SURFACE CHARACTERISATION AND PHOTOCATALYTIC REACTIVITY OF INNOVATIVE Ti/TiO$_2$ AND Ti/Pt-TiO$_2$ MESH PHOTOELECTRODES

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Abstract

Novel Ti/TiO$_2$ and Ti/Pt-TiO$_2$ mesh photoelectrodes were produced by anodising titanium mesh in H$_2$SO$_4$ solution. Their structural and surface morphology were examined by X-ray diffraction (XRD), scanning electronic microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The analytical results indicated that the crystal structure, morphology and pore size were affected significantly by the voltage and current density applied in anodisation and the percentage of platinum content. The results of XPS measurement showed that the binding energy of O 1s and Ti 2p increased slightly owing to platinum deposition (Pt^0, Pt^{2+} and Pt^{4+}) onto the surface of TiO$_2$. The photoelectrocatalytic (PEC) oxidation of methyl orange in aqueous solution using the Ti/TiO$_2$ and Ti/Pt-TiO$_2$ meshes

was investigated respectively. The experimental results demonstrated that Ti/TiO$_2$ mesh prepared at 160V and 110mA cm^{-2} achieved the best PEC oxidation. The efficiency of PEC oxidation could be further enhanced by applying an electrical bias between the working electrode and counter electrode. An optimal electrical bias voltage was found to be 0.6V, while an optimal platinum content was 3.37%.

1. Introduction

Although titanium dioxide (TiO$_2$) is an excellent photo-catalyst and slurry-based photoreactors have been successfully employed for the decontamination of some natural systems and waste streams, TiO$_2$ solids recovery from decontaminated water is still a problem. The alternative of supported TiO$_2$ gives lower efficiency due to the loss of surface area and mass transfer limitations [1-3]. Fujishima and Honda in 1972 studied TiO$_2$ as a photoanode material and demonstrated its use for photo-oxidation of water, in which an electrical bias was applied between the anode and cathode, and the photogenerated electrons on TiO$_2$ were driven away from the anode in the process [4]. After that, a number of studies demonstrated the higher efficiency of PEC oxidation processes for organic degradation, which can prevent carrier charge recombination and result in an extension of the lifetime of active holes [5-7]. In these studies, the photo-anode was prepared by coating TiO$_2$ onto a conducting glass that was initially covered by an indium tinoxide. It was found that electron mass transfer between TiO$_2$ films and supporting carriers was not very efficient due to the poor connection between the two materials. Recently, we have successfully prepared an innovative Ti/TiO$_2$ mesh electrode by anodisation and used it for the PEC degradation of rose Bengal [8]. This mesh electrode had a large microporous surface area with excellent adsorption characteristics, which achieved a better PEC

oxidation performance than using TiO_2 powder in suspension. In order to further improve its application in water and wastewater treatment, more detailed investigation is needed to determine the relationship between the preparation conditions and photoreactivity.

In this study, the Ti/TiO_2-mesh electrodes were first prepared by anodisation under different voltages and current densities, and the Ti/Pt-TiO_2 mesh electrodes were further prepared by photoreduction to deposit platinum onto the surface of the Ti/TiO_2 mesh. The objectives of this research were (1) to investigate the influence of voltage and current density during anodisation on the crystal structure, surface morphology, chemical and electronic structure of the Ti/TiO_2-mesh electrode, and (2) to seek optimal conditions to further enhance the PEC reactivity of Ti/TiO_2 mesh by surface modification.

2. Experimental

2.1 Materials

Titanium mesh (purity: 99.6%, nominal aperture: 0.19 mm, wire diameter: 0.23 mm, wires/inch: 60×60, open area: 20%, twill weave) was purchased from Goodfellow Cambridge Limited. Methyl orange was purchased from Beijing Chemical Company. Other chemicals obtained were analytical grade and used without further purification. Deionised distilled water was used throughout the experiment.

