

Polymerisation of Protonic Polyaniline/Multi-Walled Carbon Nanotubes-Manganese Dioxide Nanocomposites

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Abstract: *This study reports the synthesis and characterisation of a ternary nanocomposite of polyaniline (PANI), multi-walled carbon nanotubes (MWCNTs) and manganese dioxide (MnO₂). MnO₂ successfully filled the cavities between the MWCNTs. In situ polymerisation of aniline in the presence of MWCNTs-MnO₂ was done to form a ternary nanocomposite. The ultraviolet-visible (UV-vis) spectrum shows that MnO₂ filling does not significantly change the electronic transition of the nanocomposite. The infrared (IR) spectrum shows that the nanocomposite is rich in quinoid rings of PANI. Electron microscopy reveals the MnO₂ filling and coating of PANI. The ternary nanocomposite showed high electron conductivity compared to neat PANI and PANI/MWCNTs without MnO₂.*

Keywords: conducting polymer, polyaniline, multi-walled carbon nanotubes, manganese dioxide, nanocomposites

Abstrak: *Kajian ini melaporkan pencirian dan sintesis kompositnano terner yang terdiri daripada polianilin (PANI), tiub nanokarbon banyak dinding (MWCNTs) dan manganese dioksida (MnO₂). MnO₂ telah berjaya mengisi ke dalam ruang kosong MWCNTs. Pempolimeran telah dijalankan dengan kaedah in situ dengan kehadiran MWCNTs-MnO₂ untuk membentuk kompositnano terner. Spektra 'UV-visible' menunjukkan bahawa pengisian MnO₂ tidak mengubah transisi elektronik kompositnano dengan ketara. Spektra infra merah (IR) menunjukkan kompositnano tersebut kaya dengan cincin quinoid PANI. Mikroskop elektron menunjukkan salutan PANI dan pengisian MnO₂. Kompositnano terner tersebut menunjukkan pengaliran elektron yang lebih tinggi berbanding PANI dan juga PANI/MWCNTs tanpa MnO₂.*

Kata kunci: polimer berpengalir, polianilin, tiub nanokarbon banyak dinding, manganese dioksida, kompositnano

1. INTRODUCTION

Since their discovery by Iijima¹, carbon nanotubes (CNTs) have received much attention for their possible use in fabricating a new classes of advanced material, due to their unique structural, optical, mechanical and electronic properties.²⁻⁴ Introducing CNTs into a polymer matrix improves the properties of

the original polymer.⁵ Among these polymer/CNTs nanocomposites, many have focused on the combination of CNTs and conducting polymers.^{6,7} PANI is one of the conducting polymers that has potential in the near term, due to its good processability, environmental stability and reversible control of conductivity both by charge-transfer doping and protonation.⁸ The use of PANI together with CNTs to form nanocomposites could result in the formation of ternary materials with extraordinary properties.⁹ Though several studies have been done on PANI/CNTs nanocomposites, the electron conduction and stability of the nanocomposites still remain an issue.¹⁰ The aim of this study is to fill the MWCNTs with MnO₂ in order to improve the interaction between the MWCNTs and PANI, which may lead to an increase in the electron conductivity. Potential applications of this nanocomposite are in high energy portable electronics and supercapacitor properties.¹¹ This study also reports the synthesis of HCl-doped PANI in its emeraldine salt by *in situ* chemical oxidative polymerisation of aniline to form a ternary nanocomposite of PANI /MWCNTs-MnO₂.

2. EXPERIMENTAL

A complete description of the purification and filling of MWCNTs with MnO₂ has been explained in detail elsewhere.¹² The *in situ* nanocomposites were synthesised by the polymerisation of aniline (ACS grade, Acros) with potassium dichromate (R&M) as the oxidant in the presence of the MWCNTs-MnO₂, as described in Zein et al.¹² A solution of HCl (Aldrich) containing a predetermined amount of MWCNTs-MnO₂ was sonicated at room temperature. Aniline monomer was dissolved in HCl solution and added to the MWCNTs-MnO₂ suspension and stirred. The oxidant, potassium dichromate, was dissolved in HCl solution and then slowly added dropwise to the reaction mixture. After the suspension became green, indicating the formation of PANI in its emeraldine salt form, the nanocomposites obtained were filtered, washed several times with deionized water and dried for 24 h. The same method was used for neat PANI and PANI/MWCNTs. UV-vis spectra were performed on a Shimadzu UV-visible spectrophotometer with the samples suspended in n-methylpyrrolidinone (NMP). IR spectra were obtained by means of Fourier transform infra red spectroscopy (FTIR) from Perkin Elmer. The morphology analysis of the nanocomposites was carried out using a variable pressure field emission scanning electron microscope (VPFESEM) and transmission electron microscope (TEM). The electrical conductivity was measured by a high resistance meter from Advantest.

