Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2018

Supporting Information

Oxidized Ti_3C_2 MXene Nanosheets for Dye-Sensitized Solar Cells

Chunxiang Dall'Agnese[a,‡], *Yohan Dall'Agnese*[a,b,‡], *Babak Anasori*[c], *Wataru Sugimoto*[a,b], *Shogo Mori*[a,b]*

[a] Division of Chemistry and Materials, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan

[b] Center for Energy and Environmental of Science, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

[c] A. J. Drexel Nanomaterials Institute, Materials Science and Engineering Department, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, USA

Corresponding Author

*E-mail: shogmori@shinshu-u.ac.jp

Experimental Section

Ti_3C_2 nanosheets were synthesized by selectively etching the aluminum layers out of the Ti_3AlC_2 MAX phase in a 6M HCl/LiF solution at 35°C for 24 h, followed by 1 h ultrasonication in ultrapure water, as described elsewhere[1]. Highly concentrated viscous Ti_3C_2 paste was obtained by centrifugation at 15000 rpm for 30 min.

Prior to use the FTO glass substrates, they were first cleaned with neutral detergent solution using an ultrasonic bath for 15 min and then with distilled water for another 15 min, followed by rinsing with ethanol, and then UV/O_3 irradiation for 25 min. MXene paste was coated onto

FTO by doctor-blade method, using a clean glass pipette and tape to control the thickness. Before the complete drying of the film at room temperature, we set the apparent surface area to 0.16 cm^2 (0.4 cm x 0.4 cm). Reference TiO_2 electrodes were also prepared by the same method but commercially available TiO_2 paste (DSL-18NR-T, Dyesol) was used, followed by sintering at 450°C for 30 min. The apparent surface area of TiO_2 electrodes was 0.25 cm^2 (0.5 cm x 0.5 cm). Then the TiO_2 electrodes were annealed at 450°C for 30 min, and once cooled down to 100°C, they were dipped into an ethanol and *tert*-butyl alcohol (volume ratio 1:1) mixed solution of the Ru-complex sensitizer N719 at a concentration of 0.3 mM.

Ti_3C_2-coated FTO electrodes were oxidized in air at different temperatures from 150 ^{o}C to 550 ^{o}C. Then they were cooled down to 100^{o}C followed by immersion into the same dye solution or used without dye adsorption for other characterizations. After soaking oxidized Ti_3C_2-coated FTO or TiO_2 electrodes into the dye solution for 18 h at room temperature in the dark, the dye-adsorbed Ti_3C_2 electrodes were rinsed with acetonitrile and the surrounding photoactive area was cleaned with ethanol using cotton swabs. Then dye-adsorbed Ti_3C_2 or TiO_2 electrodes were placed onto a Pt-sputtered FTO-glass substrate (sputtered for 45 seconds twice), and they were sealed with thermal adhesive film (Himilan, Dupont-Mitsui) by heating at 120 °C on a hot plate. The electrolyte was sandwiched between dye-adsorbed Ti_3C_2 or TiO_2 electrodes and the Pt electrodes by injection from the two holes drilled in the back of Pt electrodes. The holes were also sealed with Himilan films and clean glasses. The electrolyte used in this work consists of 0.1 M LiI, 0.05M I_2, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI), and 0.5 M 4-*tert*-butylpyridine (*t*BP) in dehydrated acetonitrile.

The thickness of Ti_3C_2 or TiO_2 films were measured by a surface profilometer (Stylus profiler, Dektak 6M). Photocurrent-voltage (*I*-*V*) characteristics were measured using one sun conditions (AM1.5, 100 mW cm^2) simulator (YSS-100A, Yamashita Denso) with a mask with 0.0900 cm^2 as the aperture area on the top of the cells. Incident photon-to-current conversion efficiency (IPCE) spectra were measured with a monochromator (SM-25A, Bunko Keiki, Japan).

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed using a thermobalance (Rigaku Thermo plus TG8120) with Al pans under dry air flow rate of 10 ml/min and a heating rate of 2 °C/min from room temperature to 500 °C. X-ray diffraction (XRD) patterns were collected by a Bragg-Brentano-type diffractometer (Rigaku Rint 2500) using a Cu Kα radiation (λ=1.5406 Å) in the range 2θ = 3–60° with a 4 seconds step of 0.02°. Field emission scanning electron microscope (SEM; Hitachi S-5000) and transmission electron microscope (TEM; JEOL JEM-2010) was used to investigate the morphology and structure of the electrodes.

