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# Directed electrochemical synthesis of ZnO/PDMcT core/shell nanorod arrays with enhanced photoelectrochemical properties

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## ABSTRACT

In this paper, we demonstrate a simple two-step electrochemical deposition strategy for synthesizing ZnO/Poly(2,5-dimercapto-1,3,4-thiadiazole) (PDMcT) core/shell nanorod arrays. The as-synthesized ZnO/PDMcT samples are characterized by Fourier-transform infrared (FTIR), Raman spectroscopy, power X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The ZnO/PDMcT nanorod arrays are found to exhibit significantly enhanced photocurrent density in photoelectrochemical cell applications as compared to the pristine ZnO nanorod arrays.

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## 1. Introduction

The hybrid optoelectronic devices incorporating conjugated polymers and inorganic nanocrystals have attracted considerable attention because they offer the potential to deliver efficient energy conversion. They possess the advantages of being morphologically more stable and combine the facile solution processability, large optical extinction coefficients, and good hole mobility of polymers with the high electron affinity and electron mobility of inorganic nanostructures [1–4]. Recently, various high electron affinity inorganic semiconductors including TiO<sub>2</sub> [5,6], CdS [7,8], CdSe [9,10] and CdTe [11,12] have been widely studied for hybrid polymer nanodevices. Among them, the hybrid nanomaterials based on one-dimensional (1D) nanostructure cores are of particular

interest due to their improved or novel properties and promising applications in the fields of optics, solar cells and optoelectronics.

As an important multifunctional oxide semiconductor, 1D ZnO nanostructures have become a subject of great scientific and technological interest owing to their great potential applications in photonics, electronics, and energy harvesting [13–16]. It is now widely recognized that 1D ZnO nanostructures are among the most promising materials for the next generation optoelectronic devices operating in ultraviolet (UV) region, such as light-emitting diodes [17,18], photo-detectors [19], and solar cells [20]. However, the wide band gap (3.3 eV) of ZnO limits the utilization of visible light which occupies a large part of solar light. Many attempts have been carried out to improve the utilization of solar light by

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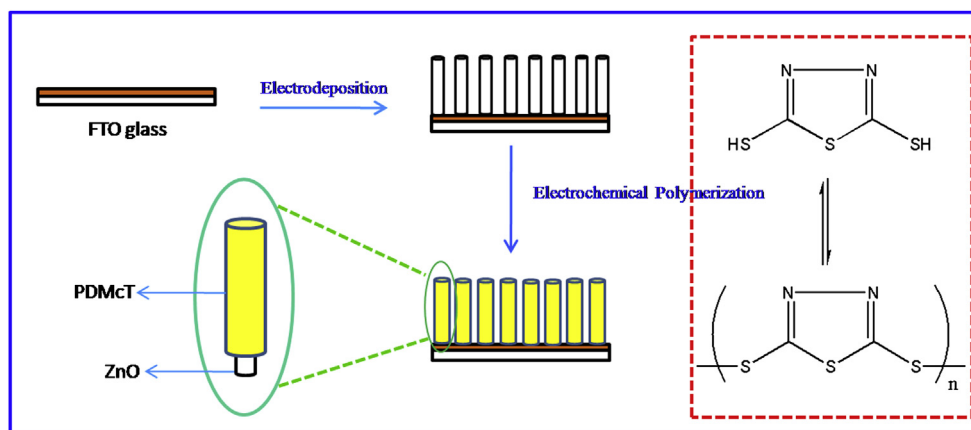


Fig. 1 – Schematic depiction of the fabrication of ZnO NRAs and ZnO/PDMcT core/shell NRAs.

extending the photoresponse of ZnO to the visible region, such as noble metal deposition [21], and narrow band gap semiconductors coupling [22,23]. 1D ZnO hybrid materials containing organic as well as inorganic components have attracted considerable attention because they promise new properties that may not easily be available from conventional materials. In these systems, the hybrid interface is shown to give rise to new electronic states which are not present in the individual components. This allows an efficient charge separation for both UV and visible light excitation [24]. Moreover, it can be expected that such devices will integrate the advantages of two materials—high electron mobility of inorganic semiconductors and photosensitivity, and high hole mobility of conjugated polymers [25], which can provide exciton (bound electron–hole pair) by photoexcitation. The exciton may be dissociated efficiently at the interface of organic–inorganic materials via a hole or electron transfer to generate the photocurrent. The distance that such an exciton is able to cover is very limited, dependent on the diffusion constant of the exciton and its intrinsic lifetime [26]. Hence, many organic solar cells are designed to have a large area interface at short distances (nanometer) to ensure a high quantum efficiency of charge generation.

