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SECM evaluations of the crystal-facet-correlated photocatalytic activity of hematites for water splitting

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ABSTRACT

Physical structure determines nanocatalytic performance. A comparative study was performed using scanning electrochemical microscopy (SECM) in imaging mode and electrochemical impedance spectroscopy (EIS), demonstrating that crystal facets play an important role in the action of hematite as a photocatalyst for water splitting. The mass specific activity of the facets was found to be in the order {110} > {012} > > {001}, regardless of whether the hematite was sensitized by cadmium sulfide quantum dots (CdS QDs). However, the photocatalytic performance of 2D nanoplates with {001} and {110} facets improved dramatically on sensitization with CdS QDs. This was attributed to spatially separated transport of photogenerated charges on different facets, as shown by the selective deposition of CdS QDs and platinum clusters on the {110} facet. The work demonstrates the importance of crystal facet engineering in nanocatalysis.

1. Introduction

Synthetic nanotechnology has made it possible to create nanomaterials with defined crystal facets; crystal facet engineering allows us to correlate physical structure with catalytic performance, which, in turn, is helpful in the design of nanocatalysts [1,2]. Metallic nanocrystals with high-index facets have been shown to have particularly high catalytic activity [2]. Semiconductor photocatalysts with well-defined morphology have also aroused extensive research interest because of their facet-correlated activity [3,4]. Recently, crystal facets have been found to play a crucial role in charge transport and transfer in photocatalytic systems [5–9]. Photogenerated electrons and holes can be transported on specific facets, as evidenced by the selective photodeposition of metallic oxides and metal nanoclusters on different crystal facets of a $BiVO_4$ photocatalyst [7]. Moreover, the synergetic effect of dual co-catalysts acting separately on different facets of $BiVO_4$ has been reported to enhance its photocatalytic performance in water splitting [8]. In brief, crystal facet engineering has become cutting edge in heterogeneous catalysis [1].

With a band gap of 2.2 eV, hematite (α-Fe_2O_3) is a prospective photocatalyst due to its visible light activation, chemical stability, environmental friendliness and wide availability [10]. However, its low light harvesting efficiency inhibits its application in photovoltaic conversion [11,12]. Crystal facet engineering was therefore used to improve its photocatalytic performance [13–18]. Various hematite samples with defined morphologies were obtained, including 1D nanowires, 2D nanosheets as well as 3D nanocubes and polyhedrons [19,20]. Heterojunctions, dye and QD sensitizers were also included in the photoanode designs [21]. In this paper we carry out a comparative study on the correlation between the crystal facet of hematite and its photocatalytic activity for water splitting. We find that facet-selective sensitization using CdS QDs on 2D hematite nanoplates can dramatically improve photocatalytic activity.

2. Instruments and experiments

Sodium sulfide (Na_2S), cadmium chloride ($CdCl_2$), sodium chloride (NaOH), chloroplatinic acid (H_2PtCl_6) and ethyl alcohol (EtOH) of analytical grade were obtained from Sinopharm Co. The 1D nanorods, 2D nanosheets and 3D nanocubes of hematite were gifts from Prof. Xingjiu Huang [20]. FTO conductive glass slides (thickness 2.2 mm, 14 Ω/cm^2) were purchased from Jing Ge Solar Tech Co., Wuhan. All aqueous solutions were prepared with deionized water (18.2 MΩ·cm, Milli-Q, Millipore Co.).

SECM and EIS were used to study the photocatalytic effect of the hematite samples. The preparation of the SECM substrate was as reported before, where an FTO slide was covered by a light mask to improve the signal/noise ratio [22,23]. 2 mg hematite and 10 μL diacetone were dispersed in 200 μL deionized water. 10 μL slurry was deposited into the spots with a microsyringe. The substrate was dried at 100 °C for 1 h. 15 Micro-SILAR cycles were performed to load CdS QDs on the hematite by alternately using 0.01 M $CdCl_2$ and 0.01 M Na_2S.

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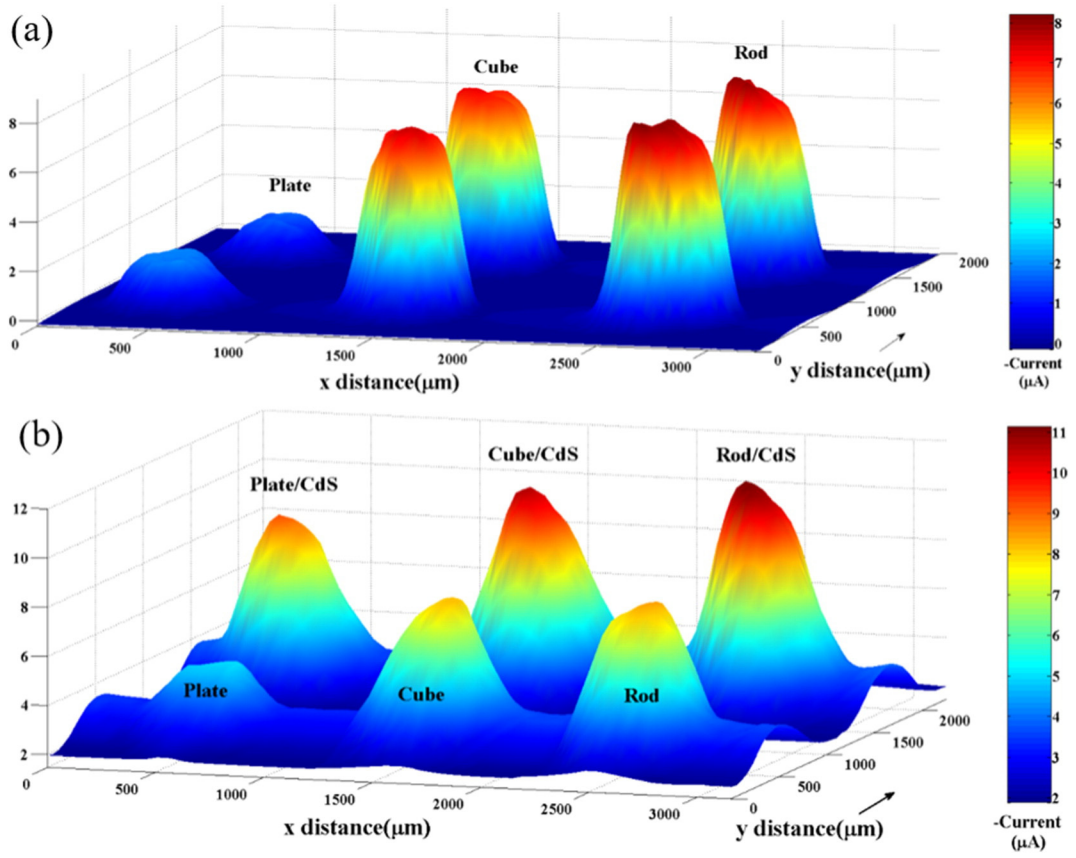

