

Synthesis, characterization and electrochemical study of Mn-doped TiO₂ decorated polypyrrole nanotubes

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Abstract. Nanostructured conductive polymers are the growing interest in the field of electrochemistry due to their superior conductivity and environmental friendliness. The existence of transition metal oxides could improve their nanostructure as well as conductive properties. In this study, polypyrrole nanotubes are synthesized in the presence of TiO₂ and manganese (Mn)-doped TiO₂ nanoparticles (NPs) to investigate their electrochemical properties. Details characterization of the synthesized composites were done by X-Ray diffraction (XRD) and TEM. The TEM analysis shows that doping of TiO₂ with Mn decrease the grain size of the TiO₂ nanoparticles and successively its effects on the synthesis of the PPy nanotubes (PPyNTs). TEM confirmed that PPyNTs synthesized in the presence of Mn-doped TiO₂ are thinner in size compare to the PPyNTs synthesized in presence of pure TiO₂. The electrochemical effectiveness of the synthesized PPy nanocomposite was investigated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV and EIS both on a modified glassy carbon electrode reveal the better electron transportability for the Mn-doped TiO₂ PPyNTs due to the synergistic effect of doping and decreased the size of PPyNTs as well as increased surface area.

1. Introduction

One-dimensional (1D) nanostructured materials such as nanowires, nanorods, nanobelts, and nanotubes have produced immense attention due to their special geometries, extraordinary physical and chemical properties. Therefore, they are highly effective for the fabrication of nanodevices, nanosensors and microelectronics [1, 2]. Polypyrrole (PPy), which is a typical conductive polymer, possess unique electrical, optical and optoelectrical properties, and is environmentally friendly. It has abundant application in energy storage, chemical sensors, biosensors and corrosion protection [3, 4]. Therefore, it has attracted extra attention in 1D nanostructured materials fabrication [5]. 1D nanostructured PPy can be synthesized through both chemical and electrochemical polymerization using template or template-free approach [6, 7] and also from electrospinning method [8].

Titanium dioxide (TiO₂) is a promising nanomaterial for many emerging applications including photocatalysis, solar cell fabrication, batteries and gas sensing. Doping of transition metal ions into TiO₂ lattice conveys different strains due to the difference between ionic radius which leads a variation in the lattice parameters and modifies its optical, electrical as well as magnetic properties [9, 10].



It has been reported that polymers synthesized in the vicinity of nanoparticles could decrease the polymer size and consequently increase the surface area [3]. It is also expected that the incorporation of TiO₂ with PPy might improve the electrochemical properties of PPy. However, only a few studies can be found in the literature. In this study, we synthesize Mn-doped TiO₂ and TiO₂ NPs decorated PPy nanotubes and studied their electrochemical properties on a glassy carbon electrode.

2. Methodology

2.1 Synthesis of Mn-doped TiO₂ nanoparticles (NPs)

Reagent grade chemicals obtained from Sigma-Aldrich and Merck, Malaysia were used to synthesize all the materials. Mn-doped TiO₂ nanoparticles were synthesized through a sol-gel method from titanium tetra-isopropoxide Ti[OCH(CH₃)₂]₄ where manganese acetate tetrahydrate was the doping precursor [11]. A well-mixed mixture of Ti[OCH(CH₃)₂]₄ and Mn precursors (3 mol %) in glacial acetic acid was poured into double distilled water and then stirred for 6 h with a constant rate. A ratio of 1: 10:200 for Ti[OCH(CH₃)₂]₄: glacial acetic acid: H₂O was maintained. After stirring the gel-like mixture was kept in an oven at 75 °C for 24 hours followed by grounded to a fine powder. The fine powder was finally calcinated for 5 h at 500 °C. In a Similar way, TiO₂ NPs were prepared for comparison.

2.2 Preparation of Mn-doped Polypyrrole nanotubes (PPyNTs)

Mn-doped TiO₂/PPyNTs were synthesized according to a previous report where methylene orange (MO) was used as a soft template during the chemical oxidative polymerization [12]. Briefly, the oxidant FeCl₃ was dissolved in 5mM MO solution and subsequently, 0.19 g of Mn-doped TiO₂ NPs was added to the mixture. To spread the NPs on the MO template, the mixture was then stirred for 30 min. After that, 0.2 ml of pyrrole monomer was added drop by drop without stirring. The whole system was immediately placed at 0-4 °C for complete the polymerization for 24 h. The resulting polymer composite then filtered and washed with distilled water and ethanol to fully remove the MO. Finally, the composite dried at 40 °C in an oven. PPyNTs were also prepared in presence of TiO₂ NPs and absence of NPs.

