BDD modified with bismuth oxyiodide quantum dots; application in photoelectrochemical water remediation and hydrogen production.

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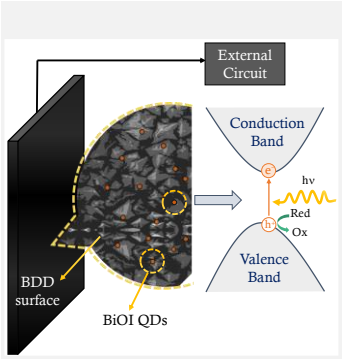

Quantum dots used as photocatalysts increase light harvesting over their bulk counterparts, and the construction of quantum dot-based photoelectrodes would improve the performance of photoelectrochemical processes. Here, we present the photoelectrochemical study of a boron-doped diamond electrode modified with BiOI quantum dots. The photoelectrode was constructed in a two-step synthesis, and its properties were evaluated by cyclic voltammetry, photocurrent and impedance. It proved to be a photoelectrode that significantly improves carrier transfer, and a maximum photocurrent of 0.23 mA . This photoelectrode would be useful for photoelectrochemical oxidation and reduction processes under visible light conditions.

Introduction

Photoelectrochemistry is about harnessing light and electricity to promote efficient energy conversion processes [1,2]. Photoelectrocatalysis as an advanced oxidation process for water decontamination is a cutting-edge technology in this field, requiring materials with superior optical and electronic properties to perform charge transfer reactions [3]. Quantum dots (QDs) are semiconductor nanocrystals that exhibit high optical yields, i.e., they harness light more efficiently than their bulk counterparts, making them valuable materials as photocatalyst [4]. By immobilizing quantum dots on an electrocatalyst substrate, the photocatalytic and electronic properties of what is known as a photoelectrode are boosted. This is the essential component of a photoelectrochemical system, as the overall performance of the process depends on it.

We present a boron-doped diamond photoelectrode modified with bismuth oxyiodide quantum dots (BDD/BiOI QDs) and explore its photoelectrochemical properties that can be exploited for the degradation of contaminants of concern, hydrogen generation or photoelectrosynthesis.

Material and Methods

All chemicals were used without further purification. A two-step synthesis was used to obtain BiOI QDs in solution. First, by coprecipitation of KI and $Bi(NO_3)_3{\cdot}5H_2O$, bulk BiOI was obtained, which was separated from the supernatant by centrifugation. Next, tween 20 was injected into the supernatant to protect the cores of BiOI QDs [5], and excess ions were filtered through a 0.22 μm millipore. The filtrate was taken to solvothermal treatment at 180 °C for 6 h to increase the crystallinity of the quantum dots. The liquid phase contained the BiOI quantum dots in solution. Bare BDD electrode was anodically activated in acidic medium prior to use. BDD modification was carried out by dip coating method followed by annealing at 350 °C to improve the junction of the QDs to the BDD electrode.

The photoelectrochemical study was carried out on a three-electrode system, the BDD or BDD/BiOI QDs as working electrode, a Pt mesh as counter electrode and Ag/AgCl as reference. Cyclic voltammetry, transient photocurrent and electrochemical impedance spectroscopy techniques were explored under both light and dark conditions.

Results and Discussion

BiOI QDs exhibit different optical and electronic properties. In this regard, Figure 1 shows the absorbance spectrum (a), and Tauc plot (b) of as-preprepared BiOI QDs (d ~ 15 nm, Fig. 1 c-d). BiOI is an indirect charge transfer semiconductor, and a value of 2.2 eV was calculated, which is wider than bulk BiOI reported in the literature (1.92 eV) [6]. This shows that it can exploit a wider range of the solar spectrum to promote electron-hole pairs generation.

