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Short Communication

Systematically investigation for synthesis of Pt doped NiO decorated single wall carbon nanotubes and effect of synthesis nanomaterials for reduction of charge transfer reduction

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Charge transfer resistance
NiO nanoparticle
Polyol

ABSTRACT

In this study, we discussed the synthesis of Pt doped NiO decorated single wall carbon nanotubes nanocomposite (Pt-NiO/SWCNTs/NC) and investigated the effect of this nanocomposite on the reduction of charge transfer resistance (R_{ct}) in electrochemical systems (solution of 1.0 mM $[Fe(CN)6]^{3-/4-}$+0.1 M KCl). For this goal, we synthesized the NiO nanoparticle, NiO/SWCNTs nanocomposite and Pt/SWCNTs nanocomposite and then morphological of these nanocomposites were characterized by TEM method. The effect of these nano-compounds on the reduction of charge transfer resistance was compared with Pt-NiO/SWCNTs/NC. The results demonstrated that, the synthesized nanomaterials could be reduce charge transfer resistance in redox reaction. Also, the Pt-NiO/SWCNTs/NC (diameter, ~ 15-20 nm) showed best condition for reduction of charge transfer resistance compare to other nanomaterials. This point confirmed that doping of Pt into NiO nanostructure and decoration of this nano-hybrid on surface of SWCNTs created high conductivity nanomaterials that are useful for fabrication of electro-catalyst in fuel cell systems.

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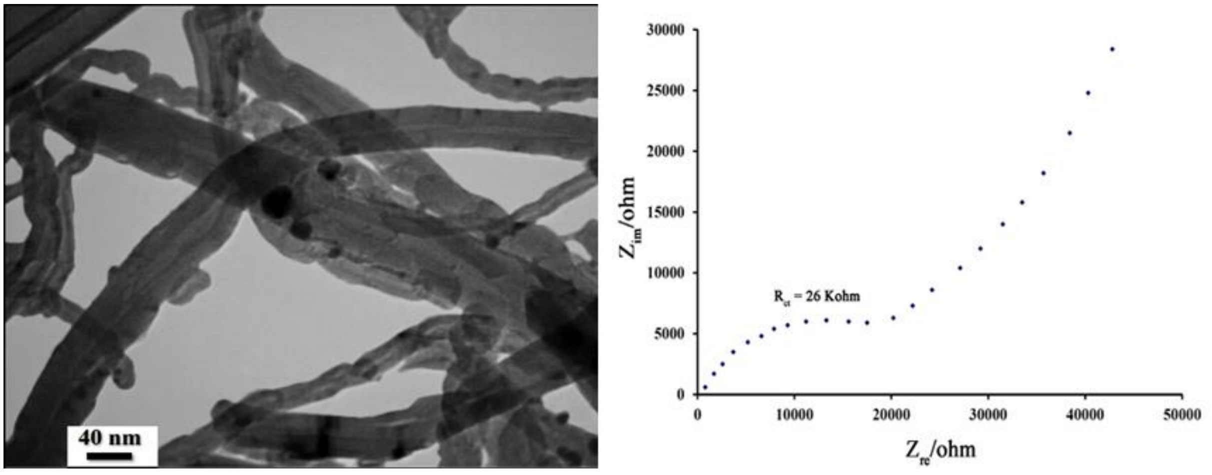
Graphical Abstract



Introduction

Nanomaterials have been introduced as a new approach in various industries, especially in the electrical industry such as batteries, supercapacitors and electrochemical sensors [1–3]. Attention to the synthesis of new nanomaterials with different and unique properties has grown significantly in recent years [4–7]. Studies have shown that nanocomposites that are formed from the combination of several nanomaterials are a suitable approach to achieve this goal [8–10]. Characteristics of hybrid nanocomposites can solve many problems in various industries, especially in the electrical industry, and be introduced as a new solution with high efficiency [11].

