

Electro Polymerization of *o*-Phenylenediamine Using Palladium Nanoparticles Coated Fabricated TiO₂ Nanotubes Modified Glassy Carbon Electrode

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Fabricated titanate nanotubes (*f*-TNT) are prepared by chemical deposition method using linen fiber. The *f*-TNTs is fabricated by TiO₂ nanoparticles, the each TiO₂ nanoparticles diameter has 80-100 nm in range. The Pd⁰ nanoparticle was coated on the surface of the *f*-TNT by chemical reduction method, using NaBH₄ as reducing agent. The prepared Pd/*f*-TNTs characterized by FT-IR, FE-SEM and HRTEM, the result shows that the *f*-TNT diameter is 1500 nm and Pd nanoparticles range in 20-50 nm. The Pd/*f*-TNT nanocomposite modified glassy carbon (GC) electrode shows quasi irreversible redox behaviours in cyclic voltammeter. Those Pd/*f*-TNTs modified electrode is utilized for electrochemical polymerization of *o*-phenylenediamine in acid medium.

Keywords: Titanate nanotube, Palladium nanoparticle, Template, Chemical deposition method, Electrochemical properties.

INTRODUCTION

Titanium dioxide (TiO₂) has been widely used in various applications, including photocatalysts, solar cells, biomaterials and environmental catalysts [1-3]. During the past decade, the research on the synthesis of nanosized porous TiO₂ materials and their application in the catalytic industry and photocells has been rather intense. Because of the important optical and electronic properties, it is useful for catalyst support [4,5], sensors [6-8] and so on. Also, it has been widely used as additives in paint, toothpaste and cosmetics because of its great biocompatibility. However, metal nanoparticles have received a great deal of attention because of their unique physical and chemical properties as well as their enormous potential applications such as catalysts, nanoelectronic devices, sensors and surface-enhanced Raman scattering [9,10].

Metal halide such as TiF₄, SnCl₄, ZnCl₂ and CuCl₂ molecule have been used for the preparation of metal oxide nanomaterials such as TiO₂ [11,12], SnO₂ [13], ZnO [14] and CuO [15,16], respectively. TiO₂ nanotubes prepared using template assisted porous alumina membrane and textile fiber [17]. The templates can be used such as an ordinary filter paper and carbon sphere, wool and cotton. The titanate nanotube is well known photo

catalysis and as the electrode for wet-type photocell applications [18,19]. Metal nanoparticles modified titanate nanotubes (TNTs) was wide range of applications such as electrocatalysis [20,21], photo catalysis [18], sensor [14] and degradation of organic pollutant or dyes and well analyzed chemical and physical properties like that thermal and chemical stability, electrical, optical, mechanical properties and also higher surface area.

The poly-*ortho*-phenylenediamine (PoPD) has been extensively developed by several researchers for many potential applications, such as protective coating for metals, electrical and electronic devices and biosensors [22,23]. It can be easily dissolved in different solvents, making it a good candidate for electro polymerization and the production of thin self-sealing insulating polymer on many electrode surfaces, such as gold, platinum, copper and indium tin oxide (ITO) [24,25]. Several reports are available in literature for the electropolymerization and characterization of conducting polymers, polyaniline, PoPD, polythiophene and polypyrrole. The PoPD electro polymerization uses common electro deposition technique in cyclic voltammetry. Among electro synthesized polymers, the electro polymerization of *o*-phenylenediamine has received a great deal of attention such as photovoltaic cells, anticorrosion coatings and biosensor application.

In this work, we have prepared linen fiber assisted fabricated *f*-TNT by deposition of TiO₂ nanoparticles. This chemical deposition process is affected by some important factors like reaction time, temperature and concentration of the TiF₄ [11,12]. This *f*-TNT has been modified by palladium nanoparticle (Pd⁰). The Pd⁰ nanoparticle formed by chemical reduction [17] using NaBH₄ as reducing agent, the palladium nanoparticle is stabilized by *f*-TNTs. The Pd/*f*-TNTs nanocomposite characterized by FTIR, FESEM, EDX and electrochemical analyzer. The Pd/*f*-TNTs nanocomposite modified GCE is used for electro polymerization of 2,3-diaminobenzine.

EXPERIMENTAL

Palladium chloride, titanium fluoride, sodium borohydride and hydrazine were purchased from Sigma Aldrich chemicals in India. Phosphate (PBS) buffer 0.1 M solution is prepared by potassium chloride, potassium orthohydrogen phosphate, sodium hydrogen phosphate and sodium chloride purchased from SD-fine chemicals. It is used for electrolyte solution to cyclic voltammeter experiment.

