

Research Article **Effect of TiO₂ Rutile Additive on Electrical Properties of PPy/TiO₂ Nanocomposite**

Trong Tung Nguyen^{1,2} and Ngoc Huyen Duong²

¹College of Television Vietnam, Thuong Tin, Hanoi 158500, Vietnam ²School of Engineering Physics, Hanoi University of Science and Technology, No.1 Daicoviet, Hanoi 112400, Vietnam

Correspondence should be addressed to Ngoc Huyen Duong; huyen.duongngoc@hust.edu.vn

Received 3 December 2015; Revised 3 February 2016; Accepted 8 February 2016

Academic Editor: William Yu

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Polypyrrole/titanium dioxide nanocomposite (PPy/TiO₂) was synthesized by *in situ* chemical polymerization of pyrrole (Py) monomer in colloidal suspension of TiO₂ rutile. TEM and SEM images show that the TiO₂ is covered by PPy forming a coreshell structure. The PPy/TiO₂ core-shell will create *n*-*p* junction and bring in an inversion layer on the PPy-shell surface. The feature is accounted for the modification in electrical properties of the PPy/TiO₂ nanocomposite. On the exposure to oxygen the conductivity of the nanocomposite exhibits an increase in 16–18-folds that are accounted for the interaction between oxygen (an electron acceptor) and the inversion layer. The cyclic voltammetry diagrams have shown that at around 15% TiO₂ and scan rate 100 mV/s the nanocomposites can reach a specific capacitance about 176 F/g.

1. Introduction

Conducting polymer (CP) is typical conjugated class that possesses the unique structure of linear chain consisting of alternative single and double bonds [1]. Due to the susceptivity of pi-electron on the double bonds to a variety of counterions as well as to surrounding environment, the conductivity of conjugated polymer can be modulated in various ways. The feature offers effective approaches to modify the electrical properties of the material for possible applications [2]. For example, the coupling of CPs with active nanostructure can be used as a mean to tailor specific properties to design new materials with desirable characteristics. Beyond a simple combination of its property, the interaction between molecules component in nanocomposite can bring in new features or synergistic effects. Common CPs, polypyrrole (PPy) and its derivatives, have attracted a great deal of attention because of their high electrical conductivity, good environmental stability, and simple synthesis and processing [3]. As a *p*-type semiconductor with bandgap $E_q \sim 3.2$ eV, PPy has been shown to be a promising material for a wide range of application such as conducting wire, sensors, electrochemical capacitor, and electronics [2, 4–6].

On the other hand, titanium dioxide (TiO_2) is a typical oxide metal and *n*-type semiconductor that exhibits strong electrochemical and photochemical activity [7]. Apart from major application in vanishes, paint, and so on relying on the brightness and high refractive index of TiO_2 , the electrochemical and photochemical features have enlarged the application of TiO₂ in photocatalyst, solar cells, and so on [8, 9]. The combination of TiO_2 with SnO_2 and $ZnSnO_3$ in heterostructures has been found to boost the adsorption abilities for water molecules via a water-collection process [10, 11]. The coupling of TiO_2 with PPy in a nanocomposite is expected to improve their unique features, namely, sensitivity, electrical conductivity, and electrochemical properties [12-17]. In general, TiO_2 crystallines have three main structural morphologies under normal conditions: rutile, anatase, and brookite. Among those three structural morphologies rutile is more stable while anatase and brookite are metastable at room temperature. The difference in morphology, crystalline, and electronic structure results in different overall properties. In terms of facial interaction and charge exchange, the rutile TiO_2 with respect to band gap $E_q \sim 3.1 \, eV$ could be more effective in the coupling with PPy [18].

It is well known that rutile is the favored polymorph under acidic conditions in hydrothermal synthesis. In this study, pure-phase rutile nanoparticles were synthesized via a low-temperature hydrothermal method using $TiCl_4$ as the Ti precursor in HCl aqueous solution which was then refluxed to facilitate the formation of pure-phase rutile [19–21].

