

In-situ Synchrotron XRD Study on TiO₂ Phase Evolution during Hydrolysis of TiCl₄

Chin-Jung Lin (林進榮), Chih-Kang Kuo (郭至剛), Wen-Yueh Yu (游文岳),
and Shu-Hua Chien (簡淑華)

Institute of Chemistry, Academia Sinica, Taipei, Taiwan
Department of Chemistry, National Taiwan University, Taipei, Taiwan

An efficient and cost-effective dye-sensitized solar cell (DSSC) based on TiO₂ film developed by O'Regan and Grätzel¹ has been extensively regarded as a promising alternative to silicon-based photovoltaic devices. A nanocrystalline TiO₂ particle layer is deposited onto a transparent conducting oxide (TCO) glass substrate as the anode of the DSSC. In this system, TiO₂ film should provide sufficient surface roughness for dye adsorption, serve as a expressway to facilitate the electron transport, and effectively confine the incident light to enhance the light-harvesting.

The conventional method to prepare TiO₂/TCO electrode requires sophisticated procedures for layer-by-layer TiO₂-coating. Herein, we report a facile process to fabricate TiO₂/TCO electrode by direct deposition of the TiO₂, which is obtained from hydrolysis of TiCl₄, onto the TCO. Moreover, the phases of deposited TiO₂ can be controlled by adjusting the concentration of H₂SO_{4(aq)}. This process is developed based on the in-situ synchrotron x-ray diffraction study on TiO₂ phase evolution during hydrolysis of TiCl₄ conducted on 17A1 and 01C2 beamlines.

Figures 1a and 1b show the in-situ XRD patterns of 0.6 M TiCl_{4(aq)} hydrolyzed in 5 M HNO_{3(aq)} at 100 °C with 0.0025 M H₂SO_{4(aq)} and 0.001 M H₂SO_{4(aq)}, respectively. As shown in Fig. 1, the formation time of anatase (A) and rutile (R) is determined by the concentration of H₂SO_{4(aq)}. When the concentration of H₂SO₄ is 0.0025 M, the diffraction peak of R emerges at time of 110 min, which is earlier than that of A at 175 min. While, when the concentration of H₂SO₄ is 0.001 M, the formation of A is advanced from 175 min to 110 min, whereas that of R is postponed from 110 min to 120 min. These results reveal that the formation time of A and R in the TiCl₄/HNO₃ aqueous system can be well-controlled by adjusting the the concentration of H₂SO_{4(aq)}.

We choose the later case, *i.e.*, anatase phase emerges before rutile phase forms, to fabricate the TiO₂/TCO electrode. Such bilayered microstructure is adopted to utilize smaller anatase particles to adsorb more dye molecules and larger rutile particles to scatter incident light. The dye used in this study is N719. The detailed experimental procedures of cell assembly and photovoltaic performance test are described in our previous study.²

Figure 2 shows the obtained photocurrent density-voltage characteristics. The energy conversion efficiency (η) is 4.11% with short-circuit photocurrent density (J_{SC}) of 10.3 mA cm⁻², open-circuit voltage (V_{OC}) of 660 mV and fill factor (FF) of 0.60. The result demonstrates that the facile process developed in this study is very promising to fabricate microstructured TiO₂/TCO electrode for effective and efficient photovoltaic devices.

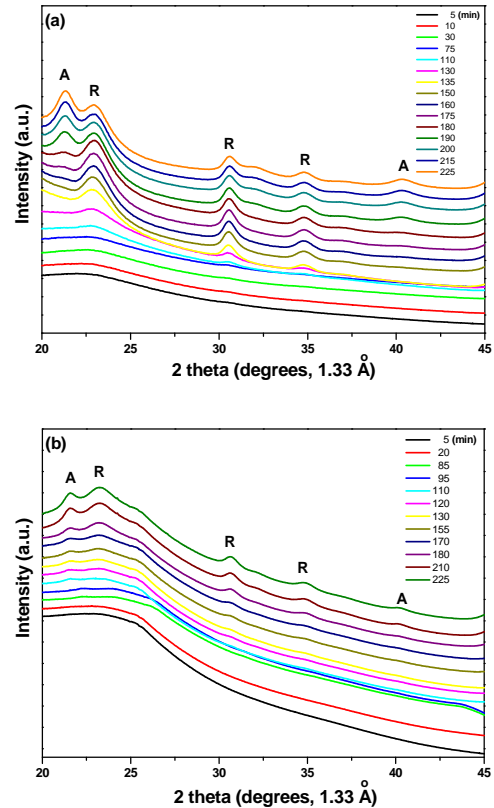


Fig. 1: In-situ synchrotron XRD studies of TiCl₄/HNO₃ aqueous system, where [TiCl₄] = 0.6 M, [HNO₃] = 5 M and [H₂SO₄] = 0.0025 M (a) and 0.001 M (b), at 100 °C. (A and R denote anatase and rutile, respectively)

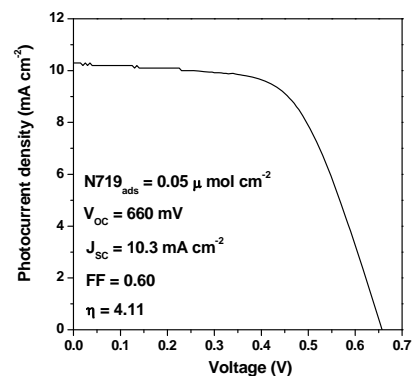


Fig. 2: Photocurrent density-voltage characteristics of dye-sensitized solar cells based on rutile/anatase/TCO under AM 1.5 simulated sunlight illumination.

- [1] B. O'Regan and M. Grätzel, *Nature* **353**, 737 (1991).
[2] C. J. Lin, W. Y. Yu, and S. H. Chien, *Appl. Phys. Lett.* **91**, 233120 (2007).