Synthesis of Pt doped TiO₂ nanoparticles: Characterization and application for electrocatalytic oxidation of L-methionine

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A B S T R A C T

In this research, we reported a novel method for synthesis of Pt doped TiO₂ nanoparticles (Pt–TiO₂) by sol–gel assisted method. The synthesized Pt doped TiO₂ nanoparticles were characterized using X-ray diffraction (XRD), transmission electronic microscopy (TEM) and FT-IR techniques. To investigate the catalytic efficiency of Pt–TiO₂ nanoparticles, the electrooxidation of l-methionine (l-Met) using the deposited film of Pt doped TiO₂ nanoparticles and carbon nanotubes composite on glassy carbon electrode (Pt–TiO₂/CNT/GCE) was studied in buffer solution (pH 7.00) using cyclic voltammetry (CV). Bare GCE shows an ill-defined oxidation wave around 1.4 V for l-Met whereas Pt–TiO₂/CNT/GCE shows a well-defined oxidation peak at 1.1 V. The modified electrode does not show any fouling effect toward the oxidation of l-Met. Amperometry method was used to determine l-Met in the concentration range of 0.5–100 μM with a detection limit of 0.1 μM (S/N = 3). The selectivity of the reaction has been assessed with no interference from tyrosine, lysine, cysteine, tryptophan, alanine and glutathione. The present modified electrode shows good recovery results for spiked l-Met in human blood serum samples.

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1. Introduction

Titanium dioxide (TiO₂) with an energy band of about 3.2 eV has various applications, such as optical coating, dye sensitized solar cell, and gas sensors [1,2]. TiO₂ has three polymorphic forms of crystal structure: brookite, anatase and rutile. The photocatalytic activity of TiO₂ is dependent on its crystal structure, crystal size distribution, surface roughness, surface hydroxyl group density, etc. [3]. The photocatalytic activity of TiO₂ can be significantly improved by doping with noble metals such as platinum (Pt), which acts as the photogenerated electron acceptor [4–9]. Thus, under UV illumination, the photogenerated electrons effectively transfer from the TiO₂ surface to the doped Pt particles to suppress the recombination of electrons and holes and promote the transfer of holes on the TiO₂ surface. This produces a longer electron–hole pair separation lifetime, resulting in improved quantum yield and photocatalytic efficiency [10].

Methionine is an essential amino acid with an important role in biological methylation reactions. It constitutes the main supply of sulfur in the diet, preventing disorders in hair, skin or nails. Moreover, it helps to reduce cholesterol levels by increasing the lecithin production in liver, being also a natural chelating agent for heavy metals. Methionine can be present in real samples at different concentration level, from near 0.1% (w/v) in some drugs to 10⁻⁵ mol⁻¹ in blood plasma [11]. Methionine deficiencies have been attributed to toxemia, muscle paralysis, hair loss, depression, schizophrenia, parkinson's disease, liver deterioration and impaired growth [12]. Since methionine cannot be synthesized in the body it must be obtained from food supplies and pharmaceutical supplements are commercially available [13].

Flow injection [14], chromatography [15], atomic absorption [16] and colorimetric [17] methods have been employed for the determination of l-Met. These methods have several disadvantages such as high cost, long analysis time and low sensitivity. Therefore, these methods were unsuitable for routine analysis. On the other hand, determination of l-Met by electrochemical method has several advantages which include high sensitivity and selectivity and reproducibility. Determination of l-Met using chemically modified electrodes is one of the attractive methods. Only few reports were available in the literature for the determination of l-Met which include screen printed graphite macro electrode [18], carbon electrode modified with ruthenium metalldendrimer multi layers [19], conducting composite electrode doped with Ru(II) metalldendrimer [20], fullerene-C₆₀ modified gold electrode [21] colloidal gold-cysteamine modified carbon paste electrode [22], boron doped diamond and glassy carbon electrodes [23], nickel powder doped carbon ceramic electrode [24] 1,8,15,22-tetraaminophthalocyanato-copper(II) modified glassy carbon electrode [25]. However, these electrodes have several drawbacks including tedious preparation.
In the present work, we focused on synthesis and catalytic activity of Pt–TiO₂ system. There are many methods adopted to prepare Pt doped TiO₂. Pt doped TiO₂ nanoparticles by sol–gel method are of considerable interest due to its low cost, easy preparation and industrial viability. The Pt doped TiO₂ nanoparticles and carbon nanotubes composite modified glassy carbon electrode was investigated for the electrochemical oxidation of methionine using cyclic voltammetry. The present modified electrode shows good results for determination of L-Met.

