EFFECT OF TiO$_2$ ANATASE NANOCRYSTALLITE ON ELECTRICAL PROPERTIES OF PPy/TiO$_2$ NANOCOMPOSITE

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Abstract. Polypyrrole/titanium dioxide nanocomposite (PPy/TiO$_2$) was synthesized by in-situ chemical polymerization of pyrrole (Py) monomer in colloidal suspension of TiO$_2$ anatase. TEM images show that TiO$_2$ anatase nanoparticles with size of around 3–4 nm are randomly imbedded on the surface and inside of PPy grain. The random distribution of TiO$_2$ anatase nanoparticle in PPy matrix forms variety of carrier barriers on the surface and inside of the materials. As expectation, the charge exchange between oxygen and the PPy affects the carrier barrier’s regions and then modify the electrical properties of PPy. Upon exposure to the open air the conductivity of the PPy/TiO$_2$ nanocomposite exhibits an increase of about 20 folds much larger than that of neat PPy. The enhancement is accounted for the modification of in the surface conductance of PPy/TiO$_2$ nanocomposite as a combination of the TiO$_2$ coupling and oxygen interaction.

Keywords: PPy, TiO$_2$ anatase, nanocomposite PPy/TiO$_2$, complex impedance spectrum.

Classification numbers: 81.07.Bc; 78.67.Sc; 81.07.-b.

I. INTRODUCTION

The unique structure of alternative single and double bonds in the linear chain of intrinsic conjugated polymers (CPs) [1,2] has found to be susceptible to the ambient chemical and physical interactions. Consequently, the polymer chain will lose or attract some electrons and then converts to either $p$-type or $n$-type semiconducting. The feature has been used as an effective approach to modify the electrical properties of the materials for possible applications [3,4]. In addition, the coupling of CPs with active constituents can be used as means to tailor functionalities and
design new materials with desirable characteristics. Beyond a simple combination of its property, the interaction between molecules component in the nanocomposite can bring in new features or synergistic effects.

Amongst of most studied CPs, polypyrrole (PPy) and its derivatives have attracted a great deal of attention because of their high electrical conductivity, good environmental stability, simple synthesis and processing [5] and shown to be promising materials for many applications such as electrical wire, sensors, electrochemical capacitors, electronic devices, [2, 4, 6–8], etc. Due to the relatively low oxidation potential the neutral PPy has found to be easily oxidized (doping) into p-doped state [9] and reduced (de-doping) back to the neutral form. As a result, the electrical properties of PPy seem to be easily modified by use of proper reduction/re-oxidation process or combination with suitable components in a nanocomposite [10].

On the other hand, titanium dioxide (TiO\(_2\)) is a typical oxide metal and n-type semiconductor that exhibits strong electrochemical and photochemical activity [11]. Apart from major application in vanishes, paint, etc., that rely on the brightness and high refractive index of TiO\(_2\), theelectrochemical and photochemical features have enlarged the application of TiO\(_2\) in photocatalyst, solar cells,… [12, 13]. Under normal conditions, TiO\(_2\) crystalline has two main structural morphologies: rutile and anatase which show a difference in crystalline, electronic structure and chemical activity. In term of chemoelectrical, photoelectrical, photochemical properties the TiO\(_2\) anatase shows stronger oxidatively while the rutile exhibits higher refractive index [14]. The coupling of more active TiO\(_2\) anatase with conducting polymers in a nanocomposite has found to improve their unique features [15–18], namely sensitivity, electrical conductivity, electrochemical properties, etc.

Based on these assumptions, in this research an attempt was carried out to investigate the effect of anatase nanocrystallites resulted from thermolysis of TiCl\(_4\) in HCl aqueous solution [19–21] on PPy/TiO\(_2\) nanocomposites synthesized by in-situ chemical polymerization.