In between of nanomaterial, carbon nanotubes and metal nanoparticles showed more conductivity and are useful for improving electrical conductivity of redox systems [12–14]. Carbon nanotubes and especially single-wall carbon nanotubes with high surface area and high conductivity were suggested in electrical industry such as batteries, supercapacitors and electrochemical sensors [15–17]. On the other hand, metal and metal oxide nanoparticles such as Pt and NiO nanoparticles wildly used for energy storage and electrochemical systems such as fuel cells [18, 19]. But, direct using of Pt nanoparticles in fuel cell systems as catalyst created some problems such as deactivation of the electrode surface [19]. Therefore, the synthesis of platinum-based nanomaterials in which platinum is not directly related to the electrode surface is of great importance in fuel cells. Doping of platinum nanoparticles in the crystalline space of metal oxide nanoparticles can be introduced as a suitable way for resolving this problem in fuel cell systems [20].

According to above and important of nanomaterials in different filed of sciences [21–26], points and important synthesis of new types of platinum-based nanomaterials with high conductivity which platinum is not placed directly on the surface of the electrode, in this project, the high conductive Pt-NiO/SWCNTs/NC synthesized by precipitation method and the effect of this nanocomposite on reduction of charge transfer resistance (R_{ct}) in electrochemical systems was investigated. The results showed that Pt-NiO/SWCNTs/NC has a greater impact than other composites such as Pt/SWCNTs, NiO/SWCNTs and NiO nanoparticle.

Experimental

Reagents and apparatus

Single wall carbon nanotubes-COOH, nickel nitrate hexahydrate, sodium hydroxide, platinum chloride were purchased for Sigma-Aldrich and used for synthesis of NiO nanoparticle, NiO/SWCNTs nanocomposite, Pt/SWCNTs and Pt doped NiO decorated single wall carbon nanotubes nanocomposite. Potassium ferricyanide, KCl and potassium ferrocyanide were purchased form Merck and used for preparation of standard solution ($[Fe(CN)6]^{3-/4-}$ (1.0 mM and KCl (0.1 M)) for electrochemical impedance spectroscopy investigation (condition; frequency range of 100 kHz to 0.10 Hz and AC voltage amplitude 5 mV). The electrochemical part of this research was performed using an electrochemical work station model Ivium-Vertex. The TEM microscope model Zeiss-EM10C-100 KV was used for morphological investigation. The $Ag/AgCl/KCl_{sat}$ (Azar Electrode) was used as reference electrode.

Synthesis of NiO nanoparticle

100 mL nickel nitrate hexahydrate (1.0 M) was stirred for 10 min. Then, 100 mL sodium hydroxide (2.0 M) was drop wise into nickel nitrate hexahydrate solution and stirring continuous for 30 min. The resulting light green precipitate was separated and washed ten times with distilled water. The precipitate was dried at 100 °C for 15 h. In the final step, green powder was calcinated at 400 °C for 2 h.

Synthesis of NiO/SWCNTs nanocomposite

1.0 g SWCNT-COOH + 100 mL nickel nitrate hexahydrate (1.0 M) was stirred for 10 min. Then, 100 mL sodium hydroxide (2.0 M) was drop wise into nickel nitrate hexahydrate solution and stirring continuous for 30 min. The resulting black precipitate was separated and washed ten times with distilled water. The precipitate was dried at 100 °C for 15 h. In the final step, green powder was calcinated at 400 °C for 2 h.

Synthesis of Pt/SWCNTs Nanocomposite

Microwave heat method was used to synthesize Pt/SWCNTs nanocomposite. 50 mL of ethylene glycol solution+0.8 mL of 0.4 M potassium hydroxide was added to the Erlenmeyer flask and stirred for 10 min to homogenize the samples. Then 2.0 mL of 0.05 M platinum chloride solution was added to the container and stirring was continued for 10 min. Then 0.1 g of SWCNTs-COOH were added to the Erlenmeyer flask and the sample of carbon nanotubes was dispersed by ultrasonics and this operation was continued for 30 min. The Erlenmeyer was placed in a microwave machine at 60 ˚C for 600 min at 600 W. The resulting powder was dried at 120 °C for 12 h. The synthesized sample was then used for analysis and subsequent studies.

Synthesis of Pt-NiO/SWCNTs/NC

1.0 g of SWCNTS-COOH was dispersed in 100 mL nickel nitrate hexahydrate (1.0 M)+0.016 g of platinum salt and ultrasonic for 10 min. Then, 100 mL of 2.0 M sodium hydroxide solution was added to the system and the sample was stirred for 10 min. The powdered sample was dried at 100 °C for 16 h and then calcined for 2 h at 400 °C.