Based on these assumptions, an attempt was carried out to investigate effect of TiO_2 nanocrystallites in rutile polymorphs on TiO_2 /PPy nanocomposite synthesized by *in situ* chemical polymerization.

2. Experimental

Pyrrole (Py) 99.5% and TiCl₄ (Aldrich Co.), ammonium persulphate (APS, Kanto Chemical Co. Inc.), and titanium chloride TiCl₄ (Aldrich Co.) were used as precursors in the experiment. The PPy/TiO₂ nanocomposite was synthesized in two steps as follows.

Firstly, TiO_2 is prepared by the thermal hydrolysis of a titanium precursor ($TiCl_4$) at relative low temperature (<100°C) in HCl acidic aqueous solution to enhance the rutile formation. The procedure was carried out as follows: A solution of 40 mM $TiCl_4$ and 1.0 M HCl in a flask was heated up to 80°C for 2 hours to make TiO_2 colloidal dispersions. After cooling down to room temperature, the colloidal dispersion was kept in refrigerator to have TiO_2 sedimentation at the bottom of the flask.

Secondly, the resulting TiO₂ sedimentation was extracted, weighted, and mixed with an aqueous solution of 0.1 M Py and 1.0 M HCl with a given TiO₂/Py ratio. Then, the polymerization was carried out by adding drop-by-drop a solution of 0.1 M APS and 1.0 M HCl to the Py solution. After 1.5 hours of continuously stirring the polymerization was terminated by pouring ethanol into the mixture. The resulting black nanocomposites formed in the solution were filtered, then cleaned by distilled water, and kept in 1.0 M HCl solution.

The morphology, structure, particle size, and size distribution of the TiO₂, PPy, and PPy/TiO₂ nanocomposite were characterized by FESEM (Hitachi S4800) and TEM (Jeol JEM1010) and X-ray diffraction (XRD D8 Advance Bruker). The change in electronic structure of the materials was analyzed by Raman spectra using LabRAM HR800 (Horiba) with a 632.8 nm excitation laser ranging from 100 to 2339 cm⁻¹ at a resolution of 4 cm⁻¹.

The change in conductivity of the PPy/TiO₂ composite was determined as its electrical resistor variation exposure to oxygen O₂ by reducing pressure. The energy storage is determined by cyclic voltammetry spectra with scanning rate of 100 mV/s, within 0.5 V to 0.5 V. The test PPy/TiO₂ layers were drop-coated on interdigital Pt electrodes and the layer resistor changes were acquired and analyzed by Keithley Digital Multimeters connecting with a personal computer.

3. Results and Discussion

The XRD made on the resulting TiO₂ shows the positions of all diffraction peaks correspond to rutile (JCP2.2CA number



FIGURE 1: XRD spectrum of $\rm TiO_2$ synthesized by pyrolysis of $\rm TiCl_4$ in 1.0 M HCl aqueous solution.

00-021-1276). As can be seen from Figure 1, a strong peak is observed at 2θ of 27.37° assigned to (110) plane refraction and the other peaks are observed at 2θ of 36.10°, 39.16°, 41.26°, 44.01°, 54.36°, 56.59°, 62.92°, 64.10°, and 68.91° standing for the refraction at (101), (200), (111), (210), (211), (220), (002), (310), and (301) planes, respectively. However, in comparison to the normal powder XRD pattern, the intensity of the (101) peak is relatively heightened and its full width at half maximum (FWHM) is shrunk. The feature likely indicates that the resulting TiO₂ rutile crystallites are major nanorods growth preferably in [001] direction and the (101) planes are the side wall of TiO₂ nanorods which are preferentially exposed to X-ray [9, 22].

