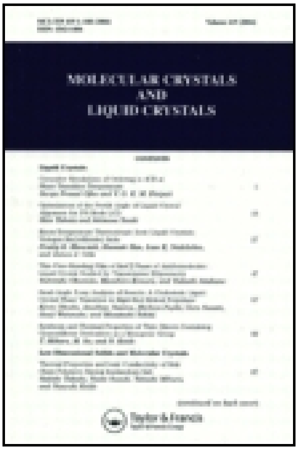

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Photocurrent Generation of Poly(3,4-ethylenedioxythiophene)-on-TiO_2 Nanoparticle

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Photocurrent Generation of Poly(3,4-ethylenedioxythiophene)-on-TiO_2 Nanoparticle

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The photocurrent generation of poly(3,4-ethylenedioxythiophene) (PEDOT) grown on TiO_2 nanoparticles were examined. PEDOT was deposited on the surface of mesoporous TiO_2 nanoparticle by chemical polymerization of 3,4-ethylenedioxythiophene (EDOT) under oxidative condition, to afford blue colored conductive particles, having average diameter of 80 nm when the feed ratio between TiO_2 and EDOT was 1:1.5 by weight. A photoelectrode coated with the PEDOT-on-TiO_2 nanoparticles showed much higher photocurrent generation for a redox couple of hydroqunone and quinone, compared to that of PEDOT or TiO_2 only. The photoelectrode prepared from PEDOT-on-TiO_2 nanoparticles (ratio 1/2) showed photocurrent higher than $2.8\,\mu A/cm^2$ upon excitation with UV light under an external potential of -0.4 V (versus Ag/AgCl). The current generation and photoswitching properties was maximized when the feed ratio between TiO_2 and PEDOT was 1:2.

Keywords: conductive polymer; nanoparticle; photoconductive; photocurrent

INTRODUCTION

Conductive polymers have been attracted much interests in the field of organic electronics and photonics for their interesting properties as well as versatile processibility conducting polymer [1–4]. Recently, attempts have been made to enhance conductivity and photoconducting properties of conductive polymers by control in nanoscale [5–11].

In our previous report, we have shown that PEDOT grown on TiO_2 nanoparticles show much improved properties such as high

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electrochromic peroperty [12] due to increased surface area. Since it is well known that TiO_2 nanoparticles show photocurrent generation [13–14] and photocatalytic properties [15–17], we extended our study of the conductive nanoparticles to investigate the photocurrent generation from them.

Therefore, we report herein the photoswitching properties of PEDOT grown on TiO_2 nanoparticles.

EXPERIMENTAL

Materials and Equipments

PEDOT, Hydroquinone and TiO_2 nanoparticles (average particle diameter of 15 nm) were purchased from Aldrich, and used without any purification. Iron(III) chloride ($FeCl_3$) was also purchased by Aldrich and sealed to be kept from light. Tetrabutylammonium perchlorate which was used as an electrolyte was obtained from TCI Inc. The electrochemical experiments were performed with a universal potentiostat [model CHI 624B (CH Instruments, Inc.)]. The photocurrent of the photoelectrodes was determined under the exposure of UV light [model Spectroline, USA, 60 mW/cm^2].

Synthesis of PEDOT-TiO_2 Nanoparticle

PEDOT-on-TiO_2 nanoparticle was synthesized by chemical polymerization of EDOT adsorbed on TiO_2 particles using a modified method from the literature methods [18–19]. 1 mmol of EDOT was added to the solutions containing 10 mL acetonitrile and TiO_2 nanoparticles, with a feed ratio of TiO_2/EDOT = 1/1.5 1/2, 1/10, 1/40, and 0 by weight (Table 1). Then, 1 mmol of $FeCl_3$ was added to the above mixture,

TABLE 1 Photocurrent Generation of PEDOT-on-TiO_2 Nanoparticles Prepared from Different Contents of TiO_2

Sample no.	TiO_2/EDOT feed ratio (by wt.)	Particle size	Photocurrent (μA)	Normalized photocurrent (μA/cm^2)
1	TiO_2	15	0.7	0.47
2	1/1.5	80	1.1	0.73
3	1/2	100	4.3	2.87
4	1/10	115	2	1.33
5	1/40	155	0.7	0.47
6	PEDOT	–	0.9	0.6

to afford immediately deep blue mixture, which was stirred further for 24 hr at room temperature to give well dispersed solution of PEDOT-on-TiO_2 particle compositions.