Preparation of *f*-TNT: The precursor solution is prepared by 0.02 M of TiF₄ dissolved 70 mL water in Teflon beaker. The 2-3 μm diameter and length 8 μm linen fiber taken in 1.00g, the fiber dispersed in aqueous TiF₄ solution. Which were maintained at 110 °C for 12 h in hot plate. Entire water molecule should be evaporating, till fiber change to black colour, TiO₂ nanoparticles deposited on surface of the linen fiber. These fibers removed by combustion at 550 °C in air. The deposited TiO₂ nanoparticles making fabricated *f*-TNT.

Preparation of palladium nanoparticles coated on *f*-TNT: The above prepared *f*-TNTs (0.1 g) was dispersed in 6 mM PdCl₂ solution (PdCl₂ dissolved in water with 80 μL conc. HCl). These mixtures are stir for 5 h in ambient conditions. In this process PdCl₂ adsorbed on surface of the *f*-TNTs, then the PdCl₂/*f*-TNTs composite dried at 100 °C, after then adsorbed PdCl₂ change to Pd⁰ nanoparticles on surface of *f*-TNTs by adding 3mM of NaBH₄ solution. Followed by the Pd/*f*-TNT nanocomposite separated using centrifuge and then dried at 100 °C. This Pd/*f*-TNTs nanocomposite is used for electro-catalytic applications.

RESULTS AND DISCUSSION

FT-IR spectrum of *f*-TNT and Pd/*f*-TNT: The FTIR spectra (Fig. 1) exhibited a peak of 3650-3000 cm⁻¹ due to adsorbed water and hydroxyl groups, which can be attributed to the stretching vibration of -OH of water. In particular, the content of water adsorbed in titania nanotubes was significantly higher than TiO₂ due to the increase of specific surface areas and pore volumes. The band observed at 1630 cm⁻¹ can be assigned to molecular water bending mode. Distinct broad bands in 700-400 cm⁻¹ region were assigned to Ti-O and Ti-O-Ti skeletal frequency regions.

The peak at 1634 cm⁻¹ is corresponding to vibrational frequency of water molecule and Ti-O vibrations peak appeared at 693, 630, 524 and 461 cm⁻¹. Similarly Pd/*f*-TNTs nanocomposite exhibited peaks at 747, 657 and 542 cm⁻¹, these peak values are slightly shifted to higher wave number region compared with *f*-TNTs [22] due to the coating of palladium nano-

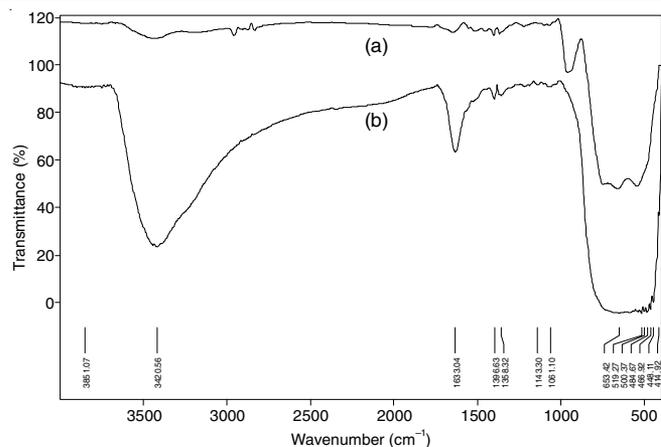


Fig. 1. FT-IR spectrum of *f*-TNT (a) and Pd/*f*-TNT (b)

particles on surface of *f*-TNTs. The palladium nanoparticles (Pd⁰) did not exhibit any vibration frequency in FT-IR spectrum, because only polarized molecule are IR active. The palladium nanoparticle is not polarized, because of its zero oxidation state (Pd⁰).

FESEM images of Pd/*f*-TNTs nanocomposite: The FESEM images exhibited the surface morphology of *f*-TNT in Fig. 2. This figure shows the thin layer nanotube and it is formed at low concentration of TiF₄ aqueous solution. The *f*-TNT diameter has 1500 nm, which tubes thin film walls diameter was 80-100 nm in size. The Pd/*f*-TNTs nanocomposite FESEM images is also showed in Fig. 2, the formed Pd⁰ nanoparticles size has in range from 20-50 nm. The surface area of the Pd/*f*-TNTs was higher than compared with *f*-TNTs [22,26]. The *f*-TNTs and Pd/*f*-TNTs elemental analysis of EDX patterns is shown in Fig. 2. The peaks of Pd are located at 2.8 KeV, the titanium TiL at 0.5 and TiK 4.5 KeV. The O₂ indicated at 0.65 KeV.