2.2 Preparation of Ti/TiO_2 mesh electrodes

A large piece of raw titanium mesh with a thickness of 0.5 mm was cut into small rectangle pieces of 25 mm x 10 mm, which were then cleaned with alcohol and acetone solution

respectively. The pretreated titanium mesh and a copper plate with the same size were submerged in 0.5M H_2SO_4 solution and an electrical current up to 200V was applied using a laboratory-made DC power supply. In the first stage of anodisation, the galvanostatic anodisation with a constant current (110 mA cm^{-2}) was applied with an increasing voltage at 1.2 V s^{-1} within the first 2 min. In the second stage of anodisation, a constant voltage (80, 120, 140, 160, 180, 200V) was then maintained, while the current density was gradually decreased from 110 to 33 mA cm^{-2}. The whole anodisation process lasted for about 10 min. The Ti/TiO_2 mesh electrodes prepared at different electrical voltages were named 80V-mesh, 120V-mesh, 140V-mesh, 160V-mesh, 180V-mesh and 200V-mesh respectively. Also, more electrodes were prepared with different current densities (80, 110, 140, 170 mA cm^{-2}) in the first stage and only 160 voltage was used in the second stage, which were named 80mA-mesh, 110mA-mesh, 140mA-mesh and 170mA-mesh correspondingly. The freshly generated TiO_2-mesh electrodes were rinsed with 0.001M nitrate acid and distilled water, then dried in an oven at 105^oC for 2 hrs.

2.3 Preparation of Ti/Pt-TiO$_2$ mesh electrode

The anodized Ti/TiO_2 mesh electrodes were further modified by photo-reduction to deposit platinum onto the TiO_2 layer. In this method, the Ti/TiO_2 mesh was placed in the 0.1M methanol solution containing a certain amount of hexachloroplatinic acid as a hole scavenger. The solution was irradiated with a 125W high-pressure mercury lamp for 20, 40, 60, and 80 min respectively. The product electrode was washed repeatedly with water and dried at 378 K for 2 hrs. The platinum content on the mesh surface was detected by X-ray photoelectron spectroscopy (XPS). Four pieces of electrode prepared had platinum

contents of 1.58%, 3.37%, 6.69% and 11.13% (mol mol^{-1}) and were labeled as Pt1#-mesh,

Pt2#-mesh, Pt3#-mesh and Pt4#-mesh correspondingly.

2.4 Characterisation of Ti/TiO$_2$-mesh electrode

To determine the crystal phase composition of the Ti/TiO$_2$ mesh electrodes, X-ray

diffraction (XRD) measurement was performed at room temperature with a Philips

PW3710 diffractometer using Cuk$_\alpha$ radiation (λ_a=0.154060 nm; λ_0=0.154439 nm);

accelerating voltage was 40 kV, and emission current was 30 mA. Scanning electron

microscopy (SEM) (Leica Stereoscan 400i Series) was used to study surface morphology,

average pore size and pore distribution. High tension was selected at 15 kV. To determine

the crystal phase composition of the mesh, X-ray photoelectron spectroscopy (XPS) was

recorded with a PHI Quantum ESCA microprobe system, using the MgK$_\alpha$ line of a 250W

Mg X-ray tube as a radiation source with the energy of 1253.6 eV, 16 mA ×l12.5 kV. A

working pressure of 1210^{-8} N.m^{-2} was applied. As an internal reference for the absolute

binding energies, the C 1s peak of hydrocarbon contamination was used. The fitting XPS

curves were analysed using the Multipak 6.0A.

2.5 Equipment

The experiment of PEC oxidation was performed in a batch photoreactor, which consisted

of a cylindrical borosilicate glass vessel with an effective volume of 165 ml, a 125W

high-pressure mercury lamp (Institute of Electric Light Source, Beijing), a potentiostat

(ISO-TECH 1PS 1810H), a mesh electrode as the anode and a Cu plate electrode (50

mm10mm) as the cathode. The high-pressure mercury lamp was positioned inside the

vessel surrounded by a circulating water jacket (Pyrex). The two electrodes were positioned in parallel and connected with a potentiostat. In the experiment, the methyl orange solution was gently aerated under UV irradiation and samples were collected at different time intervals for analyses.