3. RESULTS AND DISCUSSION

UV-vis spectroscopy was utilised to understand the electronic states of PANI in PANI/MWCNTs and PANI/MWCNTs-MnO₂. The HCl-doped PANI [Fig. 1(a)] showed a characteristic band for the polaronic transition (polaron- π^* transition) around 450 nm,¹³ indicating that the resulting PANI emeraldine salt was in the doped state. The peak around 290 nm represents the π - π^* electron orbital transition along the backbone of the PANI chain. As MWCNTs and MWCNTs-MnO₂ were incorporated with PANI [Figs. 1(b) and (c)], the characteristic peak assigned to the polaron- π^* transition of the PANI chain shifted to longer wavelengths, indicating the interaction between quinoid rings and MWCNTs.¹⁴ The π - π^* transition of PANI in the nanocomposites was also shifted to longer wavelengths. The MnO₂ [Fig. 1(c)] filling does not seem to cause any significant changes on the electronic transition of the nanocomposites.

Figure 2 shows the FTIR spectrum for the HCl-doped PANI. The spectrum exhibits the clear presence of benzoid at 1476 cm⁻¹ and the quinoid ring vibration at 1557 cm⁻¹, indicating the oxidation state of emeraldine salt of PANI.¹⁵ The strong band around 1141 cm⁻¹ is the characteristic peak of PANI conductivity and is a measure of the degree of the delocalisation of electrons.¹⁴ The very weak and broad band around 3000 cm⁻¹ is assigned to the N-H stretching mode. Figures 3(a) and (b) show PANI/MWCNTs and PANI/MWCNTs-MnO₂, respectively. There were clear differences between these and the spectrum of HCl-doped PANI (Fig. 2). The N-H stretching region near 3000 cm⁻¹ in both Figures 3(a) and (b) showed strong and broad peaks, but very weak and broad peaks were present in the neat PANI spectrum. The interaction between the MWCNTs and PANI may result in “charge transfer”, whereby the sp² carbons of the MWCNTs compete with dopant ions [Cl⁻] and perturb the H-bond, resulting an increase in the N-H stretching intensity.¹⁶ Another difference

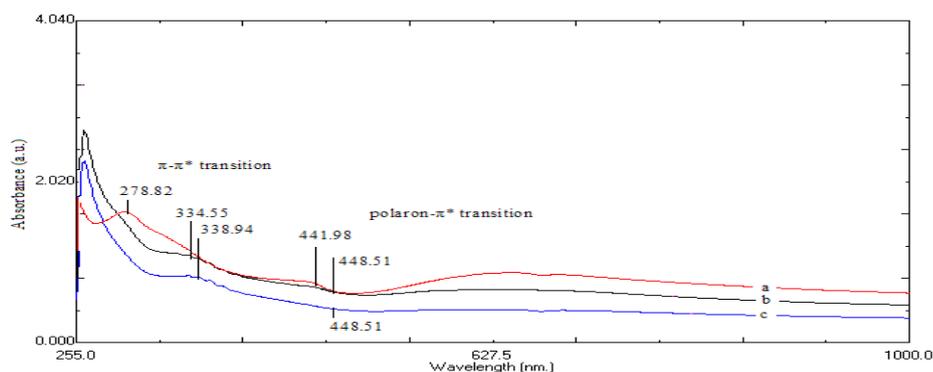


Figure 1: UV-vis spectra of: a) PANI, b) PANI/MWCNTs, and c) PANI/MWCNTs-MnO₂.