Preparation of electrode

The carbon paste electrode (CPE), carbon paste electrode modified with NiO nanoparticle (NiO/CPE), carbon paste electrode modified with NiO/SWCNTs (NiO/SWCNTs/CPE), carbon paste electrode modified with Pt/SWCNTs (Pt/SWCNTs/CPE) and carbon paste electrode modified with Pt-NiO/SWCNTs/NC (Pt-NiO/SWCNTs/NC/CPE) were prepared by mixing 0.1 g nanomaterials+0.9 g graphite powder (in any case) and hand mixed by paraffin oil as binder.

Results and Discussion

The nyquist plot of CPE in solution of 1.0 mM [Fe(CN)6]$^{3-/4-}$+0.1 M KCl is presence in Figure 1. The value of charge transfer resistance was calculated ~ 212 KOhm for unmodified electrode and this value was used as the initial value to investigate the effect of nanomaterials conductivity.

In continuous, NiO nanoparticle was characterized by TEM method. The TEM image of NiO/NPs is demonstrated in Figure 2. As can be seen, the spherical shape nanoparticles were synthesis by suggested method.

The effect of NiO nanoparticle on R_{ct} was investigated by recording nyquist plot of NiO/CPE in solution of 1.0 mM [Fe(CN)6]$^{3-/4-}$ +0.1 M KCl (Figure 3). As can be seen, the R_{ct} was reduce from 212 KOhm for unmodified electrode to 189 KOhm that confirm good electrical conductivity of NiO nanoparticle.

In addition, NiO/SWCNTs nanocomposite was characterized using the TEM analysis. The TEM image of the NiO/SWCNTs nanocomposite is shown in Figure 4. As can be seen, spherical shape nanoparticles with diameter about 15-20 nm was decorated at surface of SWCNTs by suggested method.

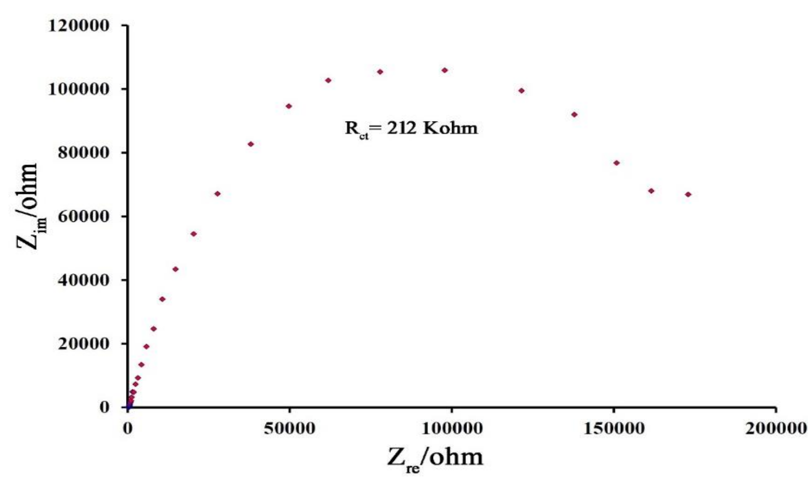


Figure 1. Nyquist plot of CPE in solution of 1.0 mM [Fe(CN)6]$^{3-/4-}$ + 0.1 M KCl

In the next step, the effect of NiO/SWCNTs on R_{ct} was investigated by recording nyquist plot of NiO/SWCNTs in solution of 1.0 mM $[Fe(CN)_6]^{3-/4-}$+0.1 M KCl (Figure 5). As can be seen, the R_{ct} was reduce from 212 KOhm for unmodified electrode to 148 KOhm for NiO/SWCNTs/CPE that confirm good electrical conductivity of NiO/SWCNTs. The result confirm that NiO/SWCNTs showed better conductivity compare to NiO nanoparticle due to presence of SWCNTs in using nanomaterials structure.