2.3 Characterization

The existence of TiO₂ and Mn-doped TiO₂ NPs in the synthesized PPyNTs was investigated through X-Ray Diffraction (XRD) in Siemens D5000 model X-Ray diffractometer. Field emission scanning electron microscopy (FESEM) in a Hitachi SU8220 microscope. Transmission electron microscopy (TEM) were taken from MIMOS Berhad, Malaysia to confirm the morphology and calculate the size of the NPs and NTs composites.

2.4 Study of electrochemical properties

As prepared Mn-doped TiO₂/PPyNTs and TiO₂/PPyNTs were dispersed in DMF (1 mg/ml) through ultrasonication. 10 µl of each dispersion were then dropped cast on a cleaned glassy carbon electrode surface and kept to dried for studied the electrochemical properties. Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in a Methrom Autolab (PGSTAT-302N) which is operated by GPES and FRA.EXE software.

3. Results and discussion

3.1 XRD and TEM analysis

The crystal phase of the synthesized TiO₂ and Mn-doped TiO₂ NPs has been identified from XRD and the corresponding lattice patterns are presented in figure 1. In pure TiO₂ NPs, all the diffraction peaks can be indexed to tetragonal anatase structure of TiO₂ with a good agreement of standard JCPDS entry code No. 00-001-0562. For Mn-doped TiO₂ NPs, no additional peak which is related to Mn or any of

its oxide were found. This confirms the phase purity of the NPs. However, most of the predominance peaks intensity (triplet) (101) (103) and (200) were increased with an increase of full width at half maximum. Moreover, the peaks were shifted slightly to a lower angle when we compared to the pure TiO_2 NPs. Hence, it could be assumed that some of the Mn^{2+} ions can enter the Ti crystal site and replaced some Ti^{4+} ions. These substitutional Mn^{2+} ions perhaps doped in regular size of Ti ions and consequently decrease the grain size of the pure TiO_2 NPs [13, 14].

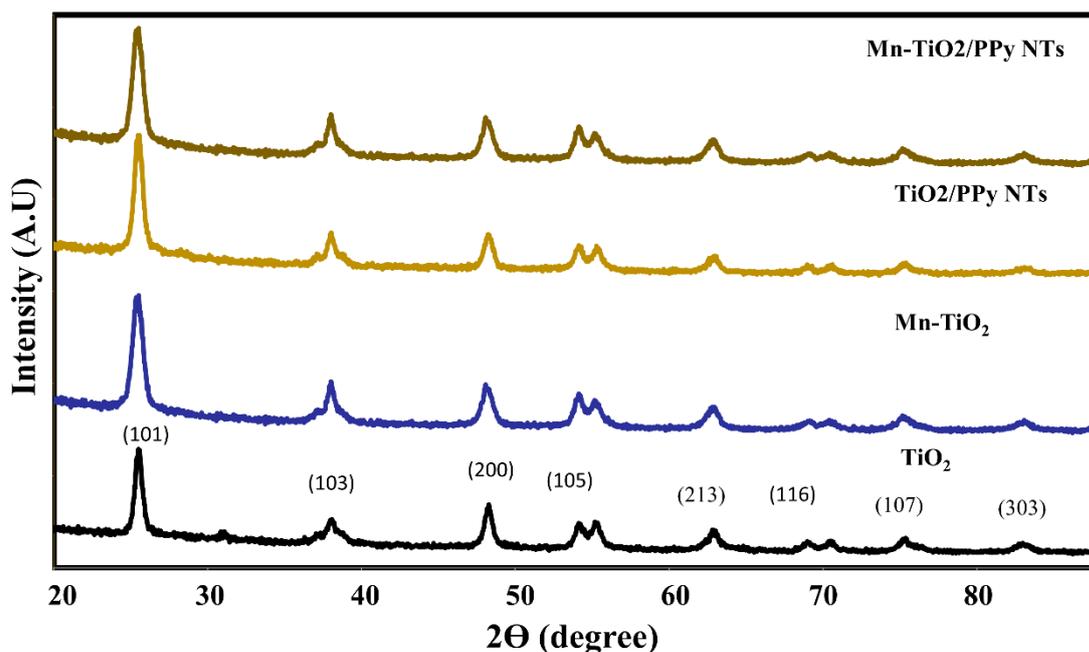


Figure 1. The powder XRD diffraction pattern of pure TiO_2 , Mn-TiO_2 NPs, $\text{TiO}_2/\text{PPyNTs}$, and $\text{Mn-TiO}_2/\text{PPyNTs}$.