**II. EXPERIMENT**

Pyrrole (Py) 99.5 % and TiCl\(_4\) (Aldrich. Co.), ammonium persulphat (APS, Kanto Chemical Co. Inc.) and titanium chloride TiCl\(_4\) (Aldrich. Co.) were used as precursors in the experiment. The PPy/TiO\(_2\) nanocomposite was in-situ chemically synthesized as followings: TiO\(_2\) nanostructure materials were firstly prepared by the thermal hydrolysis of a titanium precursor (TiCl\(_4\)). The synthesis was carried on at low temperature (\(\sim 80^\circ\text{C}\)) in acidic aqueous media of 0.1 M HCl as a usual route [19,20]. The resulting TiO\(_2\) nanomaterials were separated into two parts containing anatase nanostructures in the colloidal suspension and rutile nanostructures in the sedimentation. The anatase colloidal suspension then was extracted, dried and then mixed with an aqueous solution of 0.1 M Py and 1.0 M HCl as a given TiO\(_2\)/Py ratio. Secondly, by adding drop-by drop the same amount of an aqueous solution consisting of 0.1 M APS (as oxidant) and 1.0 M HCl into the TiO\(_2\)/Py mixing solution the polymerization of PPy was ignited. After 1.5 hours of continuously stirring the polymerization was terminated by pouring ethanol into the mixture. The resulting black PPy/TiO\(_2\) nanocomposites formed in the solution were filtered, then was cleaned by distilled water and kept in 1.0 M HCl solution.

The morphology, structure, particle size of the TiO\(_2\) anatase and PPy/TiO\(_2\) nanocomposite were characterized by X-ray diffraction (XRD D8 Advance Bruker) and Transmission Electron Microscope (TEM Jeol JEM1010). The electronic structure of the materials was analyzed by
The XRD and Raman spectra show that the TiO$_2$ extracted from the suspension solution is anatase nanocrystallite. As can be seen from the XRD spectrum in Figure 1a, the strongest peak observed around $25.29^\circ$ is assigned to (101) plane refraction of anatase and the other peaks at 37.80, 48.05, 53.89, and 62.68$^\circ$ stand for reflection at (004), (200), (105), and (204) planes, respectively (JCPDS number 00-021-1272). Using Scherrer formula to estimate the particle size, it was found that the anatase mean size is around 4.0 nm.

**III. RESULTS AND DISCUSSION**

The XRD and Raman spectra show that the TiO$_2$ extracted from the suspension solution is anatase nanocrystallite. As can be seen from the XRD spectrum in Figure 1a, the strongest peak observed around $25.29^\circ$ is assigned to (101) plane refraction of anatase and the other peaks at 37.80, 48.05, 53.89, and 62.68$^\circ$ stand for reflection at (004), (200), (105), and (204) planes, respectively (JCPDS number 00-021-1272). Using Scherrer formula to estimate the particle size, it was found that the anatase mean size is around 4.0 nm.

![Fig. 1. (a) XRD and (b) Raman spectrum of TiO$_2$ synthesized by pyrolysis of TiCl$_4$ aqueous solution.](image-url)
The Raman spectrum of the suspended TiO$_2$ in Fig. 1b exhibits Raman shift peaks at around 155, 412, 512, and 631 cm$^{-1}$ representing the $E_g$, $B1_g$, $A1_g + B1_g$, and $E_g$ vibrational modes, respectively of anatase phase [22–24]. In comparison to the standard vibration mode of anatase, the first $E_g$ mode at 155 cm$^{-1}$ shows blue shifts in frequency and increase in width at half maximum that accounts for an influence of the nanosize of the TiO$_2$ anatase crystallites.

![Fig. 2.](image-url) (a) TEM and (b) HRTEM images of TiO$_2$ nanoparticles.

As can be seen from the TEM images in Fig. 2a, the TiO$_2$ in the suspension solution forms uniform grain-like clusters consisting of anatase particles with a mean size around 4-5 nm (Fig. 2b). This estimated size of TiO$_2$ nanoparticles is consistent to the mean size calculated from XRD.

![Fig. 3.](image-url) TEM images of (a) neat PPy, (b) PPy/TiO$_2$ nanocomposite with 11% anatase TiO$_2$ and (c): PPy/TiO$_2$ nanocomposite with 33% anatase TiO$_2$.

As expected, the strong coupling between PPy and TiO$_2$ can be seen from TEM images and Raman spectra made on PPy/TiO$_2$. TEM images show that the neat PPy has common structure of granular particle with mean size around 30-40 nm (Fig. 3a); and black TiO$_2$ anatase nanoparticles with size around 3–4 nm randomly distributed on the surface and imbedded inside of PPy/TiO$_2$ particles (Fig. 3b and Fig. 3c). Due to the difference in charge carriers density between TiO$_2$ (electron, insulator) and PPy (hole, semiconductor), the present of TiO$_2$ particle could...
form a variety of carrier barriers or probably depletion junctions inside of PPy [25, 26], i.e., affecting the conductivity of the materials. In comparison to the core-shell structure of PPy/TiO2, rutile [27] the random distribution of TiO2 anatase nanoparticles in PPy matrix is expected to enhance the coupling effect between TiO2 anatase and PPy.