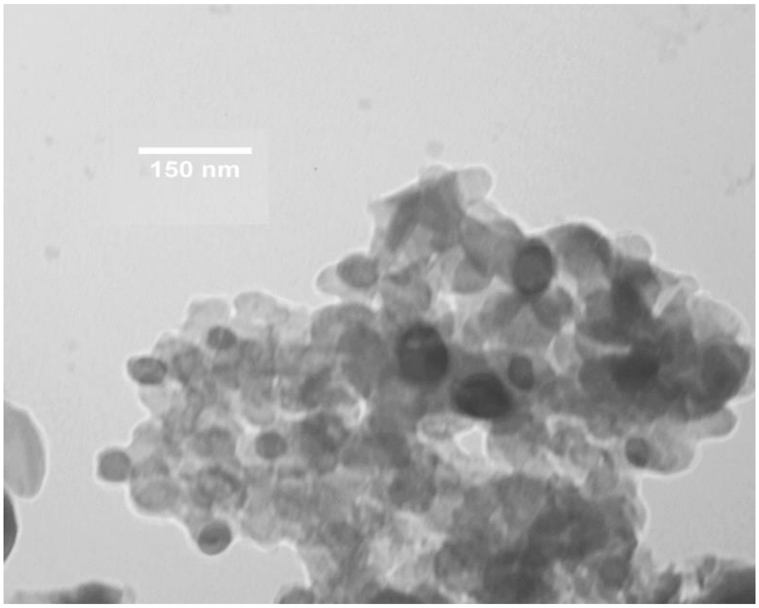


Figure 2. TEM image of the synthesized NiO nanoparticle

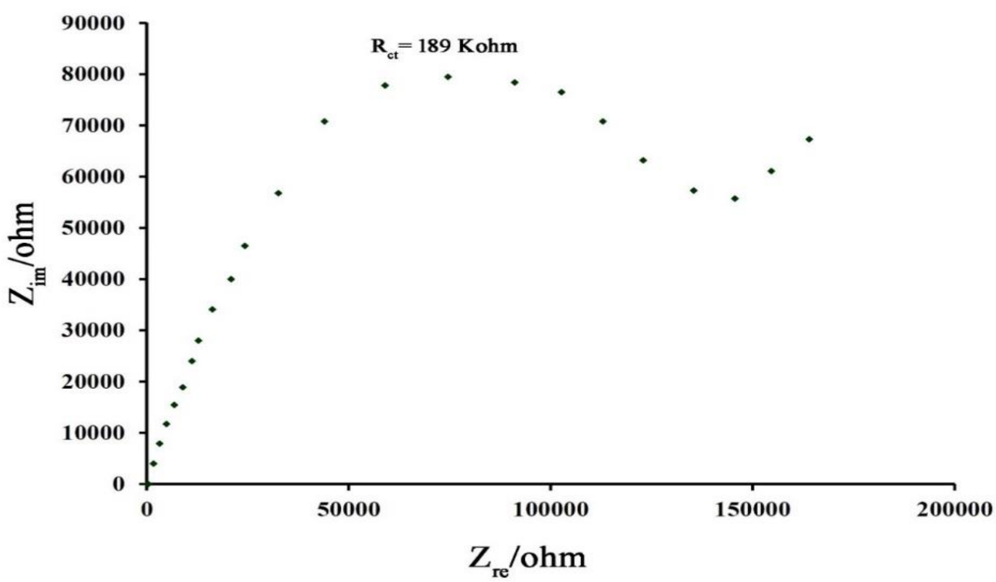


Figure 3. Nyquist plot of NiO/CPE in solution of 1.0 mM $[Fe(CN)_6]^{3-/4-}$+0.1 M KCl

The Pt/SWCNTs nanocomposite was characterized by TEM method. Figure 6 demonstrates the TEM image of the Pt/SWCNTs nanocomposite. As can be seen, spherical shape nanoparticles with diameter ~ 1-5 nm was decorated at surface of SWCNTs by suggested method.

The effect of Pt/SWCNTs on R_{ct} was investigated by recording nyquist plot of Pt/SWCNTs in solution of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ + 0.1 M KCl (Figure 7). As can be seen, the R_{ct} was reduce from 212 KOhm for unmodified electrode to 107 KOhm for Pt/SWCNTs/CPE that confirm good electrical conductivity of NiO/SWCNTs.