2. Experimental

2.1. Materials and apparatus

Titanium tetra isopropoxide with purity 98% was obtained from Acros Organics. Platinum chloride and L-Met were purchased from Aldrich. Glacial acetic acid (100%) was purchased from Merck. Carbon nanotubes were purchased from Shenzhen Nano–Technologies Port Co., Ltd. (China) and were purified using a mixture of sulfuric acid and nitric acid in a composition of 3/2 by volume. Other reagents were of analytical grade and purchased from Aldrich or Merck and used as received without further purification.

Bruker – D8 powder X-ray diffraction (XRD) was used for determination of crystal phase identification and estimation of the crystallite size. LEO-Libra 120 microscope was employed for Pt doped TiO₂ nanoparticles transmission electron microscopy (TEM) images. Fourier transform infrared spectroscopy (FT-IR) studies were carried out with BRUKER FT-IR spectrometer, OXFORD (INCA Energy 400) energy dispersive spectroscopy (EDS) was used for the elemental analysis and chemical characterization of the sample.

2.2. TiO₂ nanoparticles precursor solution

The precursor solution was prepared by dissolving titanium tetra isopropoxide (TTIP) in the glacial acetic acid (AA), followed by the addition of H₂O. The mol ratio of TTIP:AA:H₂O must be kept at 1:10:200 in order to produce a clear solution. The solution was then be stirred for several hours.

2.3. Synthesis of Pt doped TiO₂ nanoparticles

The precursor solution was made as above mentioned. Dopant (Pt) solution was prepared by dissolving platinum chloride into the deionized water at 60 °C. The amount of dopant used in this study is 5 wt.%. Then, the dopant solution was added drop wise into the precursor solution for a few minutes. The solution was dried at the temperature of 80 °C overnight. The dried gel was ground and calcined in a muffle furnace at 500 °C for 5 h.

2.4. Fabrication of Pt–TiO₂/CNT/GCE

Prior to modification, the bare GCE (geometric area = 0.025 cm²) was polished on chamois leather with 0.05 μm alumina powder. Then it was thoroughly sonicated in deionized water and absolute ethanol, respectively. 1 mg of multi wall carbon nanotube and 1 mg of synthesized Pt–TiO₂ was dispersed in 5 mL dimethyl formamide (DMF) with the aid of ultrasonic agitation. The cleaned GCE was coated by casting 5 μL of the Pt–TiO₂ and CNT composite solution and dried at 50 °C in an oven air to remove the solvent.

3. Results and discussion

3.1. Characterization of Pt doped TiO₂ nanoparticles

Fig. 1 shows XRD patterns of TiO₂ and Pt/TiO₂ powders calcined at 500 °C under air for 5 h. From the wide angle XRD pattern, the titania samples exist only in anatase phase, with their characteristic diffraction peaks of 2θ values at about 25.4 (1 0 1), 37.9 (0 0 4), 48.2 (2 0 0), 54.0 (1 0 5), 55.1 (2 1 1) and 62.9 (2 0 4), respectively. In consequence, the prepared TiO₂ and Pt/TiO₂ powders are well-crystallized pure anatase form. From the maximum diffraction peak at Fig. 1 by Scherrer’s formula \( D = \frac{K \lambda}{\beta \cos \theta} \), where \( D \) is the crystallite size, \( K \) the Sherrer constant usually taken as 0.89, \( \lambda \) the wavelength of the X-ray radiation (0.15418 nm for Cu Kα), and \( \beta \) is full width half maximum of diffraction peak measured at 2θ, the average particle sizes of pure Pt–TiO₂ (Fig. 1a) and TiO₂ (Fig. 1b) powders for (1 0 1) plane, are about 10 nm and 12 nm, respectively. In comparison with XRD pattern of pure TiO₂, Pt loaded on TiO₂ surface nearly has not influence on crystalline structure and particle size. Pt phase has not been detected in the XRD patterns of Pt/TiO₂ powders, possibly because the Pt content on TiO₂ surface is not enough to form clearly crystalline. Also, Fig. 1c shows XRD patterns of Pt–TiO₂/CNT composite that has diffraction peaks of TiO₂ and Pt/TiO₂. The peak at 2θ value of 25 is broad indicating (0 0 2) phase of CNT and (1 0 1) phase of TiO₂ have overlapped.