As shown in Fig. 4 the Raman spectrum of neat PPy shows the distinct vibrational modes at 1560 cm\(^{-1}\) (G band) and 1342 cm\(^{-1}\) (D band). The presence of TiO2 in the nanocomposite causes a change in relative intensity and a slight blue-shift of the vibration bands standing for C=C bond from 1342 cm\(^{-1}\) to 1350 cm\(^{-1}\) and 1560 cm\(^{-1}\) to 1569 cm\(^{-1}\) indicating a shift of PPy to the oxidation structure [22–24]. The higher oxidation degree of PPy is accounted for the strong coupling with TiO2 anatase in the nanocomposites. From chemical view of consideration, at the first oxidization stage the TiO2 surface in the reaction medium acts as nucleation sites for the Py radical monomers adsorbed and anchored on. As brought into contact with PPy, the higher oxidative anatase TiO2 will partly oxidize PPy and extract some electrons from PPy. Consequently, the conductance of \(p\)-type PPy and \(n\)-type TiO2 will increase and variety of consecutive \(p-n\) junctions are formed. The interfacial interaction between TiO2 and PPy in the nanocomposites is expected to modify their chemical and electronic structures.

The effect of oxygen on the electrical conductivity of PPy and its derivatives is well known [28]. As an oxidized agent, the adsorbed oxygen molecule on the PPy surface abstracts a portion of electron from the pi-bond in the polymer chain and leave positive holes in the HUMO band of PPy, then converts the PPy to be a \(p\)-type semiconductor. The more adsorbed oxygen molecules are on the surface of PPy the higher the conductance of the materials is. Change the oxygen concentration in the ambient environment by changing the air pressure, the conductance of PPy will be modified. Experiments show that the resistance of PPy and PPy/TiO2 is very sensitive to air pressure. As can be seen from the sensing profile in Fig. 5, the resistance of materials rapidly increases as air pressure reduces (the vacuum pump on) and fast recovers back to
the origin value as re-exposes to the air (the vacuum pump off). The presence of TiO$_2$ anatase in the PPy matrix significantly modifies the O$_2$ sensitivity of the materials. As can be seen from Fig. 5, the O$_2$ sensitivity of PPy/TiO$_2$ added with 11 at.% anatase TiO$_2$ exceeds 20 folds higher in comparison to that of neat PPy. This sensitivity is lightly higher than that of PPy coupling with TiO$_2$ rutile [27]. The fast response, recovery and the stability in base line from the O$_2$ sensing profile indicate the fact that the adsorption and desorption of oxygen molecules on PPy/TiO$_2$ surface is easy, namely the weak bonds (physical bonds) are dominant in the oxygen-PPy/TiO$_2$ interaction. Higher oxygen sensitivity indicates that more oxygen adsorption sites are created on the PPy/TiO$_2$ surface as anatase particles are incorporated.

![Fig. 5. The oxygen sensitivity profile of PPy/TiO$_2$ with different TiO$_2$ anatase concentration.](image)

Table 1. Values of the impedance parameters in PPy/TiO$_2$ samples.

<table>
<thead>
<tr>
<th>TiO$_2$ (at. %)</th>
<th>$R_s$ (Ω)</th>
<th>$C$ (F)</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>330</td>
<td>3.11E-12</td>
<td>5.22E6</td>
</tr>
<tr>
<td>5</td>
<td>370</td>
<td>3.15E-12</td>
<td>1.69E6</td>
</tr>
<tr>
<td>11</td>
<td>340</td>
<td>2.74E-12</td>
<td>1.23E6</td>
</tr>
<tr>
<td>32</td>
<td>250</td>
<td>3.00E-12</td>
<td>4.23E6</td>
</tr>
<tr>
<td>49</td>
<td>270</td>
<td>2.97E-12</td>
<td>1.70E7</td>
</tr>
</tbody>
</table>

In order to explain the sensing and charge transport behavior of PPy and PPy/TiO$_2$ samples, a complex impedance spectroscopy is made. As shown in Fig. 6, a good agreement is observed between the experimental results (separated dots) and the simulated data (solid lines). The Nyquist plots of PPy and PPy/TiO$_2$ are perfect single semicircles. The semicircle plots can be fitted into a simple equivalent RC circuit which consists of a frequency independent resistance ($R_s$), a parallel
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**Fig. 6.** Impedance spectra made on the PPy/TiO$_2$ nanocomposites with various TiO$_2$ anatase contents.

