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Photoresponsive polypyrrole-TiO_2 nanoparticles film fabricated by a novel surface initiated polymerization

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Abstract

A Photosensitized electrode was fabricated through a novel polymerization of pyrrole initiated by TiO_2 nanoparticles under UV irradiation. Conjugated polypyrrole (PPy) continuously grows on the surface of the TiO_2 film, resulting in fully covered film with the stably-bound PPy layer. The film structures were analysed using Raman and X-ray photoelectron spectroscopy (XPS). It was found that the film electrode exhibits improved photoresponse including the flat band potential, photocurrent and separation of charges. The lowest unoccupied molecular orbital (LUMO) level of the PPy is higher in energy than the LUMO of PPy in electrodeposited electrodes, providing a stronger driving force for the electron injection into the TiO_2.

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1. Introduction

Photoelectric devices based on dye-sensitized nanoscale semiconductors have attracted much attention [1]. It is necessary to search for new sensitizers as alternatives to the original ruthenium bipyridyl dyes because they are too expensive and hard to synthesize [2]. Potential candidates for the sensitizers are π-conjugated polymers since their photoelectric properties are suitable for various photoelectric applications including photovoltaic cells and light emitting diodes [3–5]. Our interest in polypyrrole (PPy), one of the conjugated polymers, is due to its high thermal stability and strong absorption in the range from visible light to near infrared [6,7].

Performances of the devices strongly depend on the interfacial binding between the sensitizers and semiconductors [8]. In the case of the ruthenium bipyridyl dyes, the dyes with the introduced carboxyl groups interact strongly with TiO_2 through a covalent-like binding [8]. In contrast, the interface between the conjugated polymers and TiO_2 remains an issue to be improved urgently. This is critical to their applications. It is known that strong interfacial binding favours not only charges migration but also the lifetime of the devices [8–10].

Using conjugated polymers as sensitizers encountered with an obstacle that this kind of polymer is not molten in nature and insoluble in solvents. Electrodeposition can overcome this obstacle to obtain a PPy layer on films of TiO_2 nanoparticles [11,12]. However, the as-prepared polymer simply deposits on the film without adequate binding. In this electrodeposition, a positive voltage, which allows an electrochemical polymerization of pyrrole, is applied to the flat electrode at the back contact of the TiO_2 film. Since the nanoparticles are electrical insulators at the applied potential, the polymerization only occurs in the film's mesopores where pyrrole can diffuse to reach the electrode below the TiO_2 film [13]. As a result, parts of the TiO_2 nanoparticles are usually uncovered [12]. In this case, the photosensitize effects are not optimized due to the incomplete coverage. Several groups have reported a method of chemical oxidative polymerization in which the TiO_2 surface was pretreated with H_2O_2 or Lewis acids then the polymerization of pyrrole was initiated by the

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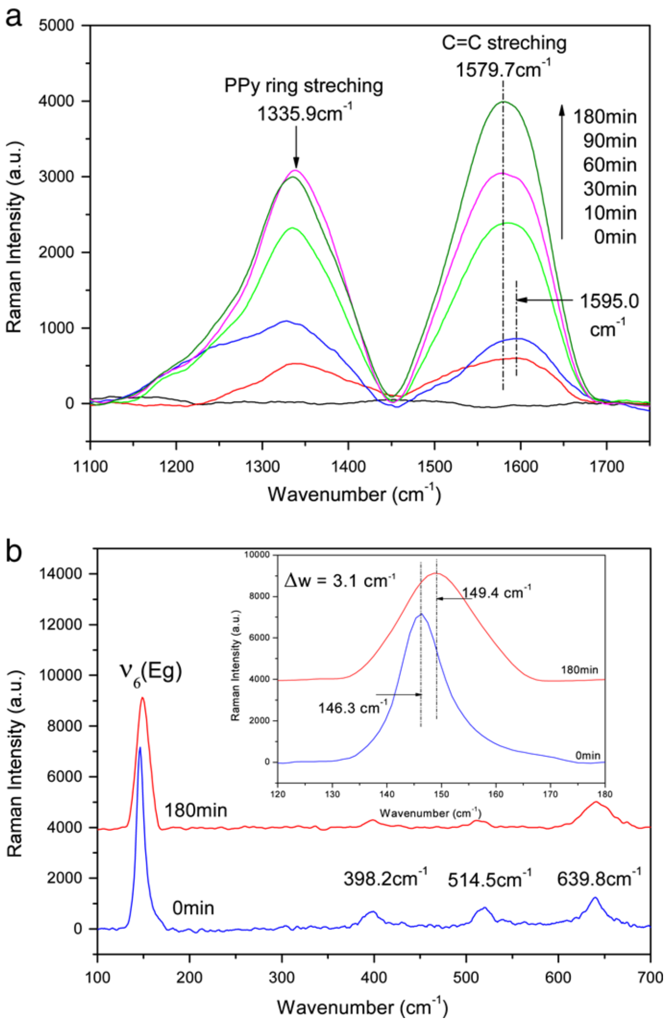

