Semi conductive Tl_2O_3 nanoparticles: Facile synthesis in liquid phase, characterization and its applications as photocatalytic substrate and electrochemical sensor

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Abstract

For the first time, we reported the facile synthesis of semiconducting thallium oxide nanoparticles using thallium (III) acetate as the starting reagent through the microwave and co-precipitation methods. Results showed that the microwave power, irradiation time and pH value plays an essential role in the control of final products size distribution. According to our knowledge, it is first time that ethylenediamine was used as pH controller agent in synthesis of Tl_2O_3 nanoparticles. Based on the current research, microwave method provided a simple and rapid method for the synthesis of Tl_2O_3 nanoparticles than to co-precipitation method, because of its homogeneous and fast-heating characteristics. As application for Tl_2O_3 nanoparticles, the photocatalytic degradation of methyl orange with maximum decolorization of 74.2% under UV light irradiation based on Tl_2O_3 nanoparticles was obtained. Also, a pencil graphite electrode was decorated using Tl_2O_3 nanoparticles and MWCNT to provide an electrochemical devise for Cu^{+2} ions sensing. This modified electrode showed agreeable responses to trace amounts of Cu^{+2} in phosphate buffer solutions which the limit of detection was found to be 4.63 nmol L^{-1} for Cu^{+2} .

Keywords: Tl_2O_3 ; Nanostructures; Microwave; Co-precipitation; Photocatalytic degradation; Electrochemical sensor.

1. Introduction

Thallium (III) oxide is a chemical compound of thallium and oxygen. Tl_2O_3 is metal with high conductivity and a degenerate n-type semiconductor with a band gap of 1.4 eV which have potential use in solar cells [1], treatment of ringworm and other skin infections, as a chemical tracer in diagnosis, particularly in cardiology [2]. It can be electrochemically or photoelectron chemically deposited on conducting or semiconducting substrates. Interest in this material has grown further with the discovery of the high-temperature superconducting material Tl-Ba-Ca-Cu oxide [3]. Thallium compounds are also used for X-ray, γ -ray and infrared detectors [4]. Toxicity behavior of thallium compound limits their medical application. Thallium is a very important ingredient of many high-temperature oxide superconductors [5] due to the wide range of stoichiometries over which super conductivity is observed in such thallium-doped materials. Because of such promising applications of Tl_2O_3 , it is very important to be able to fabricate these nanoparticles using a very simple method. Recently, semiconducting nanomaterials have generated tremendous interest in both scientific research and engineering fields. The electronic and optical properties of nanoparticles strongly depend on their size and dimensionality [6-8]. There are a few reports on the synthesis of nano-sized Tl_2O_3 using thermal decomposition [9-10], electrodeposition [11-12] and sonochemical [13] methods. In the past two decades, the use of microwave energy to heat chemical reactions has attracted considerable amount of attention due to its many successful applications in peptide, synthesis polymer chemistry, material science, nanotechnology and biochemical processes [14-18]. There are many advantages in the microwave- assisted approaches: the reaction time is very short, heat transformation is faster than that of reflux process in an oil bath and hydrothermal/solvothermal routes, local overheating can be avoided and the reaction temperature is controllable.

Copper is an essential trace element required for the human body to maintain normal, however, the extensive and excessive usage of copper may lead to toxic effect and result in serious environmental contamination [19, 20]. High levels of copper in environment could lead to accumulation within the food chain and harm to human health. So, it

is important to detect the content of Cu (II) in the water and environment. Various methods including fluorescence, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectroscopy and electrochemistry have been reported for the determination of Cu (II). In comparison with other methods, electrochemical method is particularly suited for the detection of Cu (II) due to its particular advantages, e.g. high sensitivity, inherent simplicity, miniaturization, and low cost. Anodic stripping voltammetry (ASV) has been widely recognized as a powerful technique for the determination of trace metal ions due to an effective pre-concentration step followed by electrochemical stripping measurements of the accumulated analytes [21].

In this paper, we firstly developed synthesis of thallium (III) oxide (Tl_2O_3) nanoparticles with cubic structure by a simple microwave and co-precipitation method without using any surfactants and organic solvents. After confirming nanostructure of Tl_2O_3 , their applications were studied in photocatalytic degradation of methyl orange (Me O) as organic pollution. The methyl orange significantly degraded by 74.2% in the presence of synthesized Tl_2O_3 nanoparticles. Furthermore, using immobilization of Tl_2O_3 nanoparticles and multi-walled carbon nanotube (puMWCNT) at the surface of pencil graphite electrode, a new platform for electrochemical measurement of Cu^{+2} ions in buffer solutions was prepared. This modified sensor was shown good sensitivity by detection limit of 4.63 nmol L^{-1} for Cu^{+2} in solution.