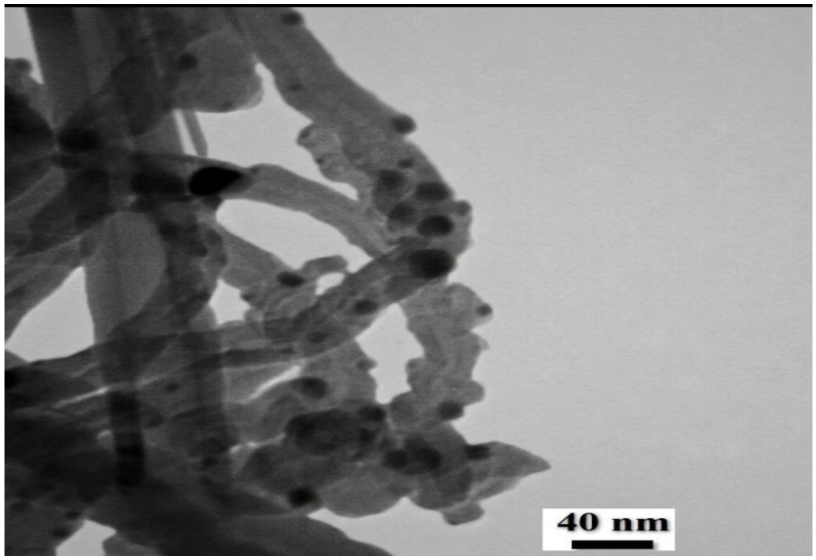


Figure 4. TEM image of the synthesized NiO/SWCNTs

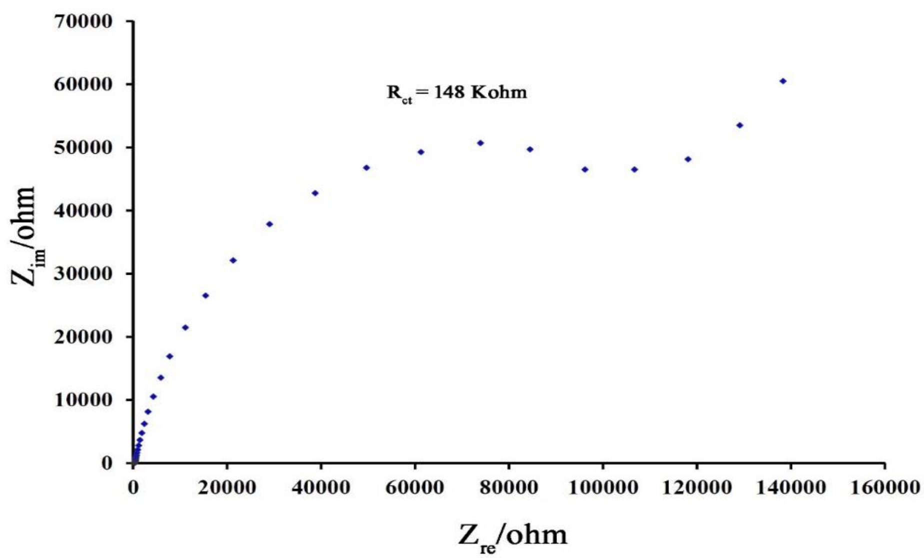


Figure 5. Nyquist plot of NiO/SWCNTs/CPE in solution of 1.0 mM $[Fe(CN)_6]^{3-/4-}$+0.1 M KCl

This value of R_{ct} showed more conductivity of this nanocomposite compare to NiO nanoparticle and NiO/SWCNTs nanocomposite due to presence of Pt nanoparticle as high conductive electro-catalyst. In the final step, the Pt-NiO/SWCNTs/NC was synthesized and characterized by TEM method. The TEM image of Pt-NiO/SWCNTs nanocomposite is presence in Figure 8. As can be seen, spherical shape nanoparticles with diameter, ~ 15-20 nm was decorated at surface of SWCNTs by suggested method. The diameter of Pt-NiO nanoparticle decorated on SWCNTs is very similar to dimeter of NiO nanoparticle decorated on SWCNTs. This diameter of NiO nanoparticle confirm Pt nanoparticle decorated into NiO crystal and donot change dimeter of nanoparticle.