Fig. 2a and b shows the FT-IR spectra of undoped and doped TiO₂–NPs in range of 400–4000 cm⁻¹ which were synthesized via
the sol–gel method. In undoped TiO₂–NPs (Fig. 2a), the peaks at 468 cm⁻¹ and 650 cm⁻¹ are for O–Ti–O bonding. The band centered at 1618 cm⁻¹ is characteristic of δ-H₂O bending. The broad absorption bands between 400 cm⁻¹ and 800 cm⁻¹ are mainly ascribed to Ti–O and O–Ti–O– flexion vibration. However, the vibration bands between 1300 cm⁻¹ and 4000 cm⁻¹ are mainly assigned to the chemisorbed and/or physisorbed H₂O and CO₂ molecules on the surface of the compound. When metal ions are doped to the surface of TiO₂, the absorption band transforms and simultaneously new absorption band appears. Upon addition of dopant, a small shift was detected for the stretching vibration of Ti–O [26].

TEM micrographs of TiO₂, Pt–TiO₂ and Pt–TiO₂/CNT composite are shown in Fig. 3. Electron microscopy analyses reveal that TiO₂ (Fig. 3a) and Pt–TiO₂ (Fig. 3b) samples exhibit similar morphology. The presence of differently sized TiO₂ grain agglomerates over the mats of carbon nanotubes is observed (Fig. 3c). It is well recognized that the TiO₂–CNTs bonding can be formed through some physic/chemical interactions such as Vander Waals force, H-bonding and other bonds. For example, Ti surface atoms on TiO₂ may possibly react with the −OH and COOH groups on the functionalized MWNs, and thus the bonding C–O–Ti or O=C–O–Ti might form through a dehydration reaction. The size histograms of the TiO₂ (Fig. 3d) and Pt–TiO₂ (Fig. 3e) are shown beside the TEM images. The histograms show that the main particle size of the TiO₂ and Pt–TiO₂ was about 13 and 16 nm, respectively. Energy dispersive X-ray spectroscopy (EDS) of Pt–TiO₂ is shown in Fig. 3f which confirms the existence of Ti, O and Pt with weight percent.

3.2. Electrochemical behavior of Pt–TiO₂/CNT/GCE

The cyclic voltammetry (CV) curve of Pt–TiO₂/CNT/GCE in 0.1 M H₂SO₄ solution at 50 mV s⁻¹ in a potential window of −0.3 to 1.2 V (Fig. 4) exhibits a typical H⁺ ion electro-adsorption/desorption region, a double layer charging current region, a Pt pre-oxidation region and a Pt oxy-species reduction region. In the proton adsorption/desorption region, current peaks observed at 0 V and −0.1 V, which corresponds to polycrystalline Pt, confirmed the existence of Pt, as evidenced by EDS, FT-IR and TEM.

The integrated area under the adsorption peak in the CV curve represents the total charge concerning H⁺ adsorption, Qₘ₄, and has
been used to determine electrochemical surface area (ECSA) by employing the equation [27]:

\[
\text{ECSA} \ [\text{m}^2 \text{g}^{-1} \text{of Pt}]= \frac{Q_0 \ [\mu \text{C m}^{-2}]}{210 \times \text{electrode loading} \ [\text{g of Pt/m}^2]}
\]

The ECSA of Pt is determined to be 84.79 m² g⁻¹ for our Pt–TiO₂/CNT catalyst, which is higher than for pt nanoparticles functionalized graphene sheets catalyst (32.13 m² g⁻¹), Pt-chemically reduced graphene catalyst (11.50 m² g⁻¹), Pt-thermally reduced graphene catalyst (20.00 m² g⁻¹), Pt-Vulcan catalyst (30.10 m² g⁻¹), Pt-graphene catalyst (44.60 m² g⁻¹) and Pt-graphene oxide catalyst (16.90 m² g⁻¹) [28,29].