**Fig. 7.** The resistance $R_p$ of PPy/TiO$_2$ as a function of TiO$_2$ concentration.
The Nyquist plots are shown in Fig. 8 and used to determine the effect of reduced air pressure on the charge transportation behavior of the PPy/TiO$_2$ sample with TiO$_2$ content of 11 at.%. As can be seen from the plots, the fitted spectrum is a semicircle with radius increasing with vacuum level. The semicircle gives the same equivalent circuit of $R_s$, $R_p$ and $C_p$. The simulated results in Table 2 show that the $R_s$ and $C_p$ are almost unchanged but $R_p$ is exponentially increased with reduced air pressure (Fig. 9).

![Impedance spectra made on the PPy/TiO$_2$ nanocomposites in reduced air pressure and N$_2$ gas.](image1)

**Fig. 8.** Impedance spectra made on the PPy/TiO$_2$ nanocomposites in reduced air pressure and N$_2$ gas.

![The resistance $R_p$ of PPy/TiO$_2$ as a function of reduced air pressure.](image2)

**Fig. 9.** The resistance $R_p$ of PPy/TiO$_2$ as a function of reduced air pressure.
Table 2. Values of the impedance parameters in PPy/TiO₂ samples.

<table>
<thead>
<tr>
<th>Air pressure [bar]</th>
<th>Rs (Ω)</th>
<th>Cp (F)</th>
<th>Rp (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1040</td>
<td>7.75E-12</td>
<td>11E+3</td>
</tr>
<tr>
<td>-0.2</td>
<td>1000</td>
<td>7.08E-12</td>
<td>83E+3</td>
</tr>
<tr>
<td>-0.3</td>
<td>980</td>
<td>6.61E-12</td>
<td>247E+3</td>
</tr>
<tr>
<td>-0.4</td>
<td>1020</td>
<td>6.68E-12</td>
<td>423E+3</td>
</tr>
<tr>
<td>-0.5</td>
<td>1050</td>
<td>6.67E-12</td>
<td>780E+3</td>
</tr>
<tr>
<td>-0.6</td>
<td>1060</td>
<td>6.60E-12</td>
<td>1,21E+6</td>
</tr>
<tr>
<td>N₂ environment</td>
<td>920</td>
<td>7.82E-12</td>
<td>4,03E+6</td>
</tr>
</tbody>
</table>

Based on the oxygen sensitivity, impedance spectra, it can be deduced that the sensing feature of PPy/TiO₂ is strongly affected by the surface states and interface layers ($p-n$ depletion region) between PPy and TiO₂. With anatase nanoparticles are randomly imbedded on the surface and inside of the PPy matrix, the PPy/TiO₂ structure will form a $n-p$ junction and depletion region depending on TiO₂ adding condition [25]. Upon exposure to the air, the charge exchange between oxygen and PPy/TiO₂ will form inversion regions of rich electron in a very thin layer near the $p-n$ PPy/TiO₂ contact and then modify the material conductance. Hence, the most sensitive $R_p$ in the equivalent circuits $R_s/C_pR_p$ is expected to be mainly associated with the material surface resistance. The modification of $n-p$ junction in the surface and inside of PPy/TiO₂ upon exposure to oxygen then is accounted for the oxygen sensitivity enhancement of the materials.

IV. CONCLUSIONS

PPy/TiO₂ nanocomposite synthesized by in-situ chemical polymerization shows that TiO₂ anatase nanoparticles with size around 3–4 nm are randomly embedded on the surface and inside of PPy grain. The PPy/TiO₂ coupling results in variety of carrier barriers on the surface and inside of PPy and then modify the PPy electronic properties. Upon exposure to oxygen (an oxidant and an electron acceptor) the charge exchange between oxygen and PPy/TiO₂ surface will form inversion layer in carrier barrier’s contact region then modify the oxygen sensitivity of PPy. Upon exposure to reduced air pressure the conductivity of the nanocomposite exhibits a variation roughly about 20 folds that are accounted for the interaction between oxygen and the PPy surface. Complex impedance spectra show that the charge transport in the materials is equivalent to a circuit consisting of a frequency independent resistance ($R_s$) in series with RC network with capacitance $C_p$ and resistance $R_p$ in which the $R_p$ is strongly sensitive to the environmental changing.

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