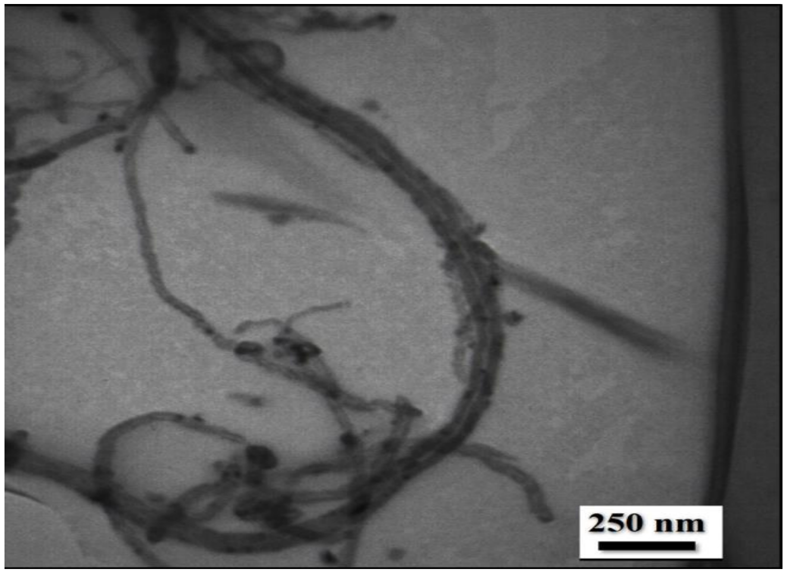


Figure 6. TEM image of the synthesized Pt/SWCNTs

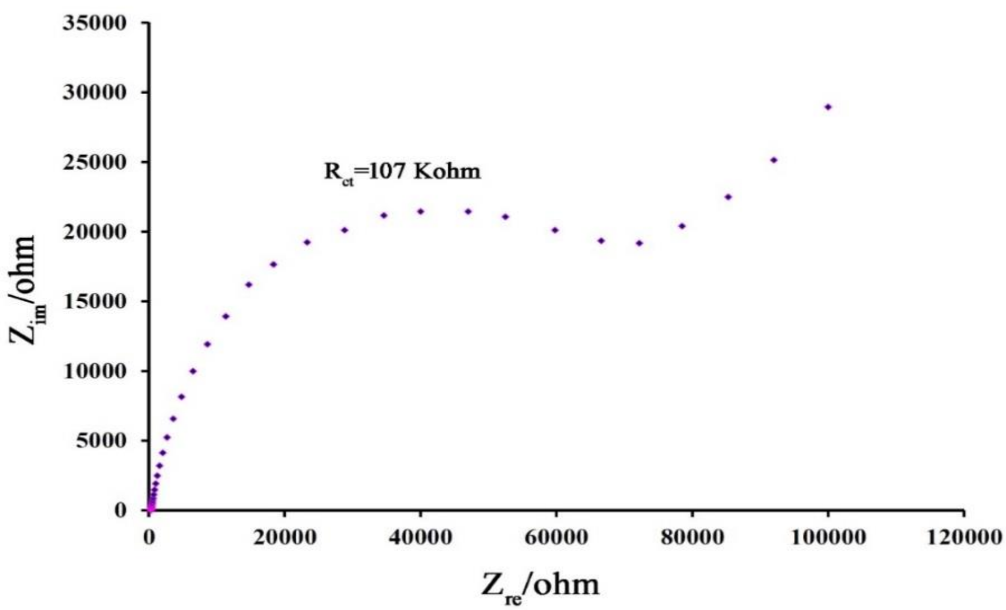


Figure 7. Nyquist plot of Pt/SWCNTs/CPE in solution of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ + 0.1 M KCl

The effect of Pt-NiO/SWCNTs nanocomposite on R_{ct} was investigated using the recording nyquist plot of Pt-NiO/SWCNTs/CPE in solution of 1.0 mM $[Fe(CN)_6]^{3-/4-}$+0.1 M KCl (Figure 9). As can be seen, the R_{ct} was reduced from 212 KOhm for unmodified electrode to 26 KOhm for Pt-NiO/SWCNTs/CPE that confirmed good electrical conductivity of Pt-NiO/SWCNTs nanocomposite. This value of R_{ct} showed more conductivity of this nanocomposite compare to NiO nanoparticle, Pt/SWCNTs and NiO/SWCNTs nanocomposite due to presence of Pt nanoparticle, SWCNTs and NiO in nanocomposite structure.