As can be seen from TEM images (Figure 2), the neat PPy has a granular structure with mean size around 30-40 nm and the TiO₂ crystallizes in the needle-like form with mean diameter around 9-10 nm and length of around 200-250 nm that is expected growth along [001] direction as discussed in XRD. The PPy granular and TiO₂ needle-like structures are commonly observed with materials synthesized in HCl medium [20]. The resulting PPy/TiO₂ nanocomposite shows a coupling core-shell structure of granular PPy covering TiO₂ needles. From chemical view of consideration, at the first oxidization stage the TiO₂ surface (donor sources) in the reaction medium acts as nucleation sites for the Py radical monomers (acceptor sources) adsorbed and anchored on. In the following stage, PPy chains grow up on the TiO₂ surface forming core-shell structures. The structures show the evidence of strong bonds between TiO₂ and PPy via donor-acceptor interaction [13, 14]. As a result, the coreshell structure will form p-n junction between PPy and TiO₂. The thickness of PPy layer growth on surface of TiO₂ then depends on the TiO₂ concentration in the reaction medium. The interfacial interaction between TiO₂ and PPy in



(a) PPy

(b) TiO₂

(c) PPy/TiO₂

FIGURE 2: TEM images of (a) PPy and (b) TiO₂ nanoparticles and (c) PPy/TiO₂ nanocomposites.



FIGURE 3: Raman spectra of TiO_2 , PPy, and PPy/ TiO_2 nanocomposite with different TiO_2 concentration.

the nanocomposites is expected to modify their chemical and electronic structures.

As shown in Figure 3 the Raman spectrum of a pure TiO_2 sample reveals three strong Raman bands 232, 446, and 609 cm⁻¹ and these three bands are in agreement with data observed in the spectra of a rutile phase. The predominance of rutile structure in the resulting TiO_2 sedimentation has accounted for the effect of HCl in the formation of TiO_2 during pyrolysis.

The Raman spectrum of neat PPy shows the instinct vibrational modes at 1590 cm⁻¹ (G band) and 1340 cm⁻¹ (D band), and 980 cm⁻¹ band indicates that certain sites of the PPy chain are still in the benzoid form (reduced state), where the vibrational mode at 938 cm⁻¹, assigned to C-H out of the plane deformation of the quinoid form, is related to the oxidized sites [23, 24]. The vibrational modes assigning a band at 1082 cm⁻¹ was correlated to the bipolaron state. The presence of TiO₂ in the nanocomposite causes a change in relative intensity and a red-shift of the vibrational bands standing for C=C bond from 1376 cm⁻¹ to 1356 cm⁻¹ and 1590 cm⁻¹ to 1578 cm⁻¹ indicating the fact that PPy shifts to reduction structure. The effect indicates the degree of reduction of PPy as the result of coupling with TiO₂ in the nanocomposites.

It is well known that the conductivity of both components (PPy, TiO₂) as well as resulting nanocomposites is sensitive to oxygen (oxidizing agent) [25]. Upon exposure to open air, oxygen is adsorbed onto the surface and abstracts electrons from the material causing ionization of the atom and yielding a positive hole; hence, the material conductance increases with oxygen concentration. Changing the air pressure means to change the oxygen concentration in the environment; the conductivity of the materials is varied. The O2 sensing profiles of PPy, PPy/TiO₂ in Figure 4 show the materials resistance rapidly increasing as air pressure reduces (the vacuum pump on) and fast returning back to the origin value as air flows in (the vacuum pump off). Typically, O_2 sensitivity of PPy/TiO₂ is 16–18 times higher than those of PPy. From the physical view of consideration, the change in conductivity involves the extraction of electrons from the valence band of semiconducting PPy as a result of oxygen interaction (physical adsorption) thus converting the materials to be *p*-type semiconductor. The adsorption and desorption of oxygen molecule on PPy/TiO₂ surface then cause the variation in conductivity of the materials. The more oxygen concentration is in the environment, the more electrons are extracted; as a result, the material conductivity is increased and vice versa. Higher oxygen sensitivity indicates the fact that more oxygen adsorption sites are created on the PPy/TiO₂ surface. The fast response and recovery and the stability in base line indicate that the physical adsorptions with weak bonding are dominant in the oxygen-nanocomposites interaction.