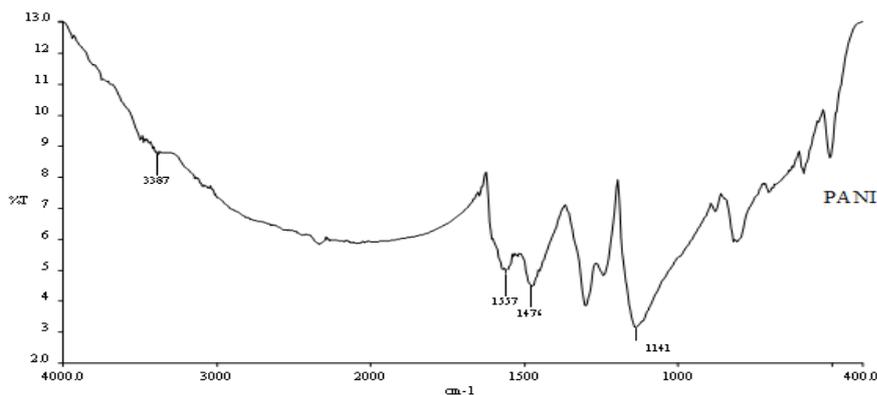


Figure 2: FTIR spectrum of HCl-doped PANI.

that can be observed is the intensity ratio of the benzoid and quinoid bands. The spectrum of pure PANI (Fig. 2) exhibits a clear difference in intensity; the quinoid band is less intense than benzoid band. The benzoid/quinoid intensity ratio for PANI/MWCNTs [Fig. 3(a)] is reduced considerably and almost equal for PANI/MWCNTs-MnO₂ [(Fig. 3(b)]. This reveals that there are fewer benzoid units in the nanocomposite of PANI/MWCNTs-MnO₂ compared to neat PANI. This may suggest that the MnO₂ promotes and stabilises the quinoid ring structure of the nanocomposite.

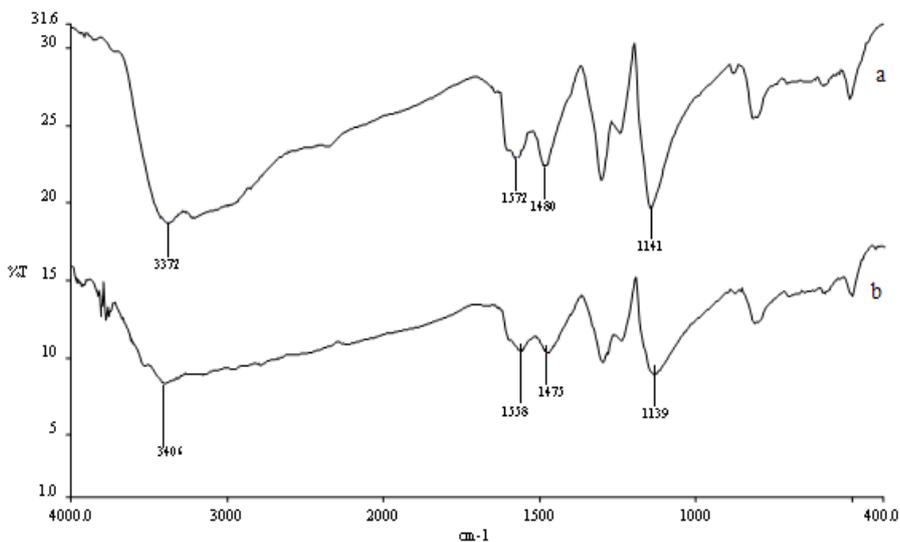


Figure 3: FTIR spectra of a) PANI/MWCNTs and b) PANI/MWCNTs-MnO₂.