2.6 The PEC oxidation of methyl orange in aqueous solution

In this study, 4 sets of tests were carried out with different objectives. The first set of tests was carried out using the Ti/TiO_2 electrodes made at the constant current density (110 mA) but different working potentials (80, 120, 140, 160, 180, 200V) under the same light intensity for 85 min to determine the optimal voltage applied in the anodising process. The second set of tests was conducted using the Ti/TiO_2 electrodes prepared with the same voltage (160V), but different working current densities (80, 110, 140, 170 mA cm^{-2}) to determine the optimal current density. The third set of tests was performed using the $Ti/Pt-TiO_2$ electrodes with different platinum content to study the optimal ratio between platinum and TiO_2 on the mesh. The fourth set of tests was conducted by applying different electrical potentials between the working electrode and counter electrode to determine the optimal voltage for the reaction.

2.7 Analytical methods

The methyl orange concentration in aqueous solution was determined by a UV-visible spectroscopy (Genesys-2) at its maximum absorption wavelength and TOC was monitored with a TOC-Analyser (Shimadzu 5000A) equipped with an autosampler (ASI-5000). The light intensity was measured by a Black-Ray UV meter (UVP Inc, Model No. J 221).

3. Results and Discussion

3.1 Crystal structure

The crystal phase composition of the Ti/TiO$_2$-mesh electrodes prepared with different voltages and current densities was examined by XRD. The diffractograms Ti/TiO$_2$ meshes are shown in Figure 2a and Figure 2b respectively, where the peaks representing anatase and rutile are labelled as A and R correspondingly. For the 80V-mesh, 120V-mesh and 140V-mesh, it was found that only anatase phase presented. When the anodisation voltage went up to 160V, rutile phase turned up at 27.405 (110), 36.105, 41.310 and 56.685 respectively. The intensity of rutile peaks increased with the increase of the anodisation voltage. Even though the anodisation voltage further increased to 200V, the 101 peak of anatase phase was very weak, and the intensity of all other anatase peaks decreased whereas rutile peaks increased. When the anodisation voltage was fixed at 160V and the current density varied from 80 to 170 mA cm^{-2}, all the peaks of anatase and rutile increased with the increase of current density. The diffractograms of Ti/Pt-TiO$_2$ meshes are shown in Figure 2c. It can be seen that the intensity of anatase and rutile peaks increased with the increase of platinum content. For all the Ti/Pt-TiO$_2$ meshes, 101 peak and 110 peak presented significantly, compared to that of Ti/TiO$_2$ mesh (160V-mesh). For the Pt4#-mesh, some Pt peaks presented.

[Figure 2a]

[Figure 2b]

[Figure 2c]

3.2 Surface morphology and pore distribution

The surface morphology of the Ti/TiO$_2$-mesh electrodes was examined by SEM and the analytical results of the meshes made at different voltages and current densities are shown in Figure 3. It was found that the surface of the oxidised meshes had a mciroporous structure and was rougher than that of the raw Ti mesh. The results demonstrated that the TiO$_2$ film formed on the mesh at a higher voltage in the anodisation was thicker. The pore size of the oxidized meshes varied from 10 to 120 nm, as the applied anodising voltage increased from 80 to 200V. In the meantime, the pore size grew fast when the voltage increased from 80 to 160V, and grew slowly when the voltage exceeded 160V. The earlier work [9] on the titanium anodisation indicated that the formation of micropore was attributed to the power dissipation in the barrier oxide layer. When anodising current density is greater than 30 mA cm^{-2} in sulphuric acid, the power dissipated in the barrier oxide layer increases considerably. It causes the overheating of local oxide, and the cooling of the oxidised anode by the electrolyte becomes insufficient. The higher temperature leads to a higher ionic current probably along grain boundaries, and the oxide may recrystalise and results in a porous surface. With current densities greater than 100 mA cm^{-2}, a fast dissolution of the oxide is believed to occur with the creation of pores, which lead to an even rougher surface.

[Figure 3]

[Figure 4]

In this study, the surface morphology of the Ti/Pt-TiO$_2$ meshes also appeared different owing to the platinum deposition on the surface as shown in Figure 4. When the mesh contained 1.58% of platinum (Pt1#-mesh), the platinum clusters were formed with a size of

15- 30 nm and only a small portion of the TiO_2 surface was covered. However, when the mesh contained the platinum up to 11.13% (Pt4#-mesh), the size of clusters increased significantly from 15 to 70 nm and the platinum deposit filled up the most pores on the TiO_2 surface.