Preparation of Photoelectrodes

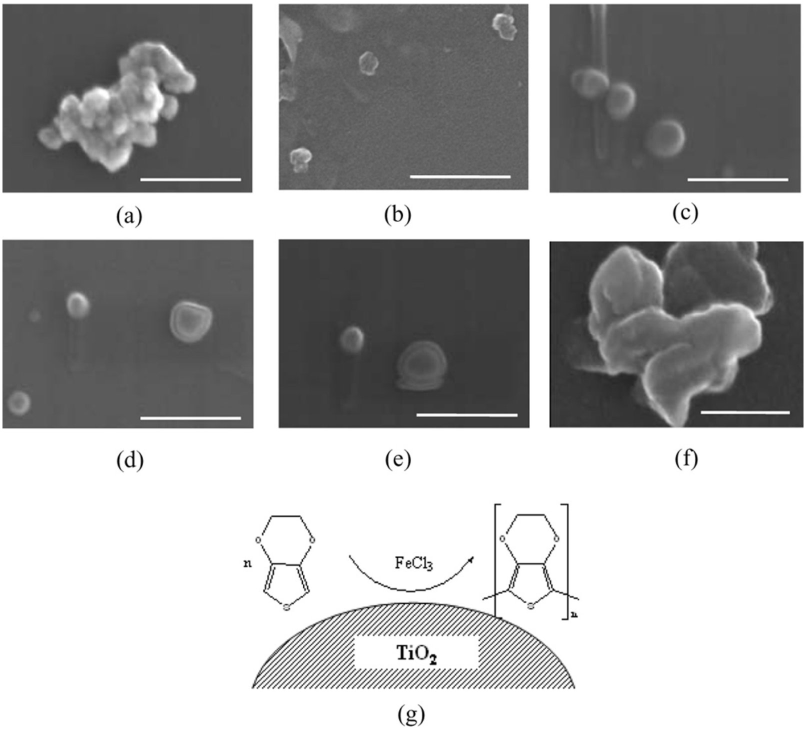
Synthesized PEDOT-on-TiO_2 particle suspensions were spincoated on an ITO glass with 1000 rpm speed. The coated electrode was dried and then washed with pure acetonitrile to remove the remaining monomer and the oxidant. The supporting electrolyte medium for photocurrent generation of the photoelectrode was a buffer solution containing 5 mM of hydroquinone and 0.2 M of potassium hydrophthalate. Pt wire and Ag/AgCl electrode were employed as a counter and reference electrode, respectively. UV light was alternatively irradiated to the sample by an automatically controlled shutter, with a switching time of 5 sec.

RESULT AND DISCUSSIONS

PEDOT monomer can be polymerized to PEDOT in the presence of oxidant $FeCl_3$. Especially in the case of mesoporous particles such as silica [4] or TiO_2, EDOT monomer adsorbs on the surface of the particles resulting in formation of conducting polymer–inorganic nanocomposite (Figure 1 (g)). Thus PEDOT was grown on the surface of mesoporous TiO_2 particles. Figure 1 shows the FE-SEM image of TiO_2 aggregated cluster (a) and PEDOT-on-TiO_2 nanoparticles prepared by different feed ratio of TiO_2 to EDOT (b-e), and chemically prepared PEDOT without TiO_2 (f). The particle size of the PEDOT-on-TiO_2 nanoparticles was increased to more than 80 nm compared to TiO_2 nanoparticles. The shape of the wall was almost same forming sphere like core-shell particle. Moreover, the particle size was increased as EDOT content was higher (Table 1).