Fig. 1. Raman spectra in the range of PPy (a) and TiO_2 (b) for the PPy-TiO_2 composite films prepared after reactions of different time.

adsorbed oxidant at the surface [11]. PPy can be bridged to the TiO_2 if proper adhesion promoters, such as 3-(trimethoxysilyl) propyl methacrylate [3] were added.

This study reports photoresponsive properties of PPy-TiO_2 films prepared by a novel surface polymerization. The film of TiO_2 nanoparticles is subjected to UV light then the photo-excited nanoparticles directly catalyze pyrrole to polymerize at the surface. This approach is of easy-to-perform and produces the composite film with the ideal structure, i.e. the TiO_2 film is fully covered by a stably bound PPy layer. This approach evolves from the finding of our recent work [14], in which methyl methacrylate (MMA) was photocatalyzed to polymerize by TiO_2 nanoparticles. Raman spectroscopy, proved sensitive to TiO_2 microstructures [15–17], is used here to analyse the strong interaction between TiO_2 and the resulting PPy.

2. Experiments

2.1. Materials

Nanoscale TiO_2 (P25) was a mixture of 20% rutile and 80% anatase with an average diameter of 21 nm (Degussa AG, Germany). Indium tin oxide glasses (ITO) with the sheet resistance of 10 ohm/sheet and transmittance of 83% were supplied by Shenzhen Nanbo Display Device Co., LTD. The ITO glasses were rinsed with acetone and ethanol sequentially, then ultrasonicated for 10 min in isopropanol and dried by nitrogen. Pyrrole was distilled before use. Chemicals of analytical grade and deionized water were employed.

2.2. Preparation of PPy-TiO_2 film

A volume of 0.1 ml of acetyl acetone in 1 ml of water was added into 3 g of TiO_2 under stirring, then the mixture was ground while 5 ml of water was added in drops in order that a lump-free paste was produced. Subsequently, one drop of Triton X100 in 1 ml of water was added to allow a uniform suspension of TiO_2. After the suspension was diluted by 10 ml of water, a few drops of the suspension were deposited onto an ITO substrate (4 × 4 cm), and spun at an angular speed of 2000 rpm for 30 s. The TiO_2 films were obtained after sintering at 450 °C for 30 min.

The TiO_2 film was placed upright in a quartz reactor containing 100 ml of pyrrole aqueous solution at 0.1 M. UV-irradiation at 365 nm towards the reactor lasted various time. The other reaction conditions were identical to those of our previous work in which MMA was photocatalyzed to polymerize by dispersed TiO_2 nanoparticles in water [14]. Darkish films were obtained, rinsed with ethanol and dried by nitrogen before tests. The blank experiment with the pyrrole aqueous solution in absence of the TiO_2 film showed that no polymer was yielded under the identical reaction conditions, as determined by UV-vis spectroscopy.

2.3. Characterization

Atomic force microscope (AFM) of NanoScope IV and scanning electron microscope (SEM) of TS 5136MM were used to image surface morphologies of the films. Fourier-transform Raman spectra were recorded on a LabRam-1B (Dilor) spectrometer. XPS was carried out with a PHI-5000C ESCA system (Perkin Elmer) with Al Kα radiation. Photocurrents were recorded on a Model 600 A potentiostat/galvanostat (software CHI660) system using a Xenon lamp of 350 W. The prepared film as the working electrode has the illumination area of 3 cm^2. A platinum plate and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The $LiClO_4/CH_3CN$ solution of 0.5 M was used as electrolyte.

3. Results and discussion

3.1. Structures and surface morphology of the film

Fig. 1(a) shows the Raman spectra of PPy region for the reacted films. The double peaks at 1590 cm^{-1} and 1335 cm^{-1} are assigned to the C = C backbone stretching and ring stretching of PPy, respectively [18]. Clearly, conjugated PPy is synthesized successfully. It is found that the peak of PPy backbone stretching slightly shifts to lower frequency,