3.3 Chemical and electronic structure

To determine the chemical and electronic structure of the mesh surface and also the valence states of various species presence therein, five meshes of 160V-mesh (no Pt), Pt1#- Pt2#- Pt3#- and Pt4# were examined by XPS and the XPS spectra of O 1s, Ti 2p and Pt 4f are shown in Figure 5. The specifications of Ti 2p, O 1s and Pt 4f for the different meshes were obtained and are listed in Tables 1 and 2. The results in Figure 5A and Table 1 demonstrated that the O 1s curves had a two-band structure. The main O 1s peak between 529.68-530.31eV increased with the increase of platinum content. Another O 1s peak at 531.78-531.85eV may be attributed to $Pt(OH)_2$ or PtO_2. Significantly, the relative area of O 1s band attributed to TiO_2 decreased with the increase of platinum content, since the platinum cluster covered the surface of the Ti/TiO_2 mesh.

[Figure 5]

[Table 1]

The results in Figure 5B showed that the Ti 2p peaks of the $Ti/Pt-TiO_2$ meshes were narrow with slight asymmetry and decreased significantly with the increase in platinum content. Meanwhile, the data in Table 1 indicated that the Ti 2p had a binding energy in the range of 458.35-458.74 eV, attributed to Ti^{4+}, which increased slightly with the increase of platinum

content. The Pt 4f spectra shown in Figure 5C demonstrated that the Ti/Pt-TiO$_2$ meshes consisted of four peaks, corresponding to Pt^0, Pt^{2+}, and Pt^{4+} respectively. The data listed in Table 2 indicated that the peaks at 70.67 - 71.40eV attributed to metallic platinum as Pt^0; the peaks at 71.96-72.69eV were peculiar to either Pt(OH)$_2$ or PtCl$_4^{2-}$ as Pt^{2+}; the peaks at 74.48-75.07eV to PtO$_2$ as Pt^{4+} and the peaks at 77.53-78.40eV to PtCl$_6^{2-}$ also as Pt^{4+}. In this photoreduction process, PtCl$_6^{2-}$ (Pt^{4+}) was adsorbed on the surface of Ti/TiO$_2$ mesh first, and then reduced into PtCl$_4^{2-}$ (Pt^{2+}) and further to metallic platinum (Pt^0). However, the photoreduction of PtCl$_6^{2-}$ was incomplete and therefore a certain amount of Pt^{4+} still remained on the Ti/Pt-TiO$_2$ meshes.

[Table 2]

3.4 The PEC oxidation of methyl orange

The first set of tests was carried out using the Ti/TiO$_2$-meshes anodised at the same current density of 110mA cm^{-2} but at the different voltages of 80, 120, 140, 160, 180V and 200V respectively to photodegrade methyl orange (MO) in aqueous solution under the light intensity of 4.38 mW cm^{-2}, but without applying any electrical bias. Six tests were performed with an initial MO concentration of 10 mg.l^{-1} and samples were collected at different reaction times (0, 10, 25, 40, 55, 70 and 85 min) for analysis of UV-visible absorption. The first-order kinetic constant k in each test was calculated based on the experimental data of methyl orange removal as shown in Figure 6. The experiment demonstrated that the Ti/TiO$_2$ electrode anodised at 160V achieved the best photocatalytic reactivity, the reaction rate in this PEC oxidation using the 160V-mesh was 3 times higher

than that using the 80V-mesh, and was almost double that using the 200V-mesh.

[Figure 6]

The second set of tests was carried out by applying the Ti/TiO$_2$ mesh anodised at the same voltage of 160V but at different current densities of 80, 110, 140 and 170 mA cm^{-2}. Other conditions were the same as those in the first set of tests. The removal of methyl orange demonstrated that the 110mA-mesh had the best photocatalytic reactivity, since the first-order kinetic constant k using the 110mA-mesh was almost double that using the 80mA-mesh and 170mA-mesh, as shown in Figure 7. The results in these two sets of tests indicated that the optimal conditions in the anodisation process to prepare a Ti/TiO$_2$ mesh with the best PEC reactivity should be set at 160V and 110 mA cm^{-2}.