The mean crystalline size was calculated from Scherrer's equation [15] and was found 18.6 and 11.90 nm for pure and Mn-doped TiO_2 NPs respectively. The XRD pattern of $\text{TiO}_2/\text{PPyNTs}$ and Mn-doped $\text{TiO}_2/\text{PPyNTs}$ were found in a similar pattern with following the similar changes, therefore, confirm the existence of NPs on the PPyNTs.

Morphology of the nanostructured materials is an important characteristic as the performance depends on the morphology. Figure 2. (a-b) shows the TEM images of pure TiO_2 and Mn-doped TiO_2 NPs. We can see clearly a uniform spherical shaped NPs has formed and Mn dopant has no influence to change the morphology. However, a less agglomeration and reduction of crystal size were observed for Mn-doped TiO_2 NPs. The mean diameter is calculated around (17.19 ± 1.07) nm for pure TiO_2 NPs and (10.97 ± 1.70) nm for Mn- TiO_2 NPs (figure 2c, 2d), which are well matched to the size calculated from Scherrer's equation in XRD. The beneficial effect of doping of Mn in TiO_2 NPs can be seen clearly from the TEM image of synthesized PPyNTs composite (figure 2e and 2f). A much thinner nanotube-shaped PPy nanocomposites were formed in presence of Mn-doped TiO_2 and the NPs are decorated on the tube surface.