2. Experimental

2.1. Materials and physical measurements

All the chemicals used for experiments were purchased from Merck and used without further purification. X-ray diffraction (XRD) patterns were recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered Cu K_α radiation at scan range of $10 < 2\theta < 80$. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy (EDXS). Transmission electron microscope (TEM) images were obtained on a Philips EM208S transmission electron microscope with an accelerating voltage of 100 kV.

Room temperature photoluminescence (PL) properties were studied on a Perkin-Elmer (LS 55) fluorescence spectrophotometer. UV-vis diffuse reflectance spectroscopy analysis was carried out using Shimadzu UV-vis scanning spectrometer.

All electrochemical experiments were carried out using an Autolab potentiostat-galvanostat PGSTAT 35 (Eco chemie Utrecht, Netherlands), equipped with GPES 4.9,006 software. The measurements were carried out in three-electrode glass cell with Ag/AgCl (3.0 M KCl) as a reference electrode, a platinum wire as counter electrode and a pencil graphite electrode (PGE) as working electrode at $25 \pm 0.1^\circ\text{C}$.

2.2. Co-precipitation synthesis Tl_2O_3 nanoparticles

For synthesis of Tl_2O_3 nanoparticles by co-precipitation method, 1.0 mmol of $\text{Tl}(\text{CH}_3\text{COO})_3$ was put into a 250 ml beaker and filled with distilled water up to 20% of its volume and keeps the pH value at about 9 with adding ethylenediamine and magnetic stirrer for 12 h. Finally, the obtained black precipitates were collected by filtration and then washed with absolute ethanol and distilled water for several times. The final product was dried in vacuum at 60°C for 6 h.

2.3. Microwave synthesis Tl_2O_3 nanoparticles

In microwave method, firstly, 0.4g of $\text{Tl}(\text{CH}_3\text{COO})_3$ was dissolved in 40 mL of distilled water and then ethylenediamine as pH controller agent was subsequently added to the solution under stirring at room temperature to reach pH value 9. Then, the mixture was loaded into a microwave Teflon container while reactions were performed in a microwave digestion system under various conditions (Table.1). After microwave irradiation, the Teflon container was allowed to cool to room temperature naturally. Finally, the black precipitate was washed with distilled water/ absolute ethanol several times and dried under vacuum at 60°C for 6 h. To investigate the effect of ethylenediamine, as pH controller agent in reaction procedure, a blank test was performed free of ethylenediamine while no noticeable precipitation was formed.

Here in Table. 1

3. Results and discussion

3.1. Characterization of Tl_2O_3 nanoparticles

Fig. 1 provides a comparison of typical XRD patterns ($10^\circ < 2\theta < 80^\circ$) of products obtained from co-precipitation (a as sample.1) and microwave (b as sample. 3) methods in an aqueous solution. All reflection peaks of XRD pattern of Tl_2O_3 nanoparticles are indexed well to cubic phase of Tl_2O_3 (space group: I213; JCPDS No. 05-0584) with calculated cell parameters $a = b = c = 10.5430 \text{ \AA}$. Extremely broaden reflection peaks were observed in Fig. 1b, which indicated fine particle nature of the obtained Tl_2O_3 nanoparticles. No other crystalline phases were detected. These peaks can be indexed as (211), (222), (400), (411), (332), (510), (440), (532), (622), (631), and (444) diffraction lines with space group of cubic (JCPDS card No. 05-0584). From XRD data, the crystallite diameter (D_c) of Tl_2O_3 nanoparticles was calculated by using the Scherer equation (1) to be 15 and 12 nm for samples. 1 and 3, respectively [22]:

$$D_c = K\lambda / \beta \cos\theta \quad (1)$$

Where β is the breadth of the observed diffraction line at its half intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in XRD. UV-vis absorption spectrum of Tl_2O_3 nanoparticles (sample. 3) is shown in Fig. 2A. The fundamental absorption edge in most semiconductors follows the exponential law. Using the absorption data, the band gap was estimated by Tauc's relationship (2):

$$\alpha = \alpha_0 (h\nu - E_g)^n / h\nu \quad (2)$$

where α is absorption coefficient, $h\nu$ is the photon energy, α_0 and h are the constants, E_g is the optical band gap of the material, and n depends on the type of electronic transition and can take any value between 0.5 and 3 [23]. The energy gap of the Tl_2O_3 nanoparticles has been determined by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ against $h\nu$ to the energy axis (inset in Fig. 2A). The E_g value was calculated for the sample 3 to be 3.2 eV.