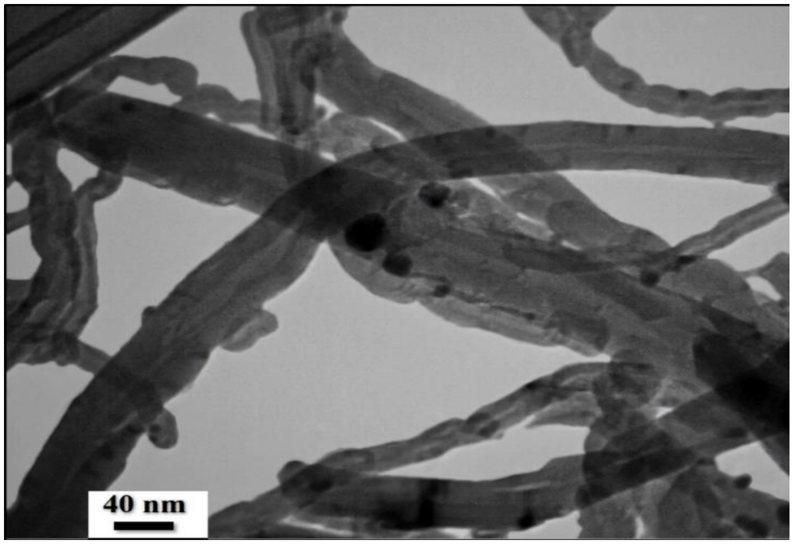


Figure 8. TEM image of the synthesized Pt-NiO/SWCNTs

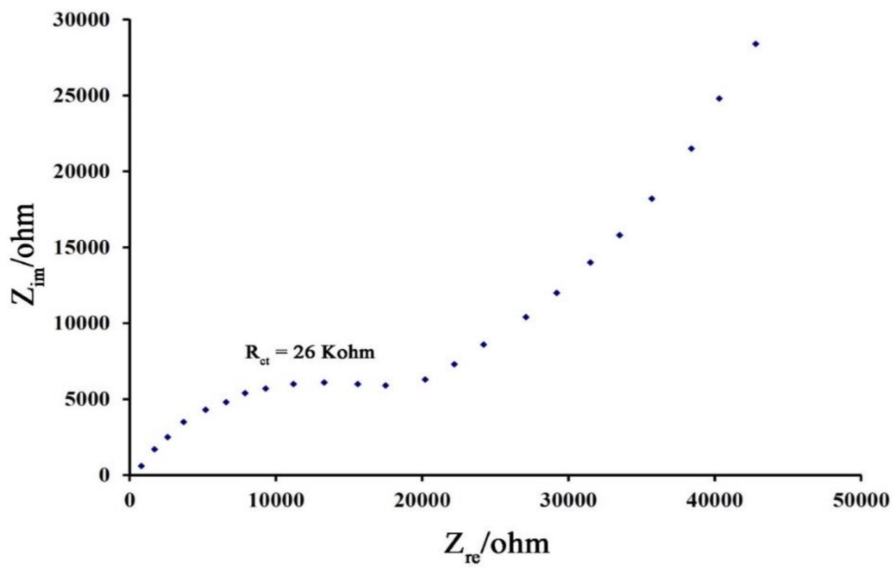


Figure 9. Nyquist plot of Pt-NiO/SWCNTs in solution of 1.0 mM $[Fe(CN)_6]^{3-/4-}$+0.1 M KCl

Conclusion

In this study, the NiO nanoparticle, NiO/SWCNTs nanocomposite, Pt/SWCNTs and Pt-NiO/SWCNTs was synthesize by chemical precipitation strategy and characterized by TEM method. The results showed that the Pt nanoparticle was decorated at the surface of the SWCNTs with the diameter of 1-5 nm. The conductivity of synthesis of nanomaterials on electrical conductivity of redox systems was investigated. Results showed that the charge transfer resistance of CPE was reduced from 212 KOhm to 26 KOhm after modification with Pt-NiO/SWCNTs nanocomposite in the solution of 1.0 mM $[Fe(CN)_6]^{3-/4-}$+0.1 M KCl. The results confirmed that this conductive nanomaterial is a good choice for modifying the electrochemical sensors.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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