Supporting Information

3-Dimensional TiO_2 Nanostructure Supports and Their Improved Electrochemical Properties in Methanol Electrooxidation

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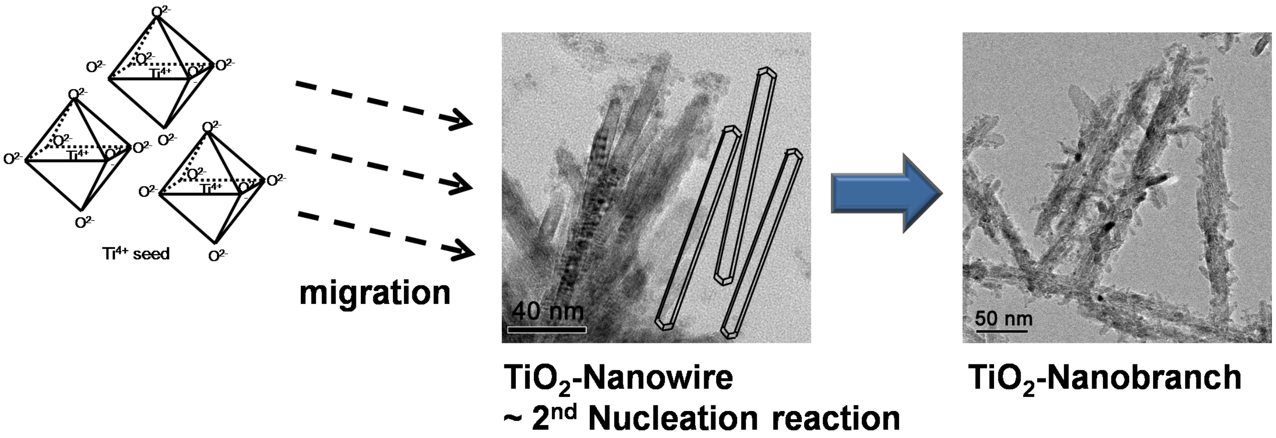
Experimental procedure

Synthesis of TiO_2 nanobranch supports. For the TiO_2-nanowire as seeds (TiO_2-NW), titanium (IV) isopropoxide (TTIP (97%), Aldrich Chemicals) was dropped in 10 M hydrochloric acid (HCl (35%), Aldrich Chemicals) with constant stirring at 25 ^{o}C for 1 h and then kept at 120 ^{o}C for 24 h. After the hydrothermal process, the resulting precipitates were cooled to room temperature and washed several times with ethanol and distilled water. The TiO_2-nanobranch as support material (TiO_2-NB) was synthesized by means of a seeding method with TiO_2-nanowires as seeds. The seed-solution (12 wt%) containing TiO_2-nanowires was injected in 0.5 M HCl with constant stirring at 25 ^{o}C and then kept constant for 15 min. After that, TTIP as precursor was dropped in mixture solution and kept constant for 1 h and kept at 95 ^{o}C for 4 h. The resulting precipitates were cooled to 25 ^{o}C, washed several times with ethanol and distilled water, and dried at 50 ^{o}C drying oven. The white TiO_2 powders were obtained after drying.

Preparation of TiO_2-nanobranch supported Pt catalyst.

The TiO_2-nanobranch supported Pt (40 wt.%) catalyst (Pt/TiO_2-nanobranch) was prepared by reducing Pt salt in ethylene-glycol (EG) solution. A solution of 2 mM H_2PtCl_6 was dissolved in 50 ml of EG and TiO_2-nanobranch as support materials and was controlled to pH 8 using 0.1 M NaOH solutions. All chemicals used were of analytical grade. The solution was rapidly raised at 180 ^{o}C and was kept for 30min at 180 ^{o}C until H_2PtCl_6 was completely reduced by EG. The resulting colloid solution was cooled at room temperature, washed with water and then with ethanol several times to remove ethylene-glycol and impurity materials.

Characterizations. For the structure analysis of the catalysts, X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray diffractometer with Cu K_α ($\lambda = 0.15418$ nm) source with a Ni filter. The source was operated at 40 kV and 100 mA. The 2θ angular scan from 20° to 80° was explored at a scan rate of 5° min^{-1}. For all the XRD measurement, the resolution in the scans was kept at 0.02°. The morphology and size distribution of the catalysts were characterized by field-emission transmission electron microscopy (FE-TEM) using a Tecnai G2 F30 system operating at 300 kV. TEM samples were prepared by placing drops of catalyst suspension dispersed in ethanol on a carbon-coated copper grid. The surface area of the TiO_2 supprots was analyzed by a nitrogen adsorption measurement (Micromeritics ASAP 2020 adsorption analyzer). Electrochemical properties of the catalysts were measured in a three-electrode cell at 25 ^{o}C using a potentiostat (Eco Chemie, AUTOLAB). A Pt wire and Ag/AgCl (in saturated KCl) were used as a counter and reference electrode, respectively. The glassy carbon electrode as a working electrode was polished with 1, 0.3, and 0.05 μm Al_2O_3 paste and then washed in deionized water. The catalyst ink was prepared by ultrasonically dispersing catalyst powders in an appropriate amount of Millipore water. The catalyst ink was dropped onto a glassy carbon working electrode. After drying in 50 ^{o}C oven, total loading of catalyst was 20 μg cm^{-2}. To clearly characterize electrochemical properties, electrochemical treatment was carried out between -0.2 and +1.0 V (30 CV cycles) with a scan rate of 50 mV s^{-1}. To compare electrochemical properties and catalytic activity of the catalysts, cyclic voltammograms (CVs) were obtained between -0.2 to +1.0 V in 0.1 M $HClO_4$ and 0.1 M $HClO_4$ + 2 M CH_3OH, respectively. For an accelerated stability test, the catalysts were kept between -0.2 to +1.0 V (total 400 cycles) in 0.1 M $HClO_4$ and then CVs were obtained in 0.1 M $HClO_4$ + 2 M CH_3OH.



Scheme S1 Formation mechanism of TiO_2-nanobranch supports using a seeding method with TiO_2-nanowires as seeds.

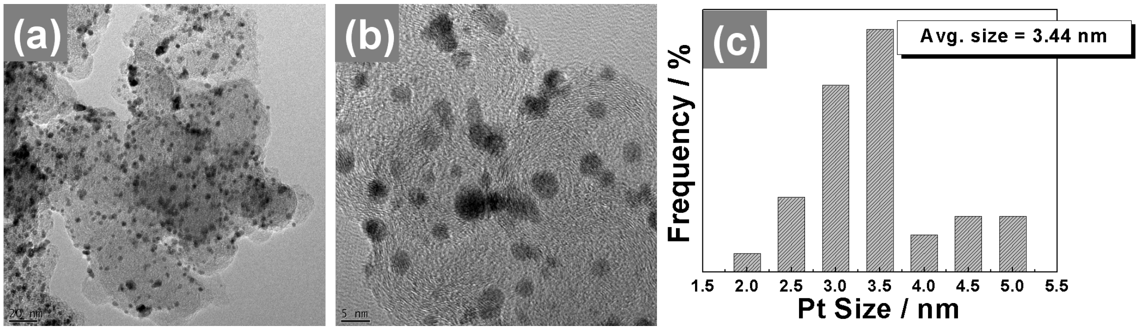


Fig. S1 (a) TEM, (b) HR-TEM images, and (c) the size distribution of Pt/C before stability test.