Here in Fig. 1

Photoluminescence spectroscopy is a non-contact, nondestructive method of probing the electronic structure of materials. By using photoluminescence spectra, band gap can be determined along with the relative energetic position of sub-band gap defect states [24]. Room temperature PL spectrum of Ti_2O_3 nanoparticles (sample 3) is shown in Fig. 2B. The emission peak at 388 nm (3.19 eV) was observed for Ti_2O_3 nanoparticles. As compared to the band gap of bulk Ti_2O_3 which is 1.4 eV [3] the absorption spectrum of Ti_2O_3 nanoparticles (sample 3) exhibits a blue-shift (3.19 eV, 388 nm).

Here in Fig. 2

In the microwave method several reaction parameters have significant effect on the size of the product such as pH value, microwave power and reaction time [25-27]. Therefore, these parameters were investigated on the particle size of as-synthesized Ti_2O_3 nanoparticles. To investigate the effect of reaction time on the particle size of Ti_2O_3 nanoparticles, several experiments were performed on the basis of time variable and pH value 9, whereas products obtained at different stages were investigated using the SEM technique. SEM images of samples 2-4 prepared at 750 W for 1 min (sample 2), 3 min (sample 3) and 6 min (sample 4) are shown in Figs. 3a-c, respectively. According to Figs. 3a and 3b, the morphology of all samples was particle-like, while by increasing the reaction time from 1 to 3 min, the particle sizes of the products were decreased. Using increasing the reaction time from 3 to 6 min, the particle size of Ti_2O_3 nanoparticles was increased (Fig 3c). Therefore, the reaction time for preparation of Ti_2O_3 nanoparticles was optimized to be 3 min.

Here in Fig. 3

Dependency of particle size of Ti_2O_3 nanoparticles to microwave power is shown in Figs. 4a and 4b by SEM images. As shown Fig. 4a, the Ti_2O_3 nanoparticles prepared at 600 W for 3 min (sample 5) are mainly composed of a large amount of agglomerated nanoparticles. With increase microwave power to 750 W (Fig. 3b, sample 3), size of the particles was decreased and separated very well. With progression of reaction to 900 W (sample 6), the

particles size of Tl_2O_3 nanoparticles was increased as shown in Fig 4b. By comparison between SEM images of microwave powers, it can be concluded that as-synthesis Tl_2O_3 in 750 W has homogeneous structure.

Here in Fig. 4

On the other hand, two reactions were performed to show the pH effect of solution on the particles size of product. SEM images of sample 7 and 8 are shown in Fig 5a and 6b, respectively. Comparison between three pH values 8, 9 and 10 shown that morphology of all samples was particle-like. Furthermore, in $\text{pH} < 9$ the products consisted small agglomerated nanoparticles while that in $\text{pH} > 9$, the sizes of products were larger than synthesized products in $\text{pH} = 9$. According to this observation, best pH value for synthesis Tl_2O_3 nanoparticles was selected to be 9. SEM image of Tl_2O_3 nanoparticles synthesis by co-precipitation method and TEM images of Tl_2O_3 nanoparticles (sample 3), with different magnifications are shown in Fig.6. According to the Fig. 6a, the morphology of product was particle like. According to the TEM images of Tl_2O_3 nanoparticles (sample 3, Fig. 6b-d), the product was mainly composed of a large amount of sphere-like nanoparticles with average particle size of ~ 10 to 15 nm.