3.3. Electrochemical determination of L-Met at Pt–TiO₂/CNT composite film modified GCE

We have examined the electrocatalytic activity of Pt–TiO₂ film deposited on GCE toward L-Met electrooxidation in buffer solution (pH 7.00) using cyclic voltammetry (Fig. 5). We obtained higher oxidation current with less positive potential for L-Met at pH 7.00. Bare GCE shows an oxidation wave at 1.4 V for L-Met (curve b). On the other hand, the Pt–TiO₂/CNT/GCE modified GCE exhibits a well-defined oxidation wave for L-Met at 1.1 V (curve c).

A comparison of the cyclic voltammograms of L-Met at bare GCE (curve b) and Pt–TiO₂/CNT/GCE (curve c) demonstrates the oxidation peak potential of L-Met at Pt–TiO₂/CNT/GCE occurs at a potential about 300 mV less positive than at a bare GCE (potential shift from 1.4 V to 1.4 V). The obtained clear voltammetric signal with higher oxidation current and less positive potential for L-Met at Pt–TiO₂/CNT/GCE electrode was attributed that the oxidation of L-Met was catalyzed by Pt–TiO₂/CNT.

3.4. Effect of pH on L-Met oxidation

It is well known, the electrochemical behavior of L-Met are dependent on the pH value of the aqueous solution [11,14]. The effect of pH value on the electrooxidation of L-Met at the surface of Pt–TiO₂/CNT/GCE was investigated through the use of different 0.1 M phosphate buffer solutions (pH 3.00–9.00). The current response of L-Met at Pt–TiO₂/CNT/GCE increases from pH 3.00 to 7.00 and then a decrease is obtained at pH values higher than 7.00 (not shown). Therefore, pH 7.00 was chosen as optimum pH and further studies were performed at pH 7.00.

3.5. Amperometric determination of L-Met

Amperometric method was used to examine the sensitivity of Pt–TiO₂/CNT/GCE toward the detection of L-Met. Fig. 6 shows the amperometric curve obtained for L-Met at Pt–TiO₂/CNT/GCE in a constantly stirred 0.1 M PBS (pH 7.00). The dependence of current response with respect to concentration of L-Met for 3 times experiments was average linear from 0.5 to 100 μM with an

![Figure 5](image1.png)  
**Fig. 5.** Cyclic voltammograms of GCE in the (a) absence and (b) presence of 0.1 mM L-Met and (c) at Pt–TiO₂/CNT/GCE in 0.1 M PBS (pH 7.00) and 0.1 M KCl at scan rate of 50 mV s⁻¹.

![Figure 6](image2.png)  
**Fig. 6.** Current–time curve of Pt–TiO₂/CNT/GCE with successive addition of L-Met to a stirred 0.1 M PBS (pH 7.00). The inset is the calibration curve.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
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<tbody>
<tr>
<td>Analytical parameters for voltammetric determination of L-Met at different modified electrodes.</td>
</tr>
<tr>
<td>Electrode</td>
</tr>
<tr>
<td>nAu-Cyst-CPE²</td>
</tr>
<tr>
<td>p-4e-Callurfa-CGE³</td>
</tr>
<tr>
<td>CHNM/GCE³</td>
</tr>
<tr>
<td>Ni-GCE⁴</td>
</tr>
<tr>
<td>Co/GCE⁵</td>
</tr>
<tr>
<td>Pt–TiO₂/CNT/GCE</td>
</tr>
</tbody>
</table>

² Colloidal-gold cysteamine-modified carbon paste electrode.
³ 1,8,15,22-Tetraaminophthalocyanato-copper(II) modified glassy carbon electrode.
⁴ Cobalt hydroxide nanoparticles modified glassy carbon electrode.
⁵ Ni doped carbon ceramic electrode.
⁶ Co₉ modified gold electrode.