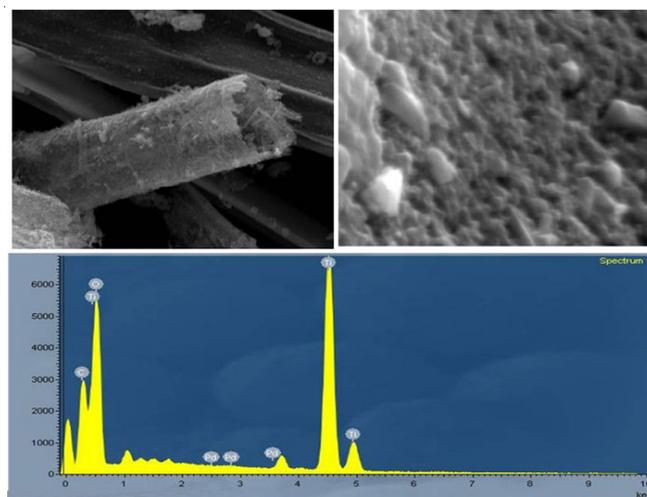


Fig. 2. SEM images and EDX pattern of Pd/*f*-TNT

Electrochemical behaviour of Pd/*f*-TNTs modified GCE: Cyclic voltammetry was done three electrode systems, powdered Pd/*f*-TNT uniformly dispersed in glassy carbon electrode and then cyclic voltammetry experiment done in the presence of 0.1 M PBS solution at different scan rate such as 20, 40, 60 and 80, the scan rate increase, while peak current

also increase [22,24]. The Pd/*f*-TNT nanocomposite modified electrode higher stability in electrochemical cell at 0.1 M PBS solutions. The Pd/*f*-TNT nanocomposite modified electrode was exhibited quasi-irreversible redox peak (Fig. 3), the oxidation and reduction potential of the modified electrode at -398 mV and -620 mV/s respectively. The formal electrode potential $\Delta E_p = 0.232$ V/s. The Pd/*f*-TNT nanocomposite modified electrode has totally changed electrochemical behaviour in presence of *o*-phenylenediamine (DAB) solution, perchloric acid 0.1 M used as an electrolyte solution. The Pd/*f*-TNTs nanocomposite modified electrode was excellent stability. The DAB and perchloric acid redox peak potential different compared without DAB at Pd/*f*-TNT modified electrode potential. Formal potential is $\Delta E_p = 0.044$ V/s (Table-1). The lower ΔE_p has higher electron transfer rate. The result indicates that Pd/

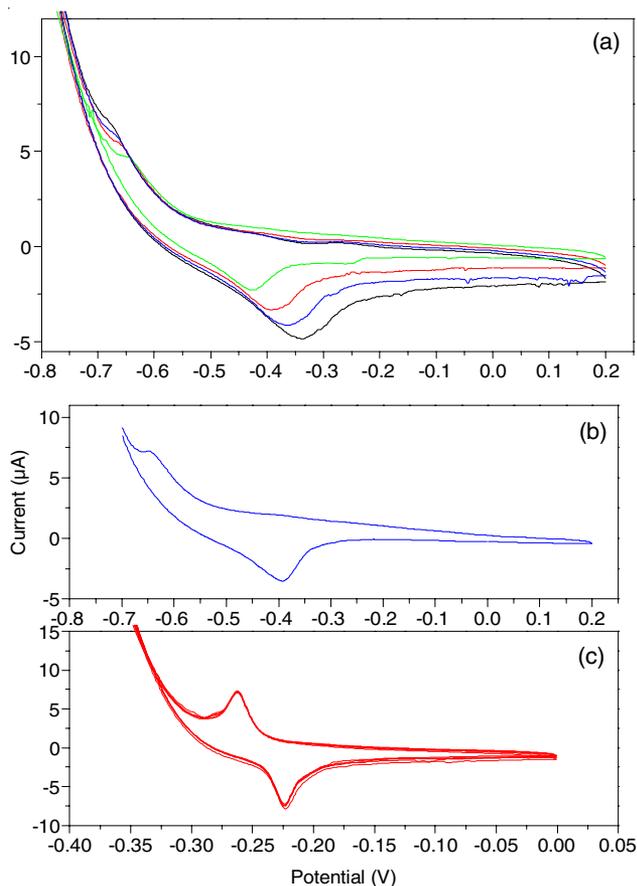


Fig. 3. Cyclic voltammety behaviour of *f*-TNTs and Pd/*f*-TNTs; (a) the Pd/*f*-TNTs at different scan date Such as 40, 60, 80, 100 mV/s, the 0.1M of PBS used as electrolytic solution; (b) The Pd/*f*-TNTs redox properties at scan rate 40 mV/s; (c) Electrochemical properties of Pd/*f*-TNTs in presence of DBA and 0.1 M perchloric acid solution scan rate 40 mV/s

Modified electrode	ΔE_{p_c}	ΔE_{p_a}	ΔE_p	$E_{1/2}$
<i>f</i> -TNT/Pd	-0.398	-0.620	0.232	-0.590
<i>f</i> -TNT/Pd-DAB	-0.220	-0.260	0.044	-0.242

f-TNT modified electrode in presence of DAB solution has higher electron transfer compared without DAB solutions contain modified electrode Pd/*f*-TNT. The peak current were proportional to the electroactive surface area, so the electro active surface area higher for Pd/*f*-TNT-DAB.