Here in Fig. 5

Here in Fig. 6

On the other hand, Energy dispersive X-ray microanalysis (EDS) used for chemical characterization of the Tl_2O_3 nanoparticles (sample 3, Fig.7A). Fig. 7A demonstrates the presence of Tl and O elements in these nanoparticles. Tl_2O_3 have been synthesized by mixture aqueous solution of $\text{Tl}(\text{CH}_3\text{COO})_3$ with trace amounts of ethylenediamine under microwave irradiation. Performed reaction without ethylenediamine under similar microwave reaction condition did not yield any noticeable precipitation. The result indicates that the reaction occurs only in the presence of ethylenediamine as pH agent. Thus, ethylenediamine was the key factor for the formation of Tl_2O_3 nanoparticles. The possible reactions to form the cubic phase of Tl_2O_3 nanoparticles can be described as follows:

3.2. Photocatalysis experiments

In order to evaluate the photocatalytic activity of the Tl_2O_3 nanoparticles, the photocatalytic degradation of methyl orange (MeO) was studied in suspension of Tl_2O_3 nanoparticles under UV light irradiation. So, 0.1 g Tl_2O_3 nanoparticles was added into 100 mL of 10 ppm MeO dye aqueous solution. Subsequently, the aqueous suspension was magnetically stirred for 45 min in 20-25°C. Then, an UV lamp (6×15 W, Philips) was switched on a 30 cm distance over the suspension. After each 5 min (n=6 times) and 10 min (n=2 times), 15 mL of the suspension was sampled and centrifuged. Then, the absorbance spectra of the MeO solutions were recorded with an UV-vis spectrophotometer. The de-colorization efficiency (%) was calculated according to Eq (3):

$$(\text{De-colorization efficiency } \%) = \frac{C_0 - C}{C_0} \times 100 \quad (3)$$

Where C_0 is the initial concentration of dye and C is the concentration of dye after photo irradiation. Fig. 7B shows the photocatalytic activity of two kinds of Tl_2O_3 nanoparticles in methyl orange solution. Utilizing synthesized Tl_2O_3 nanoparticles by microwave method as the photocatalyst, 74.2% (sample 3) of methyl orange was degraded within 40 min UV-light irradiation. However, the degradation process for microwave products was faster and better than the products of co-precipitation method (69.2%) in the first 25 minutes of irradiation time.

Here in Fig. 7

3.3. Application as electrochemical mediator

3.3.1. Fabrication of the Tl_2O_3 NPs-MWCNT/ PGE

For increasing of surface of pencil graphite electrode and more sensitivity in electrochemical determination of Cu^{+2} , synthesized Tl_2O_3 nanoparticles with purified MWCNT (puMWCNT) were applied to modify electrode. So, to purify MWCNTs and remove any residual metals in the nanostructure, 1.00 g of MWCNTs plus 20 mL of 3.0 mol

L⁻¹ HNO₃ were mixed in a 25mL flux and then the mixture was refluxed for 12 h. Then, the MWCNTs were separated from the mixture and washed with 50 mL doubly distilled water, centrifuged and dried at room temperature. The stable suspension mixture of the puMWCNTs and Ti₂O₃ nanoparticles was obtained by ultrasonication of puMWCNTs and Ti₂O₃ nanoparticles in acetonitrile solution (dispersion of 1.0 mg puMWCNTs and 1.0 mg Ti₂O₃ nanoparticles together in 2.0 ml of acetonitrile). A pencil graphite electrode (PGE) was further polished with 0.05 mm alumina powder on a polishing microcloth for several minutes. Then, it was cleaned in an ethanol/water solution (50%, v/v) in the ultrasonic bath and rinsed thoroughly with doubly distilled water prior to modification. Finally, 20μL of the stable Ti₂O₃ NPs-puMWCNT suspension was dropped onto the surface of the PGE and it was dried in a hot air flow at 50 °C. After modification, the Ti₂O₃ NPs-puMWCNT/PGE was washed with double distilled water, dried at room temperature and applied for electrochemical experiments.

3.3.2. *Electrochemical study of modifier effect*

Cyclic Voltammetry (CV) was used to characterize the different electrodes to explain the effect of Ti₂O₃ nanoparticles and puMWCNTs as two modifiers. CVs for 5.0 mmol L⁻¹ Fe(CN)₆^{3-/4-} in 0.1 mol L⁻¹ phosphate buffer solution (PBS) on the bare PGE, puMWCNT/PGE, Ti₂O₃ NPs/PGE and Ti₂O₃ NPs-puMWCNT/PGE are shown in Fig. 8A. The quasi reversible one-electron redox behavior of Fe(CN)₆^{3-/4-} ions was observed on the bare PGE with a peak separation (ΔE_p) of 0.144 V at the scan rate of 50 mV s⁻¹. After the modification of the electrode using Ti₂O₃ NPs and puMWCNTs, the peak currents for Fe(CN)₆^{3-/4-} increased about 3.24 times than bare PGE, while the ΔE_p decreased. ΔE_p was found to be 0.082 V for Ti₂O₃ NPs-puMWCNT /PGE. Comparison between peak currents obtained for different electrodes indicates that the modification of electrodes with Ti₂O₃ NPs and puMWCNT as the increasing agent caused easier and faster charge transfer at the surface of electrode.

