Photoelectrochemical Application of Multihierarchical ZnO Nanorod/Titanate Nanotube Array Heterostrutures

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Introduction

Several techniques can be used for preparing titanate nanotubes (TiNTs) films; however, a major problem is that much of the material produced onto electrode surfaces remains in the form of thick layers containing randomly-oriented nanotubes. Such characteristic leads to strong limitations for use of in electronic devices. A promising way to overcome this drawback is the introduction of aligned TiNTs onto semiconductor films.[1] In this work, vertically aligned ZnO nanorods (NRs) layers have been decorated with TiNTs to form multihierarchical electrodes. The amino acid glycine (Gly) was used as a ligand for improving attachment of TiNTs to ZnO NRs substrates. The photoelectrocatalytic performance of these hybrid electrodes was evaluated by splitting of water under Xenon lamp irradiation.

Results and Discussion

Vertically-aligned ZnO NRs and ZnO NRs+Gly films were obtained via hydrothermal method. The rods exhibited hexagonal geometry, with diameters ranging from 100 to 300 nm, and lengths between 1 and 3 µm. The functionalization consisted in the immersion of ZnO NRs (ZnONR+Gly) electrodes in aqueous TiNT (TiNT+Gly) solutions. During the process, three electrode architectures could be obtained: one without Gly; another mixing Gly and TiNT in solution; and a third one mixing Gly to the ZnO NRs during its synthesis.

Fig. 1 shows SEM-FEG images of as-grown ZnO NRs and ZnO NRs/TiNTs heterostructure-arrays obtained by mixing Gly to the TiNT solution. In 1(a), only a flat hexagonal surface of ZnO NRs is observed, whereas in 1(b) it appears a high amount of TiNTs attached along the semiconductor rods. Due to the much smaller size of TiNTs regarding the dimensions of ZnO NRs (~100 nm in length and ~10 nm of diameter), one observes only a monodispersed distribution of TiNTs onto the surface of ZnO NRs, with a $n_{TiNTs}/n_{ZnO\ NRs}$ molar ratio of 1.6.

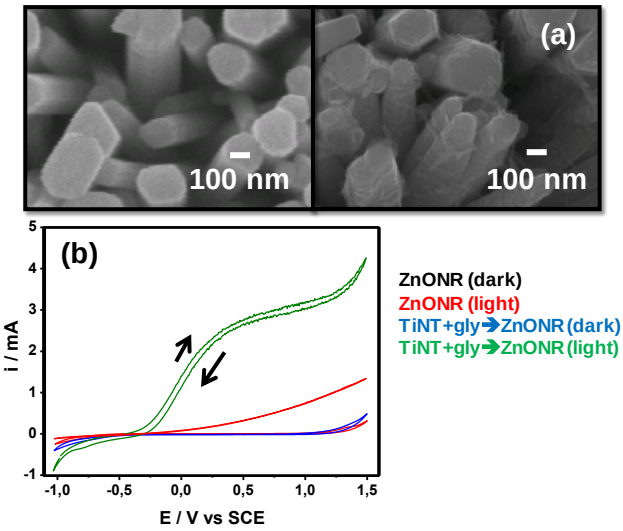

Figure 1. (a) SEM-FEG images of as-grown ZnO NRs films *(left)* and ZnO NRs/TiNTs+Gly heterostructures *(right)*; (b) Cyclic voltammetry of splitting of water using ZnONRs films and TiNT+ZnONRs films in presence and absence of UV-Vis light.

Photoelectrocatalytic performances of the modified electrodes have been evaluated for water splitting in the absence and presence of light. The potential for O_2 evolution in the dark is around +0.6 V (*vs. SCE*), while under irradiation it is -0,5 V. The generated current also suffers a significant improvement and is about 10 times higher when TiNTs is decorating the surface of ZnO NRs and ZnO NRs+Gly electrodes (Fig. 1b).

Conclusions

It was found that the multihierarchical ZnO NRs/TiNTs heterostructure exhibits significantly enhanced photoelectrocatalytic performances in comparison with their single component counterparts under UV-Vis irradiation. This increasing is owing to the synergic interaction between ZnO NRs and TiNTs.

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[1]Bavykin, D. V., L. Passoni, et al. *Chem. Commun.* **2013**, *49*, 7007.