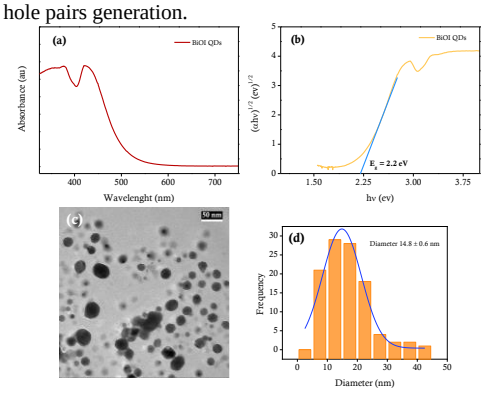

Figure 1. Absorbance spectrum (a) Tauc plot (b) TEM image (c) and size distribution (d) of BiOI QDs

Figure 2a shows the voltammetric profile of the bare BDD electrode and BDD/BiOI QDs photoelectrode. An increase in current is evident in both the oxidation and reduction peaks. In addition, the peak potential difference also decreased in the photoelectrode (0.12 V *vs.*

Ag/AgCl), which demonstrates an improvement in the conversion kinetics of the redox couple. Figure 2b exhibited different anodic and cathodic irreversible peaks corresponding to various states of Bi^{3+} at the nanocrystal surface and displays a noticeable increase in the capacitance region.

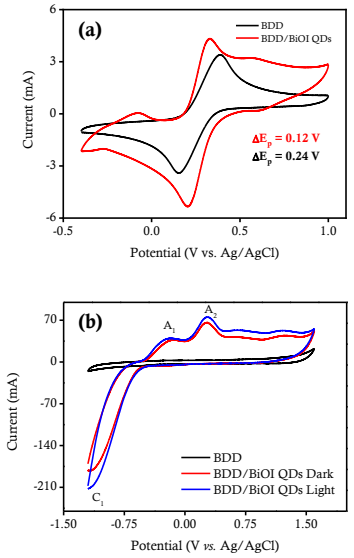

Figure 2. CV of BDD (black) and BDD/BiOI QDs (red) in 2 mM ferri/ferrocyanide in 1 M KCl (a) and CV in 0.1 M Na_2SO_4

In order to evaluate the light harvesting of the photoelectrode, the transient photocurrent (on-off system) was investigated (Figure 3). A maximum photocurrent of 0.23 mA at 1.53 V *vs.* Ag/AgCl under white light irradiation was determined. The stability of the electrode under illumination increases with time, and charge recombination ("spikes") is limited.

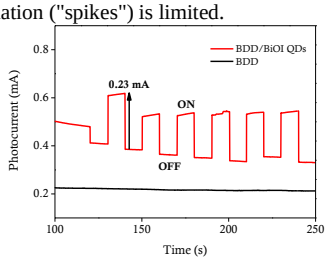

Figure 3. Transient photocurrent of BDD/BiOI QDs in 0.1 M Na_2SO_4

Figure 4 shows the Nyquist plot for the BDD/BiOI QDs photoelectrode evaluated in the ferri/ferrocyanide redox couple at open circuit potential. A value of 1.02 ohm was calculated for the charge transfer resistance of the bare electrode and 0.72 ohm for the photoelectrode. This reduction in resistance demonstrates that solid-solid junction improves the kinetics of carrier transfer, and hence charges are more available for catalysis. The nanoscale interface is expected to drive redox reactions more efficiently

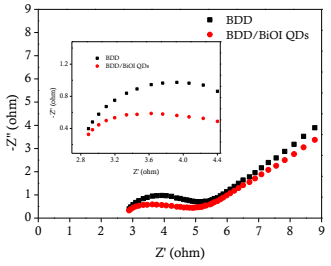

Figure 4. Nyquist plot of bare BDD (black) and BDD/BiOI QDs (red) in 2 mM ferri/ferrocyanide in 1 M KCl at open circuit potential

Conclusions

BiOI QDs were immobilized on a BDD electrode and their photoelectrochemical properties were studied. A decrease by half in the peak-to-peak potential difference was determined, and a maximum of 0.23 mA photocurrent was obtained as well as a reduction of the charge transfer resistance. This photoelectrode can be used for oxidation and reduction processes using broad spectrum light, since BiOI QDs present a wider band gap than their bulk counterpart.

Acknowledgments

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