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Fabrication of conducting polymer modified CdS photoanodes for photoelectrochemical cell

Alka Pareek[a,b], Pradip Paik[b,1], Joydip Joardar[a], K. Murugan[a], Pramod H. Borse[a,*]

[a] International Advanced Research Centre for Powder Metallurgy and New Materials, Balapur PO, Hyderabad, Telangana 500 005, India
[b] School of Engineering Science and Technology, Hyderabad Central University, Gachibowli, Hyderabad 500046, Telangana, India

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ABSTRACT

The present work focuses on the modification of a spray deposited nanostructured CdS thin films by thin layers of polyaniline (PANI) and polypyrrole (PPY) systems using electro-polymerization method. The deposition of the conducting polymer on the CdS/FTO (Fluorine doped tin oxide) film surface has been validated by X-ray diffraction, UV–Vis spectrometry and Fourier transform infrared spectrometry. As deposited PANI and PPY films exhibit a bandgap of 2.0 eV and 1.7 eV, respectively. Optimization of deposition parameters *viz.* applied field, concentration of monomer and *p*H of the precursor has been performed to obtain a uniform and an adherent coating over CdS surface. The absorption band-edge of CdS is not shifted due to its surface modification *via.* PANI and PPY. However coating of PANI enhanced the visible light absorption capacity of CdS. This additionally ensures that there exists a thin polymer coating over CdS. The photocurrent of CdS/PANI and CdS/PPY is found to be enhanced by 3.2 and 2.6 times as compared to the bare CdS. An improvement in the PEC performance could be attributed to the favorable band energetics between the conjugated polymers and CdS that effectively reduces the recombination process and thus enhances the charge transfer process.

1. Introduction

Photoelectrochemical (PEC) cell is a reliable technology to handle the ever-growing and huge energy demand for present and future era [1]. This engraving technology has triggered a surge of development in the solar active semiconducting nanostructures those suit as photoanode for their solar applications [2]. Among them CdS is one of the most studied materials due to its narrow bandgap (2.4 eV) and desirable band-edge positions for the cleavage of water molecule [3, 4]. Still it lacks the recognition of a potential candidate, as it has low charge-separation efficiency and has stability issues but not as severe as Ga-Arsenide systems. There are number of reports focussing on the improvement of CdS efficiency by means of various [5] methods *viz.* loading of noble metals (Pt, Au, Ag *etc.*) on the surface of CdS [6], doping of CdS lattice and formation heterojunction of CdS with other semiconductors [7] and/or conjugated polymers [8].

Conjugated or conducting polymers like polypyrrole (PPY), polyaniline (PANI) and polythiophene has attracted a lot of attention recently owing to their excellent electrical, optical and magnetic properties [9]. These polymers are used as photosensitizer to enhance the absorption of the semiconductor to visible range [10], form an outer layer on the surface of semiconductor to inhibit its photocorrosion [11] and further even improve the charge-transfer process at the heterojunction [12]. The conducting polymers exhibit valence bandedge position more negative than the semiconductor, which mediates an efficient hole transfer at the interface [13, 14]. This process reduces electron-hole recombination at the interface and facilitates an increase in the photocurrent. Among all the conducting polymers, *polypyrrole* (*i.e.* $–C_4H_4NH–_n$) and polyaniline are mostly studied due to important factors as:- (1) the oxidative polymerization potentials of the *pyrrole* and *aniline* are lower than other conducting polymers; (2) the electropolymerization of pyrrole and aniline can be performed in acidic aqueous solutions, while other conducting polymers requires non-aqueous solution; (3) the electrical conductivity of as deposited polymer is higher for PPY and PANI; and (4) PPY and PANI are *eco-friendly* conducting polymers [15].

There are various reports on the PPY/inorganic and PANI/inorganic semiconductors due to their high conductivity, environmental stability and their ease of synthesis [16]. Lu et al. discussed the photoluminescence properties of the nanocomposite films of PPY having

* Corresponding author.
E-mail address: phborse@arci.res.in (P.H. Borse).
[1] Present address (*lien from University of Hyderabad*): Dr. Pradip Paik, Associate Professor, School of Biomedical Engineering, Indian Institute of Technology (IIT)-BHU, Varanasi, UP, PIN 221005.