In the present study, we demonstrated the formation of highly ordered ZnO/PDMcT core/shell nanorod arrays on fluorine-doped tin oxide (FTO) substrates via a facile two-step electrochemical approach. First, ZnO nanorod arrays were grown vertically on FTO substrates via electrodeposition, and then PDMcT layers were directly formed on the surface of ZnO nanorods via a successive electrodeposition process to form the ZnO/PDMcT core/shell nanorod arrays. Furthermore, we also investigated the potential application of these nanorods in photoelectrochemical cell and their optical properties.

## 2. Experimental

### 2.1. Materials synthesis

All reagents used were analytical grade and were used directly without any purification. According to the previous reports [27,28], ZnO nanorod arrays were synthesized on FTO

substrates by galvanostatic electrolysis in an aqueous solution of  $0.02 \text{ mol L}^{-1} \text{ Zn}(\text{NO}_3)_2$ ,  $0.01 \text{ mol L}^{-1} \text{ NH}_4\text{Ac}$ , and  $0.01 \text{ mol L}^{-1} \text{ C}_6\text{H}_{12}\text{N}_4$  (HMT) with current density of  $2.0 \text{ mA/cm}^2$ . After the electrodeposition, the ZnO NRAs on the FTO glass substrates was washed with deionized water and then used as the working electrode for the second electrodeposition.

ZnO/PDMcT core–shell nanorod arrays were prepared via an electrodeposition process by using the above ZnO nanorod arrays as working electrode in a propylene carbonate anhydrous (PC) aqueous solution containing of  $10 \text{ mM}$  2,5-dimercapto-1,3,4-thiadiazole (DMcT) and  $0.1 \text{ M}$   $\text{LiClO}_4$  at room temperature. The deposition current density was  $1.0 \text{ mA/cm}^2$ . The loading of PDMcT on the ZnO nanorod surface can be tunable via the optimization of different electrodeposition time of PDMcT.

**Characterizations:** The surface morphology and composition of the prepared products were analyzed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6330F). Fourier-transform infrared spectroscopy (FTIR) of the as-prepared products was measured through a Nicolet 5700 spectrometer using KBr sample pallets. The structure of the samples was analyzed using powder X-ray diffraction (XRD, Bruker, D8 ADVANCE) with  $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and transmission electron microscopy (TEM, FEI, Tecnai G2F30). The chemical state and compositions of the products were analyzed using X-ray Photoelectron Spectroscopy (XPS, ESCALab250). The optical properties of the products were measured with a UV–Vis–NIR Spectrophotometer (UV, Shimadzu UV-3150) and Laser Micro-Raman Spectrometer (Renishaw inVia) using a visible laser ( $\lambda = 514.5 \text{ nm}$ ) with an output laser power of  $50 \text{ mW}$  as the excitation wavelength at room temperature.

All photoelectrochemical measurements were carried out in a three-electrode electrochemical cell with a flat quartz for illumination. The samples prepared on FTO substrates in the range of  $0.2\text{--}0.25 \text{ cm}^2$  were fashioned into photoanodes. The electrolyte was  $0.5 \text{ M}$   $\text{Na}_2\text{SO}_4$  aqueous solution with a pH of  $\sim 6.8$ . Linear sweep voltammograms were collected on a CHI 760D electrochemical working station, with a coiled Pt wire as the counter electrode and KCl saturated calomel electrode (SCE) as the reference electrode. The light source was a  $300 \text{ W}$  Xe lamp (PLS-SXE-300 UV, Beijing Perfectlight) supplying the

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