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Estimation of Photoelectrocatalytic Activity of Titanium Oxide Film Electrodes by *Ac* Impedance

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Abstract: In this paper, we demonstrated that the charge-transfer resistance of photoanode can be calculated through the analysis of its electrochemical impedance spectroscopy (EIS) and the photoelectrocatalytic degradation rate of aniline was inversely proportional to the value of charge-transfer resistance of photoelectrodes prepared by thermally oxidation on titanium. The value of charge-transfer resistance is smaller, the higher its photoelectro-activity is.

Keywords: Photoactivity, charge-transfer resistance, titanium dioxide, impedance

Over the last few decades, there has been a growing interest in the application of photocatalysis towards the treatment of polluted water[1-4]. It was well demonstrated that the anodic bias potential exerted on photoanode could prevent significantly the recombination rate of photogenerated carriers, consequently, it can improve the efficiency of photocatalytic degradation of organics[2-4]. For this, the study of photoelectrocatalytic degradation of pollutants has been of particular interest to researchers[1-5].

The activity of photocatalysts is a key factor for the photoelectrocatalytic degradation of pollutants. The conventional method for evaluating their reactivity is to compare their photodegradation rates of pollutants under a given experimental condition. The rate is larger, the higher photoactivity is. However, this method has several disadvantages such as long analysis time, high probability of errors due to complex procedures, and high costing. In this paper, we reported a new simple evaluation method by using the charge-transfer resistance of photocatalysts.

Experimental

Photoelectrodes were prepared by thermal oxidation of titanium sheet (thickness in 0.15 cm, polished by 1 μm diamond paper and chemically etched with an 3:1 HNO_3 (68%) /HF for 15s) at different temperature for 1h under an atmosphere of air. Specimens were made with an electrical contact on their backsides. The working area was 3.9 cm^2 and 60 cm^2 for photoanode A and B, respectively, and the rest was covered with expoxy. Photoanode A and B were used for the photoelectrochemical measurements and photo-degradation of aniline, respectively. The crystal structure of specimens was carried out by using a X-ray diffractometer (XRD, Rigaku D/max –3B, CuK α, 40 kV~40 mA, 8° min^{-1}, 2θ = 20~80°). The composition of specimens was estimated by X-ray photoelectron spectroscopy (XPS, VG Escalab MKII, AlK α 15 kV, 20 mA). Photoelectrochemical measurements were performed on CH Instrument 660 electrochemical station driven by a personal computer, which was carried out in a conventional borosilicate glass three-electrode cell (a platinum foil as counter electrode (CE), saturated calomel electrode (SCE) as reference, deaerated 0.5 mol dm^{-3} Na_2SO_4 as supporting electrolyte). The amplitude of the sinusoidal wave was of 10 mV and the frequency range examined was 100 kHz to 0.1 Hz. For all cases, the applied potential was kept constant in the dark for 30s before illumination. The light source was 6W UV lamp (Emax=365nm). The photocatalytic degradation of aniline was carried out in a rectangle photoreactor (photoanode B as working electrode, Ag sheet as CE, SCE as reference, 0.5 mol dm^{-3} Na_2SO_4 as supporting electrolyte, solution 100cm^3). The aniline concentration was estimated colorimetrically as reported in Ref 5. The photons of the incident light inside the reactor in TiO_2/Ti free solutions measured employing potassium ferrioxalate actinometry[5] was 2.38×10^{-7} and 2.53×10^{-8} mol s^{-1} for the photoreactor and conventional three-electrode cell, respectively. All chemicals and solvents were of at least reagent grade and used without further purification. Deionized and double distilled water was used throughout the work.

Results and Discussion

The analysis of XPS shows that the composition of photoanodes is TiO_2 (hereafter denoted as TiO_2/Ti), and their crystal structure is rutile TiO_2 confirmed by XRD measurement. This is agreement with the results as reported in Ref 6.

Figure 1 shows a typical EIS plot for TiO_2/Ti electrode. It was found that only one capacitance arc and one peak can be observed on the EIS Nynquist plot and on the Bode plot, respectively, whether with or without illumination the working electrode. Bisquert *et al.*[7] found that the interfacial impedance of photoelectrode TiO_2 could be modeled by a charge transfer resistance (R_{ct}) in parallel to the constant phase angle element (Q). Liu Hong *et al.*[8] also explained that the R_{ct} of photoelectrodes could be calculated by the size of arc (at low frequency) in Niquist plot. By using the equivalent circuit as above mentioned to fit the impedance data, it was found the results were satisfactory (error less than 5%). The value of R_{ct} for TiO_2/Ti electrode formed at different oxidation temperature was shown in **Figure 2**. Without illumination, the value of R_{ct} was very large as implied by the large arc (an approximate line) in **Figure 1**. However, it can be found that photogeneration promoted a decrease of the charge-transfer resistance, as implied by the change of size of the low-frequency arcs in **Figure 1**. With illumination, the value of R_{ct} decreased with increasing the oxidation temperature from 300°C to 600°C and then increased when the temperature was higher than 600°C as indicated in **Figure 2**. However, the value of R_{ct} was very large (not shown) when the temperature was up to 800°C.