Here in Figure. 8

On the other hand, Fig. 8B depicts the redox behavior of 2.45μmol L⁻¹ Cu⁺² at the surface of bare PGE (curve a), puMWCNT/PGE (curve b) and Ti₂O₃ NPs-puMWCNT /PGE (curve c). As can be seen from CV curves, the

oxidation peak current of Cu at Ti_2O_3 NPs-puMWCNT /PGE is greater than oxidation peak current of Cu at puMWCNT /PGE while the response on the bare PGE was almost no detectable or very weak. This clearly demonstrates the favorable signal-enhancing effect of the Ti_2O_3 NPs-puMWCNT/PGE. So, to obtain the lowest limit of detection at Ti_2O_3 NPs-puMWCNT /PGE for Cu^{+2} ions, the anodic stripping voltammetry method was chosen for analytical characterization.

3.3.3. Optimization of conditions

While copper oxidation is dependent on the pH of the solution, thus to optimize pH of the solution, the electrochemical behavior of copper was studied in 0.1 mol L^{-1} PBS in different pH values ($2.0 < \text{pH} < 7.0$) at the surface of Ti_2O_3 NPs-puMWCNT /PGE by CV. It was found that the electro-oxidation of Cu at the surface of Ti_2O_3 NPs-puMWCNT /PGE was more dependent to $\text{pH} = 3.0$.

Anodic stripping differential pulse voltammetry (ASDPV) method was used to improve the sensitivity of Ti_2O_3 NPs-puMWCNT /PGE in determination of Cu^{+2} . The results showed to acquire voltammograms of a relatively high sensitivity and well-shaped waves with a relatively narrow peak width, a -0.5 V by duration 160 s for deposition potential, a modulation amplitude of 80 mV, a step potential of 4 mV, a scan rate of 10 mV s^{-1} , an interval time of 0.5 s and modulation time of 0.05 s should be chosen.

3.3.4. Analytical characterization of Cu^{+1} and Cu^{+2}

Under the optimized conditions described above, ASDPVs for the oxidation of different concentrations of Cu^{+2} were carried out in 0.1 mol L^{-1} PBS at $\text{pH}=3.0$. As can be seen in Fig. 9, the results showed that electro-oxidation of copper at the surface of Ti_2O_3 NPs-puMWCNT /PGE occurred at three different potentials. The adsorptive stripping peak currents were directly proportional to the bulk concentration of Cu^{+2} in the range 0.075-0.50 $\mu\text{mol L}^{-1}$ for reaction of $\text{Cu} \rightarrow \text{Cu}^{+1}$ ($E_{\text{ox}} = +0.22$ V) and in the range 0.45- 2.45 $\mu\text{mol L}^{-1}$ for reaction of $\text{Cu} \rightarrow \text{Cu}^{+2}$ ($E_{\text{ox}} = +0.042$ V). Electro-oxidation of Cu in higher the concentration ranges of 1.45 $\mu\text{mol L}^{-1}$ was occurred at the potential of -0.085 V, While it could be related to the reaction of $\text{Cu}^{+1} \rightarrow \text{Cu}^{+2}$ according to standard reduction potentials of

copper. According to our knowledge, no reports have been published so far for three states of oxidation of copper at modified electrodes. Therefore, in this paper, this effect could be due to the presence of high conductive Ti_2O_3 NPs nanoparticles on the surface of electrode. The limit of detection is defined as $C_L = 3S_b/m$, where C_L , S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively. S_b was estimated by 10 times determination of blank signals. So, the limit of detection (LOD) for Cu was found to be 4.63 nmol L^{-1} . This value of LOD is comparable with the values reported by other research groups for the electrocatalytic oxidation of Cu at the surfaces of chemically modified electrodes by other mediators [28-32].

Here in Figure. 9

The stability of Ti_2O_3 NPs-puMWCNT /PGE was checked in optimized experimental conditions, by successive ASDPV determination of Cu^{+2} for once in every day. The relative standard deviation of the peak currents for seven-time measurements ($n = 3$) was found to be 1.07%. The repeatability of electrode responses was estimated by making repetitive determinations of $0.48 \text{ } \mu\text{mol L}^{-1} \text{Cu}^{+2}$ using Ti_2O_3 NPs-puMWCNT/PGE. The RSD of the peak currents ($n = 10$) was found to be 1.36%.