Fig. 1. SECM images of hematite nanocatalyst array on the FTO substrate: (a) two parallel images of the non-sensitized hematites; (b) the contrasting images of the non-sensitized and the CdS QDs sensitized hematites. Substrate potential is biased at 0.2 V vs. Ag/AgCl reference electrode, the electrolyte is an aqueous solution with 0.1 M NaOH, the illumination intensity is 50 mW/cm^2, tip — substrate distance is 100 μm, and the scanning rate is 200 μm/s.

The photoanodes for the EIS experiments were prepared by blading hematite on an FTO slide (area: 0.5 cm^2) and sensitizing it with CdS QDs using normal SILAR procedures [22,23]. Since the experiments were finished in a short period of time, the effect of CdS QD corrosion can be neglected.

SECM experiments were performed using a CHI 920C workstation (CH Instr. Co.). The FTO substrate, an Ag/AgCl wire and a platinum wire acted as the working, reference and counter electrodes, respectively. A 200-μm-diameter optic fiber was used as the SECM tip and the photocurrent response was recorded. EIS experiments were carried out using a Solartron 1260 workstation (Ametek Co.). A Xenon lamp (100 mW/cm^2) was the light source. Transmission electron microscopy (TEM, JEM-2100, JEOL Co.) was employed to characterize the morphology of the materials.

3. Results and discussions

The morphologies of the hematite samples were characterized by TEM as reported elsewhere [20]. The 1D nanorods and 3D nanocubes have a single crystal facet {110} and {012}, respectively. The 2D nanoplates have a major facet {001} and a minor one {110}. Under illumination, the photogenerated electrons transfer to the counter electrode and reduce water to hydrogen, and the residential holes oxidize water to oxygen on the photocatalyst spots [10]. The SECM images (Fig. 1) reflect visually the photocatalytic activity of the hematite samples. The photocurrents of the 1D nanorods, 2D nanoplates and 3D nanocubes are 8.2 μA, 2.1 μA and 7.1 μA, showing a mass specific activity in the order {110} > {012} > > {001}. However, when sensitized by CdS QDs the photocurrent of the 2D nanoplates increases dramatically and is almost comparable to those of the 1D nanorods and 3D nanotubes (Fig. 1b).

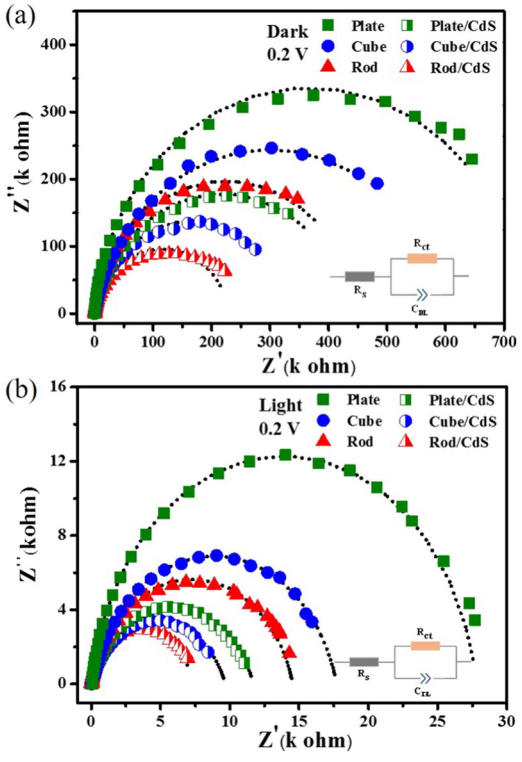

Fig. 2. Electrochemical impedance spectra of the six types of photoanodes obtained in the dark (a) and under illumination (b) in an aqueous solution with 0.1 M NaOH. The amplitude of the sinusoidal perturbation is 5 mV, the frequency ranges from 100 KHz to 0.01 Hz and the potential bias of the photoanodes is 0.2 V vs. Ag/AgCl reference electrode.