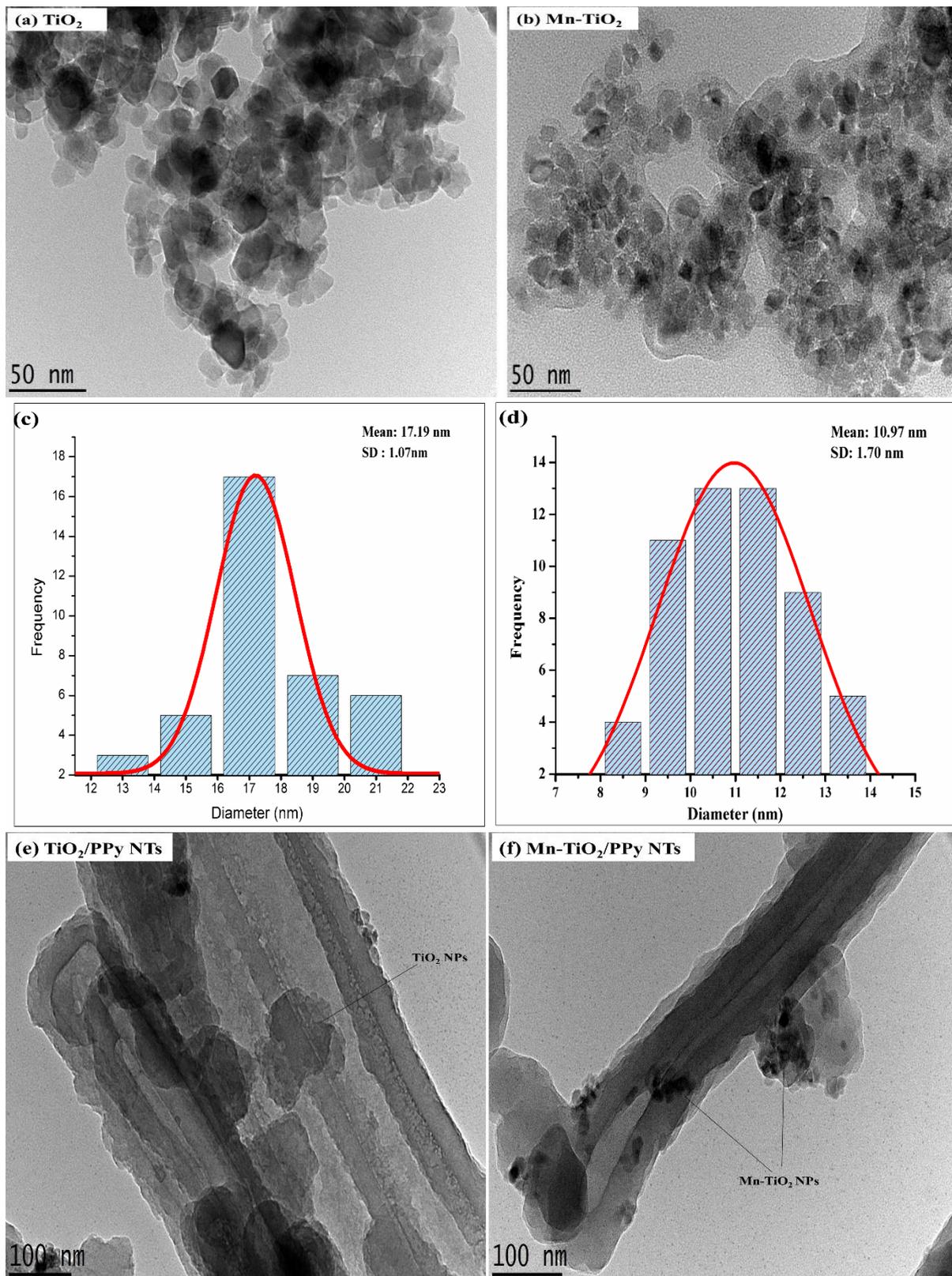


Figure 2. TEM images of TiO₂ NPs (a), Mn-doped TiO₂ (b), TiO₂/PPyNTs (e), Mn-TiO₂/PPyNTs (f) and particle size distribution of TiO₂ NPs (c), Mn-doped TiO₂ NPs (d).

3.2 Electrochemical performance of synthesized PPyNTs

CV was performed in 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ (1:1) in 0.5 M KCl as supporting electrolyte within 0 to 0.6 V at a scan rate 50 mV/s. Figure 3. shows the CV profile of bare GCE, TiO_2/PPy NTs, and Mn- TiO_2/PPy NTs modified GCE. An increase anodic (I_{pa}) and cathodic (I_{pc}) peak current were observed for TiO_2/PPy NTs modified GCE compared to bare GCE. In addition, the oxidation-reduction potential also shifted to a lower voltage, which is always beneficial. A further increase in the peak current was observed for Mn- TiO_2/PPy NTs modified GCE. This could be due to the synergistic effect of Mn-doped TiO_2 and the decrease of NTs diameter as well as the increased surface area.

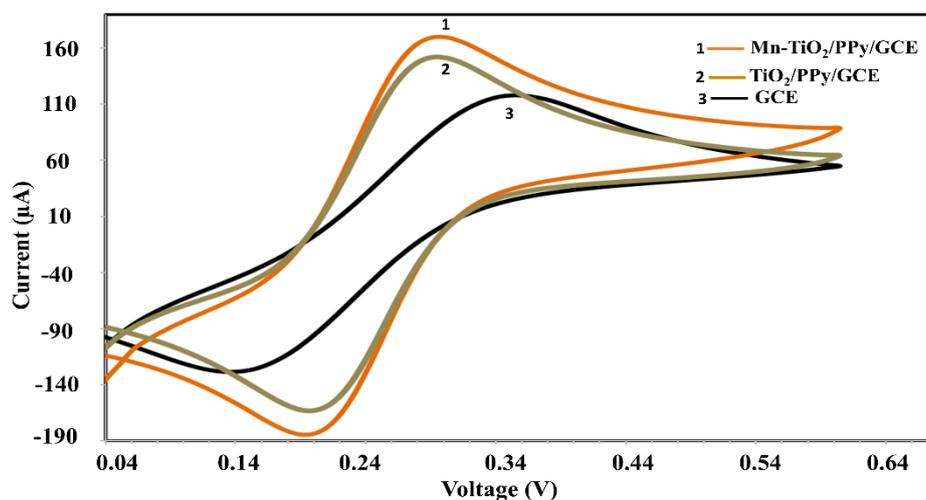


Figure 3. CV in 10 mM $\text{Fe}^{2+/3+}$ and 0.5 M KCl as supporting electrolyte.