Reference
[22]  
[25]  
[24]  
[21]  
This work
Table 2
Recovery test for l-Met in human blood serum samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spiked (µM)</th>
<th>Found (µM)</th>
<th>Mean recovery (n = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.0</td>
<td>10.1</td>
<td>101.0 ± 4</td>
</tr>
<tr>
<td>2</td>
<td>25.0</td>
<td>24.8</td>
<td>99.8 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>50.0</td>
<td>49.8</td>
<td>99.6 ± 3</td>
</tr>
<tr>
<td>4</td>
<td>100.0</td>
<td>97.3</td>
<td>97.3 ± 6</td>
</tr>
</tbody>
</table>

detection limit of 0.1 µM at Pt–TiO2/CNT/GCE, a high sensitivity of 29,085.66 µA mM⁻¹ cm⁻² and an correlation coefficient of 0.991 (Fig. 6, inset).

The observed linear range and detection limit of l-Met were compared with the reported papers and are given in Table 1 [21,22,24,25,30]. As can be seen from Table 1, the present modified electrode shows better sensitivity than the other modified electrodes. Further, the present modified electrode was highly stable and no tedious procedure was involved in electrode modification.

3.6. Reproducibility and stability of the Pt–TiO2/CNT/GCE

The operational stability of Pt–TiO2/CNT/GCE was tested by the CV method every 2 days in 2 weeks. The response of 0.1 mM l-Met decreased less than 12% after 2 weeks, so it has good stability. The fabrication reproducibility of five electrodes independently made, showed a RSD of 6.1% for detecting 0.1 mM l-Met. The excellent reproducibility and stability of Pt–TiO2/CNT/GCE may be mainly attributed to the strong deposition of the Pt–TiO2/CNT.

3.7. Recovery test for l-Met in human blood serum samples

The practical application of Pt–TiO2/CNT/GCE was tested by measuring the concentration of l-Met in human blood serum samples. The human blood serum samples were collected from nearby hospital. 1 mL of the serum sample was diluted to 10 mL of 0.1 M PBS. The standard addition technique was used to examine the recovery of l-Met in serum samples. The recovery results were obtained and the results are summarized in Table 2. The proposed method showed a good recovery for spiked l-Met in serum samples, indicating that the present modified electrode could be applied to determine l-Met in different human fluids.

3.8. Interference study

Possible interferences for the detection of l-Met at the Pt–TiO2/CNT/GCE was investigated by the addition of various compounds such as glycine, alanine, ascorbic acid, dopamine, uric acid, l-cysteine, glutathione, p-penicillamine, cystamine, N-acetyl-l-cysteine and lysine into pH 7.00 PBS in the presence of 1.0 mM l-Met. The results showed that these mentioned compounds did not show interference.

4. Conclusion

In summary, we demonstrated that Pt doped TiO2 nanoparticles can be readily formed by sol–gel method. The method is simple, scalable and applicable to a variety of systems. The Pt–TiO2 has a catalytic activity, making it an ideal candidate for sensor applications. The present study demonstrates the sensitive determination of l-Met using the Pt–TiO2/CNT modified GCE. The bare GCE showed an ill-defined oxidation wave for l-Met whereas the modified electrode not only showed a well-defined stable oxidation peak but also enhanced its oxidation current. Further, using the amperometry method, a detection limit of 0.1 µM (S/N = 3) was achieved for determination of l-Met. The modified electrode showed good recovery for l-Met in blood serum samples, indicating that the present method may be used for practical applications.

References


Biographies

Fereshteh Chekin received her Ph.D. degree in analytical chemistry from Mazandaran University under supervision of Prof. J.B. Raoof in 2010. She joined in Islamic Azad University as a professor assistant in 2010. Her research interests include electrochemistry, analytical chemistry, biosensors, nanobiosensors, nanocomposite materials. Her current research is focused on synthesis of nano materials.

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