[Figure 7]

To investigate the effect of platinum content on the photocatalytic reactivity, the third set of tests was conducted using the 160V-mesh(0%), Pt1#-mesh(1.58%), Pt2#-mesh(3.37%), Pt3#-mesh(6.69%) and Pt4#-mesh(11.13%) under light intensity of 4.38 mW cm^{-2}, but without applying any electrical bias. Methyl orange solutions with the initial concentration of 10 mg.l^{-1} were irradiated for 85 min and the results are shown in Figure 8. The results demonstrated that the photocatalytic oxidation of methyl orange was significantly affected by the platinum content contained in the meshes from 1.58 to 11.13%. It seemed that there was an optimal platinum content of around 3.37% to achieve the highest photocatalytic

reactivity.

[Figure 8]

The fourth set of tests was carried out using the 160V-mesh with the same light intensity
and the same initial methyl orange concentration, but applying different electrical bias (0.0,
0.1, 0.3, 0.6 and 1.0V) between the two electrodes. One test was also carried out as PC
oxidation, in which the Ti/TiO$_2$ electrode and counter electrode were not connected wirely.
All tests lasted for 85 min and the experimental results are shown in Figure 9. The
experiment demonstrated that 0.6V was the best voltage for application of the electrical
bias, although the first-order kinetic constant k had only a slight increase in the range of 0.0
- 1.0V. Actually, we found there was a significant difference between PC and PEC
oxidation, which means that whether the two electrodes were wired for connection was
more important than the voltage variation between the two electrodes for the reaction rate.
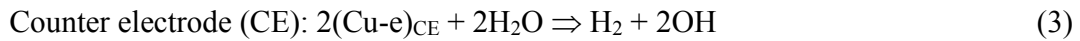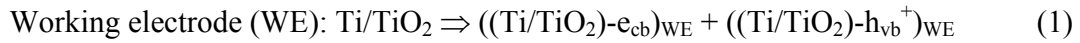
[Figure 9]

To investigate the mineralisation of methyl orange, TOC in methyl orange solutions was
also monitored in the reactions using the 160V-mesh and Pt2#-mesh electrodes
respectively with the light intensity of 4.38 mW cm^{-2} and 0.6V bias. Samples were
collected at 0, 20, 40, 60, 80, 100, and 120 min for TOC analysis. The results shown in
Figure 10 presented that the TOC was removed by 78.5% and 93.1% respectively, when
160V-mesh and Pt2#-mesh were used. It conformed that the TiO$_2$ mesh electrode with

platinum impurity (Pt2#-mesh) had a better PEC reactivity than the mesh with TiO_2 only (160V-mesh) in the mineralisation of methyl orange. The experiment demonstrated that a complete mineralisation of methyl orange could be achieved within 120 min under this experimental condition.

[Figure 10]

3.5 The mechanism of the PEC oxidation using Ti/TiO₂ and Ti/Pt-TiO₂ mesh electrodes

In our investigation, we propose that the mechanism of PEC oxidation by using the Ti/TiO_2 working electrode and the copper counter electrode can be expressed by Equation (1)-(7).

Working electrode (WE): $Ti/TiO_2 \Rightarrow ((Ti/TiO_2)\text{-}e_{cb})_{WE} + ((Ti/TiO_2)\text{-}h_{vb}{}^{+})_{WE}$ (1)

$$((Ti/TiO_2)\text{-}e_{cb})_{WE} \Rightarrow (Cu\text{-}e)_{CE} \qquad (2)$$

Counter electrode (CE): $2(Cu\text{-}e)_{CE} + 2H_2O \Rightarrow H_2 + 2OH$ (3)

where the subscripts of cb and vb denote the conduction and valence bands of the TiO_2 respectively