Figure 2 shows UV-Vis spectra of dispersed solution containing TiO_2 (a), chemically polymerized PEDOT (b) and PEDOT-on-TiO_2 nanoparticle (sample No. 3) (c). PEDOT has absorption peaks at 310 nm and 350 nm while no specific peak was observed at TiO_2 containing solution. Increased absorption in UV region was observed when PEDOT was coated on TiO_2 [20]. PEDOT-on-TiO_2 showed characteristic peaks of PEDOT without any spectral shift which indicated the growth of PEDOT on TiO_2 particles [21–23].

As TiO_2 has capability of photocatlytic property, photoelectrode coated with PEDOT-on-TiO_2 particles could show photocurrent generation in the presence of a redox couple. Furthermore, the photocurrent



(a) (b) (c)

(d) (e) (f)

(g)

FIGURE 1 FE-SEM images of (a) TiO_2, (b) ~ (e) sample 2 ~ 5, and (f) chemically synthesized pure PEDOT. The scale bar corresponds to 300 nm. The bottom figure (g) shows the schematic diagram of polymerization process on the TiO_2 particles.

generation can be rationalized by a redox process of hydroquinone/quinnone, which can quench the photogenerated hole carrier from polymer film. In acidic electrolytes, quinones undergo a reversible redox reaction according to the following overall reaction. (Scheme 1) [24–27]. Irradiation of the photoelectrodes under a potential of $-0.4\,V$ (versus Ag/AgCl) in the electrolyte solution containing hydroquinone (HQ) resulted in photocurrent generation. Figure 3 shows current generation of the photoelectrodes under different external voltage. The current generation was repetitive by a light/dark switching and most efficient under the bias potential of $-0.4\,V$.

Interestingly the photocurrent of the photoelectrode coated with PEDOT-on-TiO_2 nanoparticles was higher than that of TiO_2 only. The electrode with PEDOT film only showed unstable photocurrent without switching properties under the same condition. Thus the

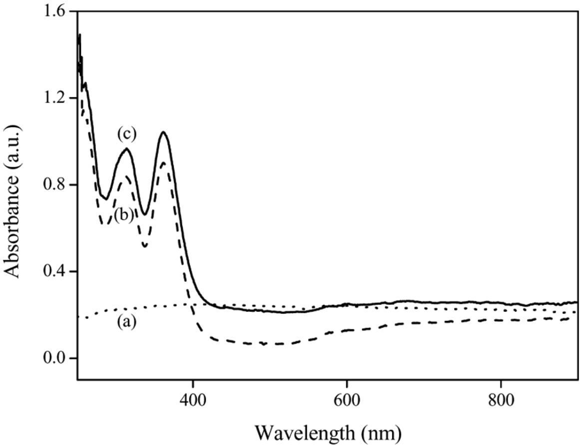
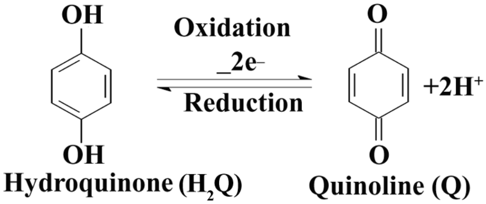


FIGURE 2 UV-Vis Absorbance spectra of suspension of (a) TiO_2, (b) PEDOT, (c) PEDOT-on-TiO_2 (sample No. 3).

increased photocurrent generation of PEDOT-on-TiO_2 nanoparticles indicates that TiO_2 could be activated by the PEDOT layer. Such a photocurrent generation was related to the absorbance of the film, indicating that the photocurrent generation originates from the carrier generation by photoexcited PEDOT units. Among the photoelectrode prepared from PEDOT-on-TiO_2 nanoparticles sample No. 3 showed photocurrent higher than $2.8\,\mu A/cm^2$ upon excitation with a light under an external potential of $-0.4\,V$ (versus Ag/AgCl). The current generation and photoswitching propertiy was maximized when the feed ratio between EDOT and TiO_2 was 2:1.

However, when the content of TiO_2 was further decreased the photocurrent generation was decreased as the non-active PEDOT layer become thicker. Indeed FE-SEM image of sample 4 showed thicker conductive layer and even double layer. Thus when TiO_2 content was high, the PEDOT layer block the absorption of light,



SCHEME 1 The overall redox reaction scheme of Q/HQ.