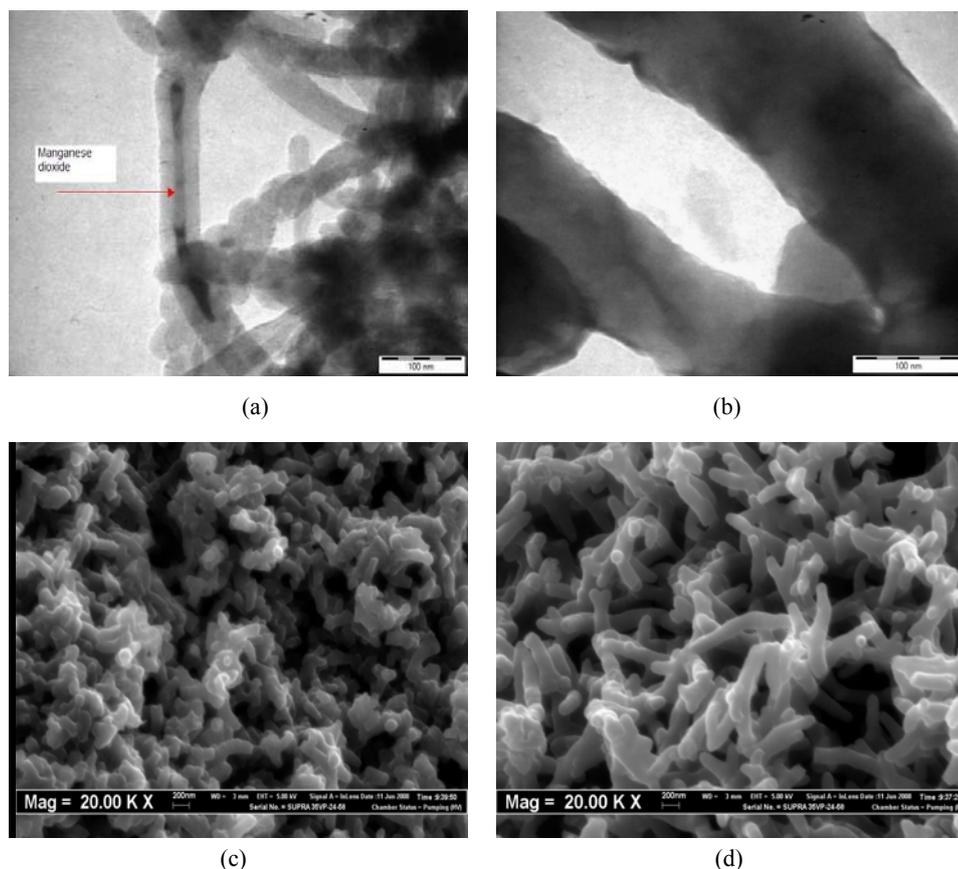


Figure 4: TEM images of: a) MWCNTs-MnO₂ and b) PANI/MWCNTs-MnO₂, and SEM images of: c) PANI/MWCNTs and d) PANI/MWCNTs-MnO₂.

TEM images of the MWCNTs after being filled with MnO₂ are shown in Figure 4(a). The filled MWCNTs show dark contrast, suggesting that the filling of MnO₂ in the inner cavity of MWCNTs did take place. The outer walls of the filled MWCNTs were smooth with no observable crystallised MnO₂. Figure 4(b) shows the ternary nanocomposite, PANI/MWCNTs-MnO₂. It shows that the PANI was uniformly coated on the surface of the MWCNTs-MnO₂, forming a tubular structure with a thickness of a few nanometers. Figure 4(d) reveals that the PANI/MWCNTs-MnO₂ was well-dispersed. During the polymerisation, the growing PANI polymer chains wedged away the MWCNTs-MnO₂ bundles and then broke the bundles down into individual MWCNTs-MnO₂. The interaction between the quinoid ring of PANI and the MWCNTs-MnO₂ causes PANI polymer chains to be adsorbed at the surface of MWCNTs, thus forming a tubular core surrounding the MWCNTs-MnO₂.

The electrical conductivities of neat PANI, PANI/MWCNTs and PANI/MWCNTs-MnO₂ were measured according to the standard four-point probe method. The conductivity of the samples were measured and calculated to be 38.34 Scm⁻¹, 50.56 Scm⁻¹ and 57.74 Scm⁻¹ for neat PANI, PANI/MWCNTs and PANI/MWCNTs-MnO₂, respectively. The enhancement in conductivity of PANI/MWCNTs compared to neat PANI is due to the charge transfer effect from the quinoid rings of the PANI to the MWCNTs. Furthermore, the MWCNTs may serve as “conducting bridges”, connecting the PANI conducting domains. A further increase in conductivity was observed for PANI/MWCNTs-MnO₂, which may be due to the role of MnO₂ in stabilising the interaction between the PANI and MWCNTs, thus leading to an increase in electron conductivity.

4. CONCLUSION

Ternary nanocomposites of PANI/MWCNTs-MnO₂ were successfully prepared through the *in situ* chemical oxidative polymerisation of aniline. PANI/MWCNTs-MnO₂ showed good interaction, based on the shift in the electronic transition described by UV-vis and FTIR spectra, which showed that PANI/MWCNTs-MnO₂ was rich in quinoid rings. TEM revealed the filling of MWCNTs with MnO₂ and the uniform coating of PANI. SEM showed less bundling among the nanocomposites. The conductivity of PANI/MWCNTs-MnO₂ was higher than that of neat PANI and PANI/MWCNTs. PANI/MWCNTs-MnO₂ showed better results than neat PANI and PANI/MWCNTs without MnO₂. Further study should focus on investigating the interaction mechanism and possible applications of this PANI/MWCNTs-MnO₂ nanocomposite.

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