

Evaluation of a High Conductivity TiO₂/Ag Fibrous Electrode with EIS Measurements

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Since the breakthrough of wet photoelectrochemical (PEC) solar cells by Grätzel and co-workers[1], a great deal of attention has been paid to nanoporous-nanocrystalline semiconductor electrodes especially for DSCs owing to their low cost. One of the key factors which influence the photoelectrocatalytic efficiency of these systems is the specific surface area of the electrode[2], which increases the amount of dye loading and light absorption. The other key factor is the electron transport efficiency[3]. This has led us to a structure consisting of Ag fibers deposited with TiO₂ nanoparticles. The photo-generated electrons are expected to be easily scavenged into the neighboring Ag and be transferred into the circuit through low conductivity Ag fibers.

Ag fibers were made by reduction of Ag complexes on cellulose fibers, followed by burning out the template. The formed membrane of Ag fibers was fixed on a stainless steel sheet using conductive carbon tape and was used as the substrate for electrophoretic deposition of TiO₂ nanoparticles. Colloidal suspension of 30-50 nm TiO₂ nanoparticles was synthesized by Sol-Gel method and TiO₂ photocatalyst layers were grown on the fibers by electrophoretic deposition of TiO₂ nanoparticles at current density of 500 $\mu\text{A}/\text{cm}^2$ and deposition time of 90 sec.

SEM and BSE images of TiO₂/Ag fibers show the presence of a uniform coating of TiO₂ on the fibers with the thickness of a few hundred nanometers. Electrochemical characterization of EIS Nyquist plots were performed in a three electrode system (Zahner elektrik IM6ex) using Ag/AgCl as the reference electrode, Pt as the counter electrode, and TiO₂ thin film or TiO₂/Ag membrane as the working electrode. Na₂SO₄ (0.5 M) aqueous solution was used as the electrolyte. Analysis of the EIS data was performed using ZView2 software. For illumination of samples in photoelectrochemical tests, an 8 W low pressure mercury lamp was employed. The intensity at the sample was 11 mW/cm^2 . The frequencies for EIS measurement were scanned from 10⁴ Hz down to 0.01 Hz. These characterizations were performed for both TiO₂/Ag fiber electrode and a TiO₂ thin film electrode. Figure 1 shows the results of EIS Nyquist plots of TiO₂/Ag fibers as well as the TiO₂ thin film on a stainless steel substrate in the dark and under UV illumination. EIS data were analyzed in terms of an equivalent circuit model. By fitting the impedance spectrum to a model of an equivalent electrical circuit, useful information on the electrical response of the working electrode can be obtained. The equivalent circuit shown in Figure 2 has been proved effective in simulating this structure [4]. Here, R_s is the solution resistance; R_f and CPE_f are resistance and capacitance of the film; R_{ct} is electron charge transfer resistance; and CPE_{dl} is the double-layer capacitance. Both C_f and C_{dl} were replaced with constant phase element (CPE) in the fitting procedure due to the nonideal capacitance response of these interfaces. The impedance of CPE is given by $Z_{CPE} = 1/C_0(j\omega)^m$, where C_0 is the admittance magnitude of CPE and m is an exponential term. Pure capacitance behavior is represented by $m=1$ [5].

Table 1 shows the results obtained by fitting the Nyquist plots with the equivalent circuit shown in Figure 2 in the absence and presence of UV light. As a simple comparison, the values of R_f for TiO₂/Ag fibers, are significantly smaller than those of TiO₂ thin films. This shows that the electrode resistivity for TiO₂/Ag fibers is lower, which can be attributed to thinner TiO₂ layer thickness. Also, the values of R_f under UV illumination, in both cases, are smaller than those in the dark. The difference in R_f in dark and under UV is a 5-fold difference for TiO₂ thin film samples and 20-fold for TiO₂/Ag fibers. If the 5-fold difference is attributed to higher concentration of photogenerated electrons and holes in TiO₂, the 20-fold difference in TiO₂/Ag fibers indicates that more efficient separation of electrons and holes has occurred[4, 5]. This might be due to smaller TiO₂ thickness and effective capture of electrons in the neighboring Ag. The efficient transfer of photogenerated electrons to Ag is expected to cause nonideality in the film

capacitance, in the presence of UV illumination. This is manifested by the considerable decrease of m_f for TiO_2/Ag fibers to about 0.6, under UV illumination. This value is about 0.8 for TiO_2 thin film samples. This also evidences better charge transfer efficiency for TiO_2/Ag fibers.

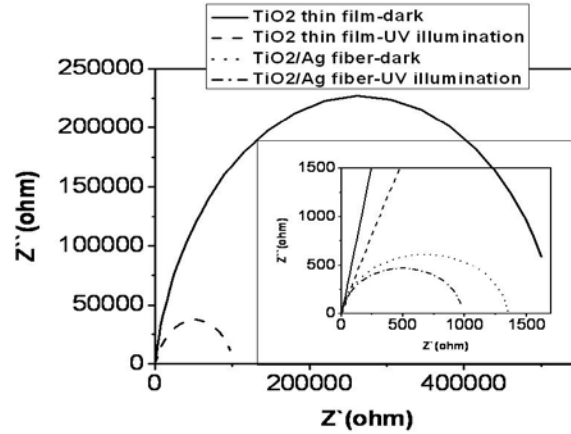


Figure 1. EIS Nyquist plots of the TiO_2/Ag fibers and TiO_2 thin film prepared in a similar condition. The low impedance part is magnified in the inset.

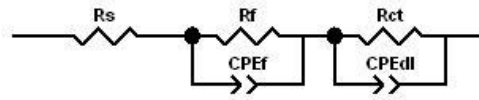


Figure 2. The equivalent circuit of TiO_2 thin film and Ag-TiO_2 fibers. R_s is electrolyte resistance; R_f and CPE_f , resistance and capacitance of film; R_{ct} , charge transfer resistance; CPE_{dl} , double layer capacitance.

Table 1. Fitted results of EIS spectra for TiO_2 thin film and TiO_2/Ag fiber.

paramet ers	TiO_2 thin film		TiO_2/Ag fiber	
	Dark	UV illumin ation	Dark	UV illumin ation
R_s (Ω)	4.24	4.19	4.22	4.29
R_f (Ω)	530 K	100.8 K	90	4.4
C_f (F)	3.45e-5	8.16e-5	0.019	0.019
m_f	0.9	0.81	0.94	0.6
R_{ct} (Ω)	2500	1696	1260	975.7
C_{dl} (F)	0.001	0.0004	0.002	0.015
m_{dl}	0.93	0.91	0.94	0.97

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