Nanostructured hierarchical hematite photoanode from hydrothermal synthesis for efficient solar water oxidation

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Hematite (α-Fe2O3), which is most common form of iron oxide, is a promising material for a photoanode in electrochemical solar water splitting because of its small band gap (~2.1 eV) that enables absorbing visible light and its excellent stability in aqueous conditions. However, the photoactivity of hematite is limited by its low conductivity, slow water oxidation kinetics and short diffusion length of holes. Typically, nanostructuring and adopting appropriate dopants and catalysts are used to overcome the drawbacks. Here, we fabricated all-iron oxide based triple-layered hematite photoanode, because iron is one of the most abundant elements in earth, which makes it an appropriate material for photoanode. We introduced undoped hematite underlayer that lowered onset potential and improved photocurrent, and β-FeOOH overlayer which also improved photocurrent by catalyzing water oxidation.

The hierarchical nanostructure was fabricated by controlling only composition of iron-oxides using the hydrothermal synthesis from an aqueous solution with 0.15 M of iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and 1 M of sodium nitrate ($NaNO_3$). β-FeOOH nanorod array were uniformly formed on FTO substrates by the synthesis at 95 °C for 13 hours. The hematite photoanode can be fabricated by a thermal treatment of β-FeOOH at 550 °C, whereas without the thermal treatment, β-FeOOH itself can be used for an electrocatalyst for OER. Doping in hematite was performed by adding titanium butoxide ($Ti(OBu)_4$) into the precursor solution. Undoped hematite underlayer, was formed by shortening the synthesis time to 50 min. β-FeOOH catalyst was formed on hematite nanorods using the synthesis for 20 min from undoped precursor solution.

Photoelectrochemical characterization were performed in 1 M NaOH (pH 13.6) electrolyte using a three-electrode electrochemical cell configuration with a SCE reference electrode and Pt foil counter electrode. The 300 W xenon lamp and AM 1.5G filter were used to illuminate with intensity of 100 mW·cm^{-2}.

Figure 1 shows the SEM images of Ti-doped hematite (DH), Ti-doped hematite with undoped hematite underlayer (U/DH), Ti-doped hematite with undoepd hematite underlayer and β-FeOOH overlayer (U/DH/A). Hematite nanorods has the diameter about 50 nm and the neight of 500 nm. Structure of DH and U/DH were pretty similar, so the underlayer did not changed the morphology of nanorods. β-FeOOH bumps on hematite nanowires were observed in U/DH/A and the feature size were the order of nanometer scales.

Figure 2 shows the photocurrent density from hematite photoanodes. Because it is known that undoped hematite shows no photoactivity and DH shows photocurrent of 1.32 mA/cm^2 at 1.23 V vs. RHE, Ti was successfully doped into the hematite nanowires.

The undoped hematite underlayer was effective for both increasing photocurrent and lowering onset potential.

The photocurrent of U/DH at 1.23 V vs. RHE was improved to 1.51 mA/cm^2, and onset potential was reduced about 40 mV from 0.88 V to 0.84 V vs. RHE. Because undoped hematite has large resistivity enough to block the back dirrusion of electrons from FTO substrate, the improvements by the underlayer can be caused by the suppressed recombination of holes near the interface with FTO. In addition, because undoped hematite forms homojunction, the concern for the matching of band edge can be ruled out, and also the interface should have less defect than heterojunction thereby generating less recombination centers.

β-FeOOH overlayer also increased the photocurrent. The photocurrent of U/DH/A at 1.23 V vs. RHE was improved to 1.64 mA/cm^2, but onset potential was shifted anodically to 0.93 V vs. RHE. The reason for anodic shift is because β-FeOOH has lower conduction band edge and lower valence band edge than hematite, photogenerated carriers have to overcome the barrier to be transported to β-FeOOH overlayer. However, with the applied potential that is high enough to thin the barrier so that the photogenerated holes can be transferred through it, more holes can react and the sharper increasement of photocurrent was observed.

In this study, we fabricated highly photoactive iron oxide based photoanode only differing the composition and phase of it. The photocurrent and onset potential was improved with adopting undoped hematite underlayer by reducing recombinations from back diffusion of electrons of FTO. β-FeOOH overlayer also improved photocurrent by catalyzing the water oxidation kinetics.
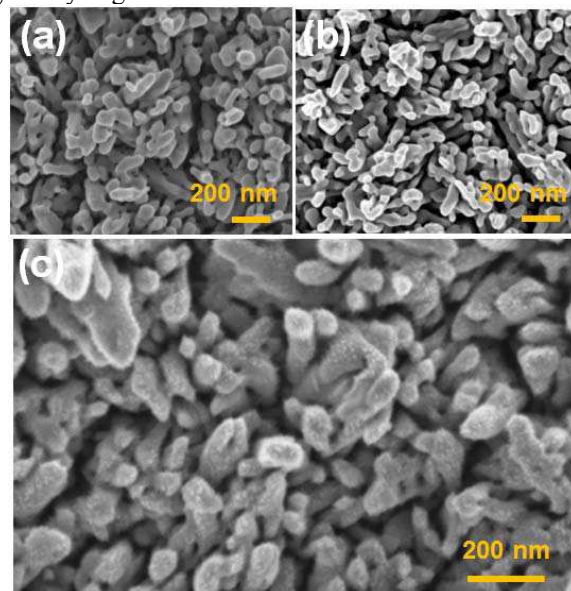
Figure 1. SEM images of the hematite formed by hydrothermal synthesis, (a) DH, (b) U/DH, (c) U/DH/A.
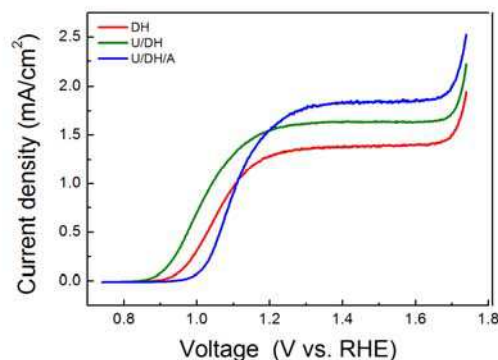
Figure 2. Photocurrent density versus voltage curves of the hematite photoanode. Red line indicates DH, green line indicates U/DH, and blue line indicates U/DH/A