4. Conclusions

In this paper, Ti_2O_3 nanoparticles were successfully synthesized through facile microwave and co-precipitation methods. Besides, the effect of different reaction parameters such as microwave power, irradiation time, and pH value on the particle size of the resulting Ti_2O_3 nanoparticles was studied. Moreover, this method was free from any surfactants and organic solvents and in comparison with co-precipitation method; microwave method is the fast, convenient, and suitable method for synthesis Ti_2O_3 nanoparticles. In addition, we have used ethylenediamine to control pH value of reactions. Furthermore, Ti_2O_3 nanoparticles were effectively applied in photo degradation of methyl orange. Finally, a pencil graphite electrode was fabricated using Ti_2O_3 nanoparticles and MWCNT to provide a sensitive electrochemical device for Cu^{+2} ions sensing. Using this device, vary oxidation states of copper were studied.

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Table.1. Reaction conditions for synthesized Ti_2O_3 nanoparticles using microwave method.

Sample no	Power (W)	Time (min)	pH	Method	Decolorization of methyl orange
1	—	720	9	co-precipitation	69%
2	750	1	9	Microwave	73%
3	750	3	9	Microwave	74%
4	750	6	9	Microwave	67%
5	600	3	9	Microwave	66%
6	900	3	9	Microwave	68%
7	750	3	8	Microwave	71%
8	750	3	10	Microwave	73%

Figure captions

Fig.1. XRD patterns of synthesized Tl_2O_3 nanoparticles using (a) co-precipitation method and (b) microwave method.

Fig.2. (A) Diffuse reflectance spectrum of Tl_2O_3 nanoparticles (sample no. 3). (B) Room temperature PL spectra of Tl_2O_3 nanoparticles (sample no. 3).

Fig.3. SEM images of Tl_2O_3 nanoparticles in different reaction times: (a) 1.0 min for sample no. 2, (b) 3.0 min for sample no. 3 and (c) 6.0 min for sample no. 4.

Fig.4. SEM images of Tl_2O_3 nanoparticles in vary of microwave powers: (a) sample no. 5 in 600 W and (b) sample no. 6 in 900 W for 3.0 min.

Fig.5. SEM images of Tl_2O_3 nanoparticles synthesized in different pH: (a) sample no. 7 in pH=8 and (b) sample no. 8 in pH=10.

Fig.6. (a) SEM images of synthesized Tl_2O_3 nanoparticles by co-precipitation methods (sample no. 1) and (b-d) TEM images of synthesized Tl_2O_3 nanoparticles by microwave method (sample no. 3).

Fig.7. (A) EDS pattern of Tl_2O_3 nanoparticles (sample no. 3). (B) Photo de-colorization of methyl orange in absence and presence of Tl_2O_3 nanoparticles under UV irradiation.

Fig.8. (A) Cyclic voltammograms of bare PGE (a), puMWCNT/PGE (b), Tl_2O_3 NPs/PGE (c) and Tl_2O_3 NPs - puMWCNT/ PGE (d) in the presence of 5.0 mmol L^{-1} $\text{K}_4\text{Fe}(\text{CN})_6$ / $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 mol L^{-1} PBS. Scan rate: 50 mV s^{-1} . (B) redox reaction of $2.45\text{ }\mu\text{mol L}^{-1}\text{Cu}^{+2}$ in 0.1 mol L^{-1} PBS at the surface of bare PGE (a), puMWCNT/PGE (b) and Tl_2O_3 NPs - puMWCNT/ PGE (b) by scan rate of 8.0 mV s^{-1} .

Fig.9. ASDPVs of Tl_2O_3 NPs - puMWCNT/ PGE in 0.1 mol L^{-1} PBS solution (pH=3.0) containing different concentrations of Cu^{2+} . The letters a-u corresponds to 0.075, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.95, 1.45, 1.95, 2.45 and $3.70\text{ }\mu\text{mol L}^{-1}$ of Cu^{2+} . Insets (A) and (B) show the plot of the oxidation peak current as a function of Cu^{1+} and Cu^{2+} concentrations, respectively.

Fig.1

Fig.2

Fig. 3

Fig. 4

Fig.5

Fig. 6

Fig.7

Fig. 8

Fig.9