To investigate the interfacial properties of the nanocomposite-modified GCE electrode, EIS was used as it is one of the efficient technique. Figure 4(a). shows the Nyquist plots of Mn-doped TiO_2/PPy NTs (1), TiO_2/PPy NTs (2) and bare GCE (3). In EIS, the Nyquist plot consists of a semicircle at a higher frequency which signifies the electron transfer limited process on electrode/electrolyte interface. Also, an inclined line at lower frequency correlates the mass transfer process.

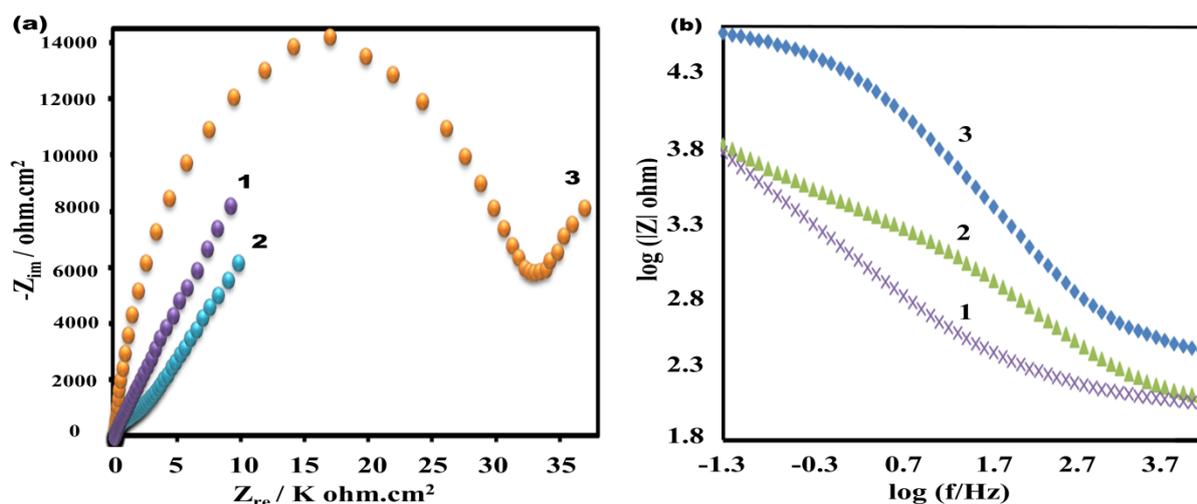


Figure 4. EIS of Mn-doped TiO_2/PPy NTs (1), TiO_2/PPy NTs (2) and bare GCE (3) 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ (1:1) in 0.1 M KCl as supporting electrolyte at OCP within a frequency range 100 kHz to 0.1 Hz.

The electron transfer resistant can be evaluated by comparing the diameter of the semicircle. It is well known that decrease the semicircle diameter corresponds to lower the electron transfer resistant which means higher conductivity [16]. This can exactly see in the comparison of three electrodes. The semicircle diameter decreased a lot for pure TiO₂/PPyNTs. However, a further decreased can be observed for Mn-TiO₂/PPyNTs.

The effect of Mn doping is also confirmed from Bode plots in figure (4b). Whenever we compare the log |Z| of the three electrodes it can be seen that the charge transfer resistance shows the same direction: GCE > TiO₂/PPyNTs/GCE > Mn-TiO₂/PPyNTs/GCE, that is good agreement with the result obtained from the Nyquist plot.

4. Conclusion

Nanostructured polypyrrole in nanotube morphology were synthesized in the presence of pure TiO₂ and Mn-doped TiO₂ NPs. XRD and TEM analysis showed that the average diameter of pure TiO₂ and Mn-doped TiO₂ NPs is 17.19 nm and 10.97 nm respectively. They also confirmed the presence of Mn-doped TiO₂ NPs produced significantly thinner size PPyNTs composite. CV measurement and impedance analysis on GCE electrode showed the higher electron conductivity and minimum charge transfer resistance for Mn-TiO₂/PPyNTs due to high surface area. Therefore, Mn-doped TiO₂/PPy NTs could be utilized as effective electrode materials for the development of sensitive electrochemical sensor. However, further investigation is required to establish the optimum dopant concentration for best electrochemical properties.

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