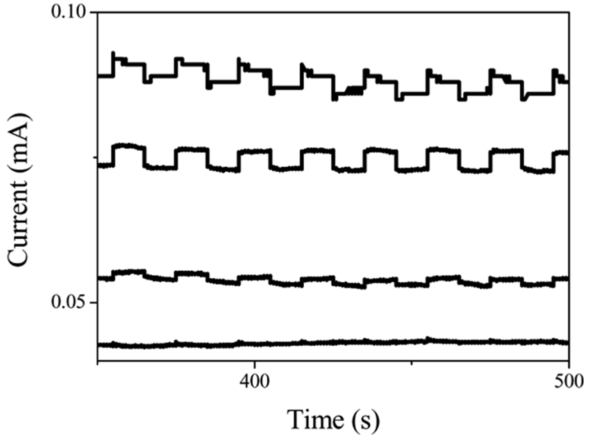


FIGURE 3 Photocurrent generation of the photoelectrode which coated with PEDOT-on-TiO_2 under different bias voltage (−0.6 V, −0.4 V, −0.2 V and 0 V, from top to bottom) in buffer solution containing HQ.

inactivating the photo carrier generation. Figures 4 and 5 shows the photocurrent generation for photoelectrode of PEDOT-on-nanoparticles having different PEDOT content. Such a photoactivity of PEDOT-on-TiO_2 particles opens a potential application of PEDOT nanoparticles into an organic photovoltaic device and photosensor.

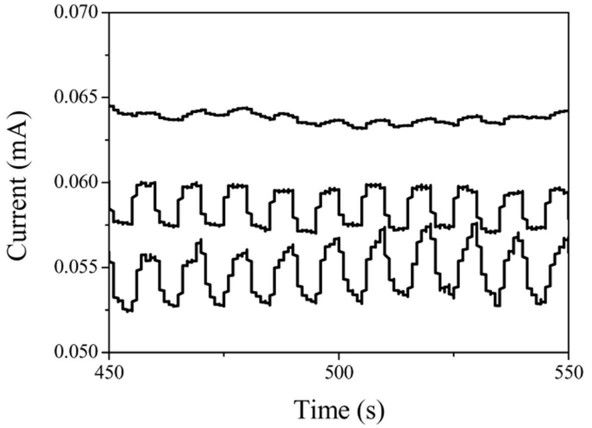


FIGURE 4 Photocurrent generation of the photoelectrode containing different TiO_2 ratio (sample No. 5, 4, 3 from top to bottom).

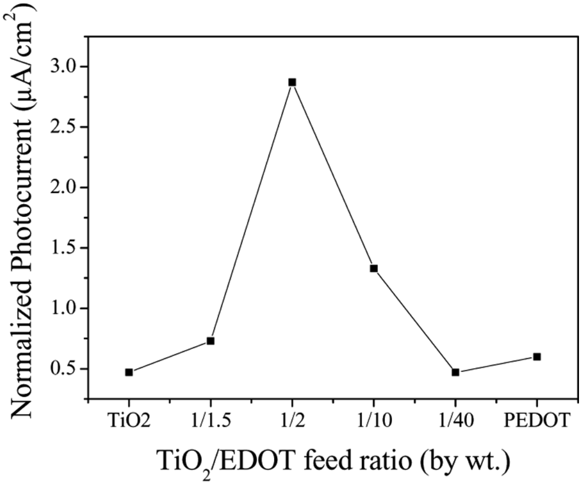


FIGURE 5 Plot of the photocurrent generation from the photoelectrode against the content of TiO_2.

In conclusion, PEDOT nanoparticles were prepared using TiO_2 as a nanotemplate, on which PEDOT was coated grown as a layer, forming sphere-shaped particle. The diameter of the particle was up to 155 nm. The photoelectrode covered with PEDOT-on-TiO_2 showed much higher and more stable photo-induced current generation compared to that of PEDOT only or TiO_2. Such a photoactivity of PEDOT-on-TiO_2 particles opens a potential application of PEDOT nanoparticles into an organic photovoltaic device and photosensor.

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