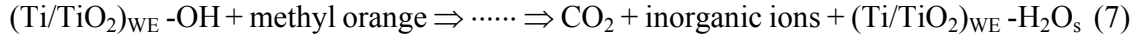Overall reaction: $Ti/TiO_2 + H_2O \Rightarrow 1/2\ H_2 + OH + ((Ti/TiO_2)\text{-}h_{vb}{}^{+})_{WE}$ (4)
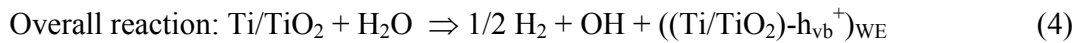
Then the holes on the WE react with the hydroxide or H_2O molecules adsorbed on the TiO_2 surface (OH_s and H_2O_s) to generate hydroxyl radical (OH·).
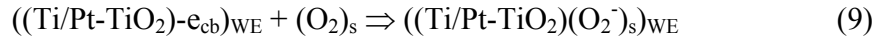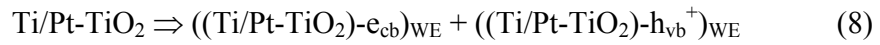
$$OH^{-}{}_{s} +\ ((Ti/TiO_2\text{-}h_{vb}{}^{+})_{WE} \Rightarrow (Ti/TiO_2)_{WE}\text{-}OH· \qquad (5)$$

$$H_2O_s + ((Ti/TiO_2)\text{-}h_{vb}^+)_{WE} \, (Ti/TiO_2)_{WE}\text{-}OH\cdot + H^+ \qquad (6)$$

Finally the hydroxyl radicals (OH·) oxidise the methyl orange adsorbed on the WE surface.

$$(Ti/TiO_2)_{WE}\text{-}OH + \text{methyl orange} \Rightarrow \cdots\cdots \Rightarrow CO_2 + \text{inorganic ions} + (Ti/TiO_2)_{WE}\text{-}H_2O_s \quad (7)$$

When the Ti/Pt-TiO$_2$ mesh is used, the excited electrons from valence band to conduction band migrate to platinum clusters, and then further migrate to O$_2$ molecules adsorbed on the surface of mesh to form O_2^-. The O_2^- is an active particle to oxidise the methyl orange as shown in Equations (8)-(10).

$$Ti/Pt\text{-}TiO_2 \Rightarrow ((Ti/Pt\text{-}TiO_2)\text{-}e_{cb})_{WE} + ((Ti/Pt\text{-}TiO_2)\text{-}h_{vb}^+)_{WE} \qquad (8)$$

$$((Ti/Pt\text{-}TiO_2)\text{-}e_{cb})_{WE} + (O_2)_s \Rightarrow ((Ti/Pt\text{-}TiO_2)(O_2^-)_s)_{WE} \qquad (9)$$

$$(O_2^-)_s + \text{methyl orange} \Rightarrow \cdots\cdots \Rightarrow CO_2 + \text{inorganic ions} \qquad (10)$$

In addition, the recombination between the excited electrons and holes as a reverse reaction of Equation (1) is a significant factor in reducing PEC oxidation efficiency. Therefore, reducing the recombination of electrons and holes becomes essential to promote PEC efficiency. In this experiment, the connection between the working and counter electrodes by the potentiostat made it possible to efficiently drive the photo-generated electrons away from the Ti/TiO$_2$ surface and extend the lifetime of the holes.

4. Conclusions

Two novel photoelectrodes of Ti/TiO_2 mesh and $Ti/Pt-TiO_2$ mesh were successfully prepared by anodising Ti mesh in 0.5M H_2SO_4 solutions. The results of XRD analysis indicated that the anatase phase of TiO_2 was dominant on the surface of the electrodes, while the results of SEM examination showed that this Ti/TiO_2-mesh electrode had a microporous surface structure and its pore size was affected by the anodising voltage and current density. The analytical results of XRD also showed that the intensity of all anatase and rutile peaks increased with the increase of platinum content on the Ti/TiO_2 mesh surface. The results of XPS measurement showed that the binding energy of O 1s and Ti 2p increased slightly owing to platinum deposition and that Pt^0 as metallic platinum, Pt^{2+} as $Pt(OH)_2$, and Pt^{4+} as either PtO_2 or $PtCl_6^{2-}$ presented on the surface of $Ti/Pt-TiO_2$ meshes. The Ti/TiO_2 mesh prepared at 160V and 110mA cm^{-2} had the best PEC reactivity in the methyl orange photooxidation. The PEC reactivity was significantly promoted by applying an electrical bias between the working electrode and counter electrode, since the recombination of electrons and holes was hindered.

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