

A facile preparation method of the BiVO₄ film photoelectrode

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Introdução

Bismuth vanadate (BiVO₄) is an n-type semiconductor, which is usually used as a yellow pigment, but which has recently also attracted attention for use in solar water splitting photoelectrolysis and in the photolytic destruction of organic pollutants.¹ The advantages offered by BiVO₄ are (i) a relatively low band gap (2.4 to 2.5 eV), (ii) inexpensive components, and (iii) stability in aqueous media, making this material a promising photoanode for applications in visible light.

In most of the synthesis methods proposed in literature several hours of reflux and use of aggressive chemicals such as concentrated nitric acid are required. In addition, often BiVO₄ is obtained as powder material and when it is employed as photo-electrode an extra preparation step (conversion of powder to thin film) is necessary. In this paper we propose a relatively simple and direct one-step route to photo-active BiVO₄ nanostructure films based on combining Bi(NO₃)₃ and NH₄VO₃ directly in poly-ethyleneglycol (PEG300) as solvent, applying this precursor solution to ITO coated glass, and thermal treatment at 500 °C in air. Films were characterised by SEM, EDX, RAMAN and cyclic voltammetry.

BiVO₄ films on ITO substrate were prepared dissolving Bi(NO₃)₃.5H₂O and NH₄VO₃ in PEG. The deposition was carried out by employing a drawing roller (hard rubber lino printing roller. After deposition the ITO was heated at 500 °C for 1 hour in tube furnace in presence of O₂. The ITO glass film substrate was fully covered by yellow and adherent film after the preparation process. The electrodes used were a platinum wire counter electrode and a potassium chloride saturated calomel (SCE) reference electrode.

Resultados e Discussão

Typical cyclic voltammograms for the BiVO₄ film on ITO in aqueous 0.5 M Na₂SO₄ solution in light and in the dark are shown in Figure 1A. A characteristic redox system centred at -0.4 V vs. SCE is indicative of reduction and re-oxidation of V⁵⁺ to V⁴⁺ surface states (or possibly also accumulation of charges in the conduction band. An anodic photo-current is observed commencing from ca. 0.0 V vs. SCE and increasing with increase in bias potential when the light is on. The anodic photocurrent is associated with photo-oxidation of water. Hysteresis in the photo-current profile is likely to be linked to local pH changes within the porous film structure. At 1.0 V vs.

SCE a typical value for the photocurrent is 300 μA cm⁻² under solar simulator conditions. The photocurrent observed in this work is larger than most results reported in the literature for pure BiVO₄ films. The Raman spectrum and XRD data showed that film formed is a pure monoclinic phase of BiVO₄.² Scanning electron micrographs (SEMs) of BiVO₄ films are shown in Figure 1B, where agglomeration of individual nano-crystallites is observed. The SEM image shows that the film is dense, crystalline, and with particles typically around 100 to 200 nm in diameter. The energy-dispersive X-ray spectroscopy (EDX) data analysis revealed the presence of the elements Bi, V, and O in the film with approximately 1:1 atomic ratio for Bi:V. The band gap can be estimated as 2.52 eV from diffuse reflectance spectra.

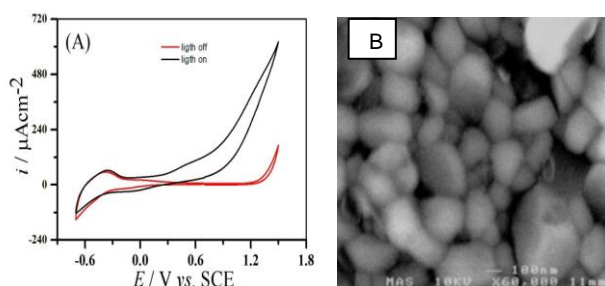


Figura 1. (A) Cyclic voltammetry in 0.5 M Na₂SO₄ in the dark and light. (B) FE-SEM image for the BiVO₄ thin film electrode formed on ITO.

Conclusões

A nanocrystalline, homogeneous, and adherent BiVO₄ thin film with monoclinic structure was produced on ITO substrate electrodes using a one-step method based on a PEG300 precursor solution. The method is experimentally simple, fast, and inexpensive. The photo-anode material obtained exhibits photocurrents over a large potential range. It can be concluded that the synthesis of nanostructured BiVO₄ films presented in this work is promising for use as photoelectrodes in water splitting or in photocatalytic degradation of organics.

Agradecimentos

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¹ Ding, C.; Shi, J.; Wang, D.; Wang, Z.; Wang, N.; Liu, G.; Xiong, F.; Li, C. *Phys. Chem. Chem. Phys.* **2013**, *15*, 4589.
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