Cyclic voltammetry spectra with scanning rate of 100 mV/s, within -0.5 V to 0.5 V, are used to determine the specific capacitance of PPy/TiO₂ in comparison with a capacitor 1000 μ F as reference. The CV spectra of samples are shown in Figure 5. The equivalent capacitance of samples is calculated by C = dQ/dV = i/S, where S = dV/dt and current *i*. The specific capacitance of PPy/TiO₂ is calculated by C/m, where *m* is the nanocomposite weight used in the sample. Experiments show that the specifics capacitance of neat PPy is 135 F/g and changing when TiO₂ is added. The capacitance achieves the peak as TiO₂ content is about 15% and reduces when TiO₂ is increased 12 F/g with 70% TiO₂.

The change in conductivity, sensitivity, and specific capacitance of PPy/TiO₂ nanocomposite can be explained by the impact of core-shell structure as shown in Figure 6. The PPy/TiO₂ core-shell structure will form n-p junction and



FIGURE 4: (a) The sensitivity of of PPy/TiO₂ upon exposure to oxygen, (b) the oxygen sensitivity of the materials as function of TiO_2 concentration.



FIGURE 5: (a) CV diagram of PPy/TiO₂ nanocomposites with scanning rate of 100 mV/s, (b) calculated specific capacitance of the materials as function of TiO₂ concentration.

depletion region with a width of around 10–20 nm that depends on doping condition [26, 27]. The PPy shell with thickness of 20–30 nm actually locates the space charge region. Similar to CMOS capacitor, the change in the depletion width can be used to explain the change in specific capacitance of the PPy/TiO₂. As a result of the diffusion, electrons from *n*-type TiO₂ diffuse into *p*-type PPy and form an inversion region of rich electron in a very thin layer near the PPy surface. Upon exposure to the air, the interaction between oxygen (an electron acceptor) and the rich electron layer results in an additive electron extraction from PPy valence

band and then changes the PPy conductivity. The adsorption and desorption of oxygen molecule on PPy surface then cause the variation in conductivity of the materials. The more oxygen concentration is in the environment, the more electrons are extracted; as a result, the material conductivity is increased and vice versa. Higher oxygen sensitivity indicates the fact that more oxygen adsorption sites are created on the PPy surface. The fast response and fast recovery in the oxygen sensitivity profile indicate that the physical adsorptions with weak bonding are dominant in the oxygen-nanocomposites interaction.



FIGURE 6: TEM image of the core-shell structure of $\mathrm{PPy/TiO_2}$ nanocomposite.

Thus, the PPy/TiO₂ coupling result in the formation of the inversion layer then creates more additive oxygen deficiency on the PPy-shell surface. The feature is accounted for the modification in conductance, oxygen sensitivity, and specific capacitance of the PPy/TiO₂ nanocomposite.

4. Conclusions

PPy/TiO₂ nanocomposite synthesized by *in situ* chemical polymerization was created in the form of granular PPy and embedded TiO₂ nanoparticles forming core-shell structure. The PPy/TiO₂ core-shell results in thin *n*-*p* junctions in which the TiO₂ core effectively modifies the PPy band gap as well as overall the electrical properties of the coupling. Consequently, the conductance and specific capacitance of the nanocomposite change as a function of TiO₂ concentration. The *n*-*p* contact between TiO₂ and PPy brings in an additive oxygen deficiency to the PPy shell surface and then increases the oxygen sensitivity. The process is revertible as a result from the physical O₂ adsorption and desorption which act as doping and dedoping on semiconducting PPy.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors gratefully acknowledge financial support from Basic Research Project Grant no. 103.02-2012.32 in Aid by National Foundation for Science and Technology Development (NAFOSTED), Vietnam.

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