. The absorption spectrum of the RhB solution was measured every 15 min using the UV–vis spectrophotometer, with absorption used to calculate the concentration of the remaining RhB. Photocatalytic reactions were also conducted in a N–L–S system, with the air phase of the triphase interface replaced with nitrogen.

4.4. Characterization. Morphologies were observed by SEM (Hitachi S4700, Japan) and TEM (Tecnai G2 F20 S-Twin, America). XRD analysis was performed using an X-ray powder diffractometer (X’Pert Pro MPD, Holland Panalytical). A CA goniometer (JC2000D6, Powereach, Shanghai, China) was used to measure the water CA. Plasma treatment was performed using a plasma cleaner (SAOT, 5D, China). Photocatalytic degradation was measured by a UV–vis spectrophotometer (Evolution 220, Thermo, America).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03234.

XRD patterns of samples deposited at current density of ~10 mA/cm²; experimental setup for the photocatalytic reaction; emission spectrum of UV lamp used in photocatalytic experiments (black curve line) and UV-Vis absorption spectras of the RhB solution (red curve line); degradation of RhB using two different triphase photocatalytic systems under UV light (PDF).

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Notes

The authors declare no competing financial interest.

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