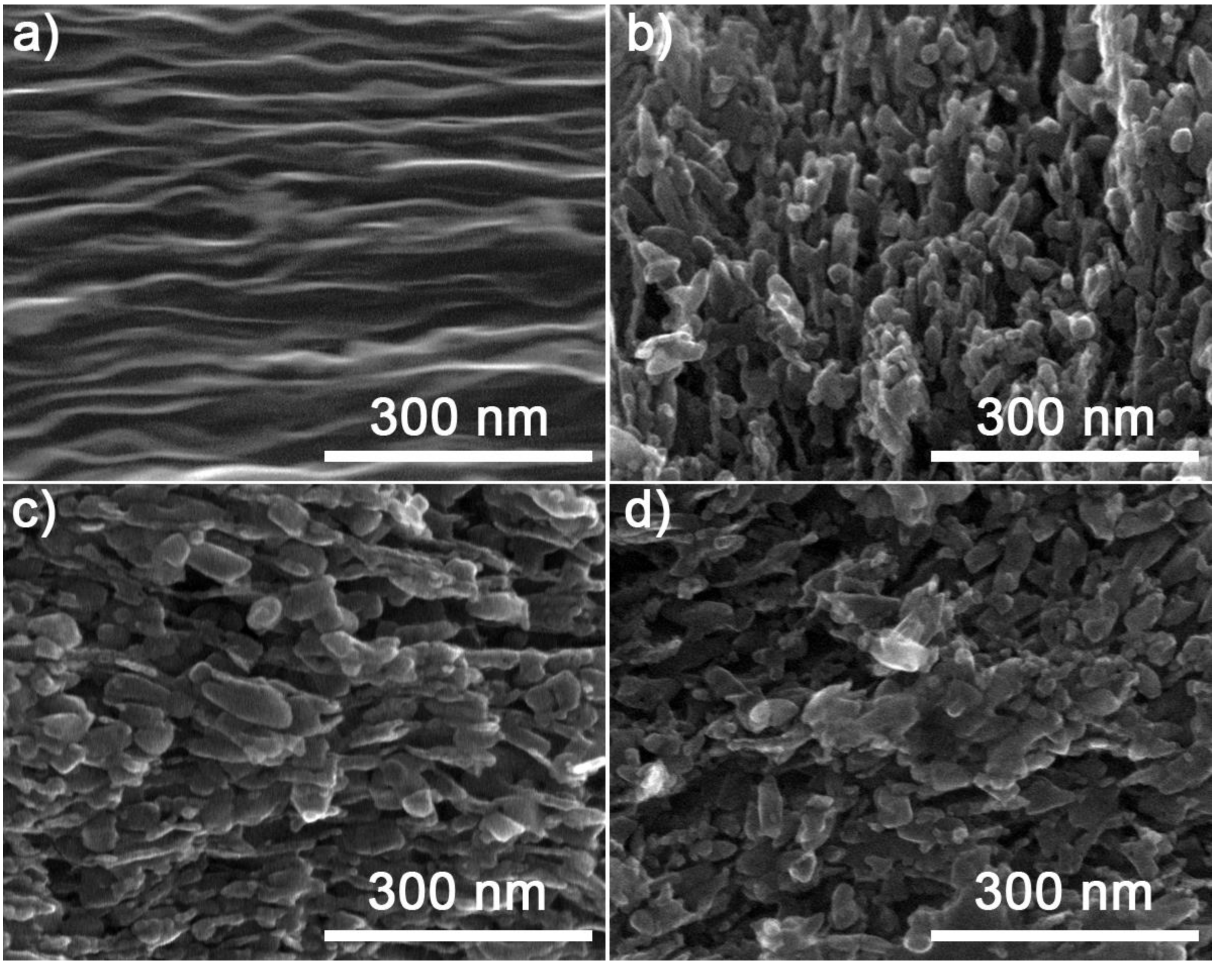

Figure S1. FE-SEM images of coated Ti_3C_2 film dried at room temperature (a), treated at 450°C for 80 min (b), at 500°C for 30 min (c) and at 550°C for 30 min (d).

Reference

1. M. Ghidiu, M. R. Lukatskaya, M.-Q. Zhao, Y. Gogotsi and M. W. Barsoum, *Nature*, 2014, **516**, 78-81.