Electro polymerization of *o*-phenylenediamine at Pd/*f*-TNTs modified GCE: Electro polymerization of DAB at Pd/*f*-TNT modified GC electrode is shown in Fig. 4. The Pd/*f*-TNTs nanocomposite modified electrode polymerized DAB at 0.1 M perchloric acid. The reduction and oxidation peak appeared at -220 and -264 mV respectively, the polymerization current gradually increase or grown with increasing of the cyclic number, this indicates poly-phenylenediamine is formed [25]. This Pd/*f*-TNT modified electrode has higher stability, higher electron transfer behaviour and higher surface area. The polymerization reaction is given in **Scheme-I**.

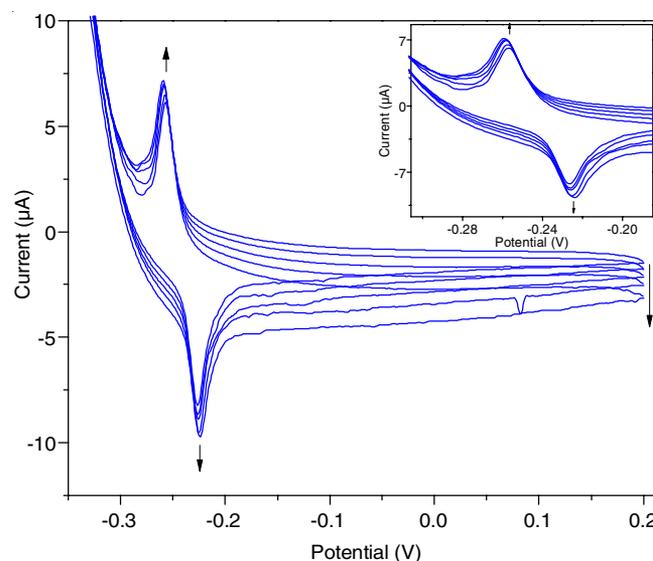
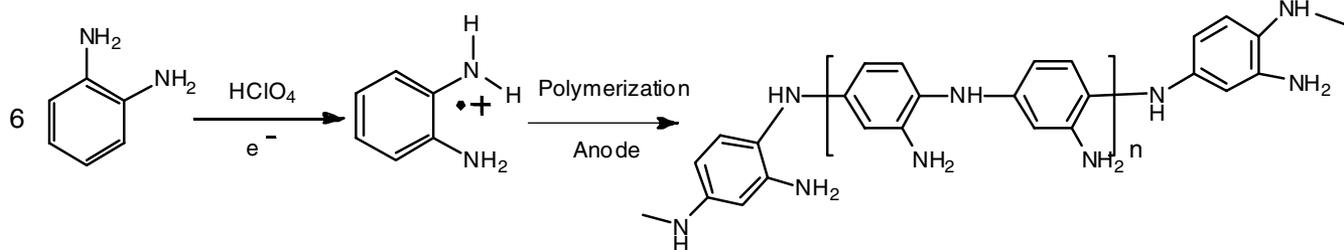


Fig. 4. Electropolymerization of *o*-phenylenediamine in presence of 0.1 M perchloric acid solution at *f*-TNT/Pd modified electrode. The scan rate at 0.05 mV/s

Conclusion

We developed and improved template assisted preparation of *f*-TNT and palladium nanoparticle coated onto surface of



Scheme-I: Electropolymerization reaction of *o*-phenylenediamine at Pd/*f*-TNTs modified GCE

f-TNT. The palladium nanoparticles were formed by chemical reduction by NaBH₄. Some physical factors affect the formation of *f*-TNT and Pd/*f*-TNT, those formation mechanisms clearly described in schematic diagram. The *f*-TNT and Pd/*f*-TNT characterized by FT-IR, FE-SEM and EDX pattern. The Pd/*f*-TNT modified electrode is utilized for electrochemical polymerization of *o*-phenylenediamine in acid medium. Those behaviours were investigated in cyclic voltammetry.

CONFLICT OF INTEREST

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

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