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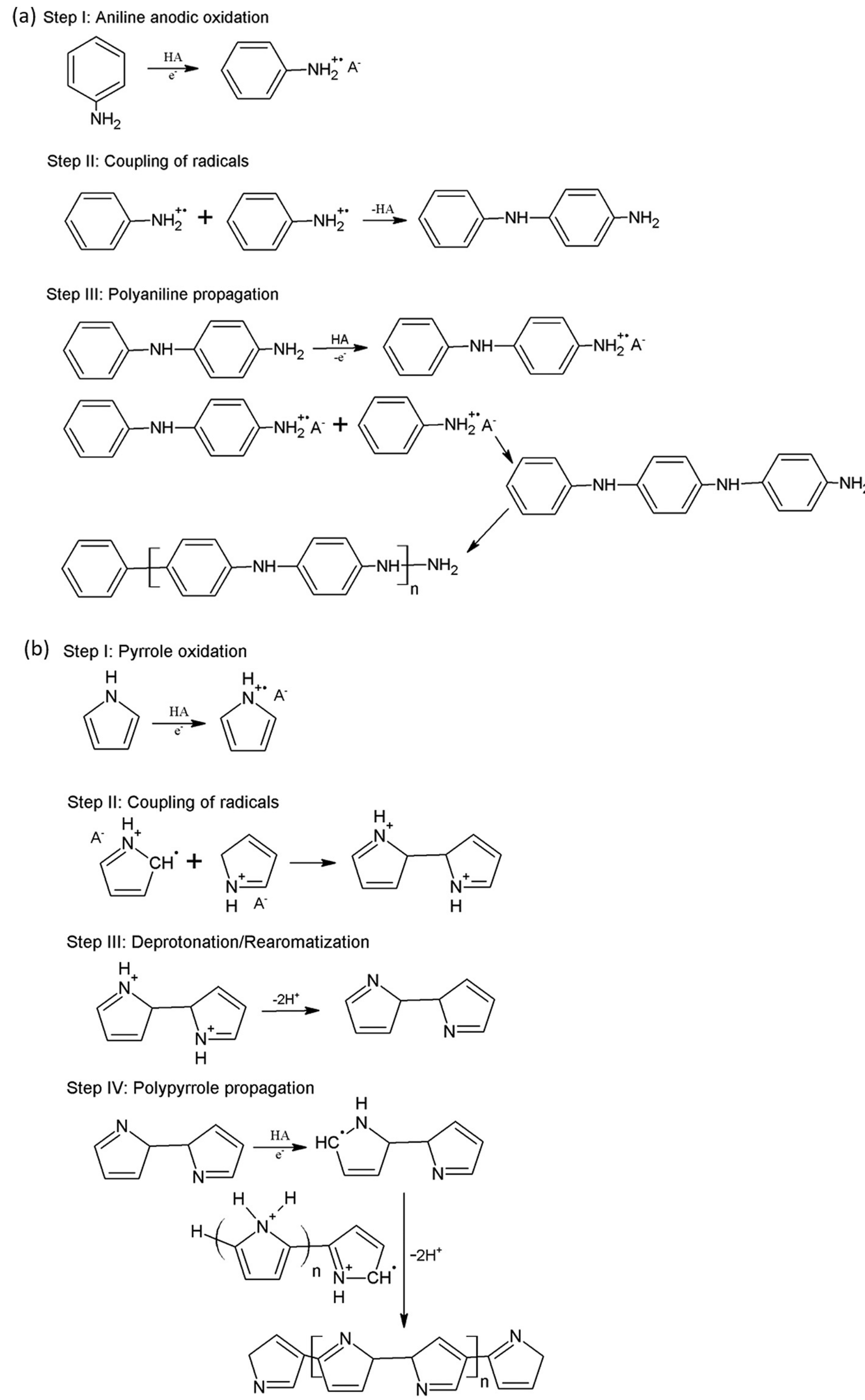

Scheme 1. Schematic diagram showing the mechanism of (a) electro-polymerization of PANI, and (b) electro-polymerization of PPY.

multilayers of CdSe and CdTe [17]. Chang et al. reported the rheological and dielectric properties of the PPY encapsulated in the channels of porous silica (MCM-41) [18]. Zhang et al. reported a very fast response and high sensitivity to ammonia gas detection by PPY modified SnO_2 hollow spheres [19]. Gu et al. synthesized highly efficient AgCl/PPY nanocomposite [12]. Zhang et al. reported an improved photoactivity of PANI/PdS-CdS and investigated the visible light activity and anti photocorrosion properties [4]. Das et al. found an enhanced electrical conductivity of CdS-polyaniline multilayer nanocomposites [20]. They reported an efficient charge separation and charge transfer between CdS and PANI that makes these polymer a highly desirable candidate in optoelectronic applications. Kose et al. studied the electrical properties of the CdS/polyaniline nanocomposite *via.* an oxidative polymerization [21]. He et al. reported an efficient photocatalytic hydrogen evolution using PANI/CdS composites [22]. Dey et al. studied the effect of Cd concentration on the photocatalytic performance of the PANI/CdS [23]. Patidar et al. studied the electrical properties of CdS/PANI heterojunction [24]. This clearly indicates that PANI and PPY are important systems affecting the performance of CdS photoelectrode.

In the present work, we have synthesized and deposited the PPY and