Figure 2 shows the relationship between the apparent first-order rate constant

K_{app} for the photoelectrocatalytic degradation of aniline and the oxidation temperature of TiO_2/Ti electrode. It is found that the value of K_{app} increased with increasing the oxidation temperature from 300°C to 600°C and then decreased sharply when the temperature higher than 600°C. In other words, the photodegradation rate of aniline is inversely proportional to R_{ct} of photocatalyst. This can be explained by that the the value of R_{ct} increases, the charges transfer across the interface between the semiconductor and solution becomes difficult, the recombination rate of photocarriers increases, thus the amount of photoactive species available reduces and the degradation rate of aniline decreases. In fact, as indicated in **Figure 3**, the photocurrent against the oxidation temperature for TiO_2/Ti electrode has the same rule as R_{ct} changing with oxidation temperature. In a word, the value of R_{ct} is smaller, the higher the degradation rate of pollutant is, namely, the value of charge-transfer resistance reflects the activity of photocatalyst. So it can be evaluated the photoelectrocatalytic activities of catalysts by the value of charge-transfer resistance. This is of interest due to at least not needing to carry out the experiments for the photodegradation of pollutants.

Figure 1 EIS plot obtained under potentiostatic control at anodic bias 0.0 V for TiO_2/Ti electrode (oxidation at 600°C). (a) Niquist plot; (b) Bode plot.

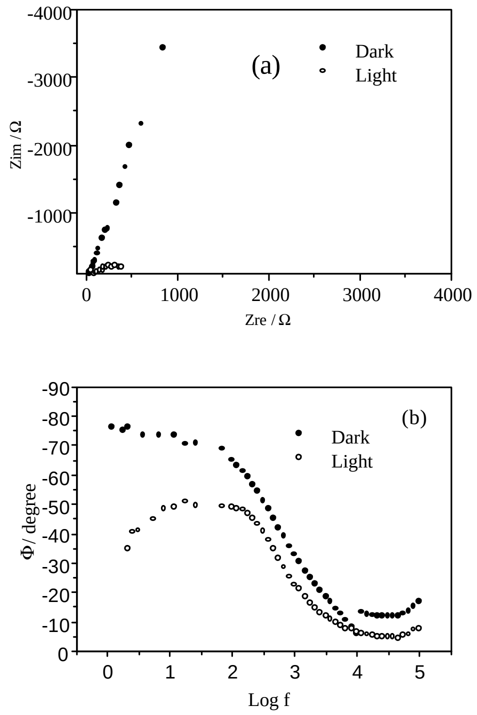
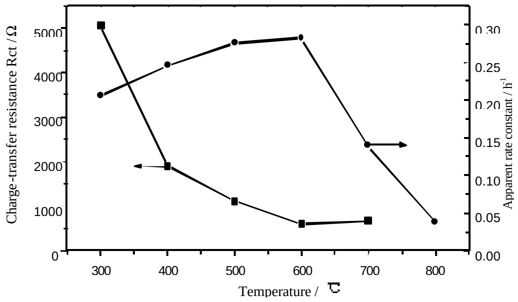
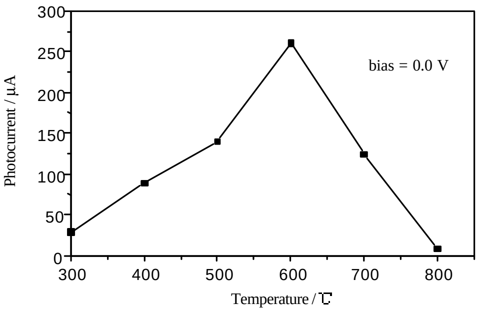


Figure 2 Charge transfer resistance and apparent rate constant for photoelectrocatalytic degradation of aniline against oxidation temperature of TiO_2/Ti electrodes



(EIS experiments see **Figure 1**; aniline degradation: C_0=10 mg dm^{-3}, pH6.0, anodic bias=0.5 V)

Figure 3 Steady-state photocurrent against oxidation temperature for TiO_2/Ti electrodes



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