

Supporting Information

A new approach to surface activation of porous nanomaterials using non-thermal helium atmospheric pressure plasma jet treatment

Farkfun Duriyasart, Masataka Ohtani, Jun-Seok Oh, Akimitsu Hatta, and Kazuya Kobiro**

F. Duriyasart, Dr. M. Ohtani, Prof. K. Kobiro
School of Environmental Science and Engineering
Kochi University of Technology
185 Miyanokuchi, Tosayamada, Kochi, 782-8502, Japan
E-mail: ohtani.masataka@kochi-tech.ac.jp, kobiro.kazuya@kochi-tech.ac.jp

Dr. M. Ohtani, Prof. K. Kobiro
Laboratory for Structural Nanochemistry
Kochi University of Technology
185 Miyanokuchi, Tosayamada, Kochi, 782-8502, Japan

Dr. M. Ohtani, Prof. K. Kobiro
Research Center for Material Science and Engineering
Kochi University of Technology
185 Miyanokuchi, Tosayamada, Kochi, 782-8502, Japan

Dr. J.-S. Oh, Prof. A. Hatta
Research Center for Nanotechnology
Kochi University of Technology
185 Miyanokuchi, Tosayamada, Kochi, 782-8502, Japan

Dr. J.-S. Oh, Prof. A. Hatta
School of Systems Engineering
Kochi University of Technology
185 Miyanokuchi, Tosayamada, Kochi, 782-8502, Japan

Dr. J.-S. Oh
Faculty of Science and Engineering
Meijo University
1-501 Shiogamaguchi, Tempaku, Nagoya, 468-8502, Japan

Experimental Section

Materials: Methanol, ethanol, titanium tetraisopropoxide, formic acid, phthalic acid, methylene blue, triethylamine, and potassium chloride were purchased from Wako Pure Chemical Industries Co., Ltd. Commercial SiO₂ nanoparticles (Sciqas 1.0 μm) were received from Sakai Chemical Industry Co., Ltd. All chemicals were used as received without further treatment. Water purified by reverse osmosis was used throughout the experiments.

Synthesis of TiO₂ nanoassemblies: TiO₂ MARIMO, cheek-brush, and urchin-like assemblies were prepared using previously reported methods.^{1,2} Precursor solutions containing organic additives (0.5 mol L⁻¹) were prepared by mixing an aliquot of each organic additive with methanol (3.5 mL) using a Vortex mixer, followed by addition of titanium tetraisopropoxide (105 μL , 0.353 mmol). The precursor solution was transferred to an SUS-316 stain-less-steel tubular reactor with an inner volume of 10 mL. The reactor was sealed with a screw cap and heated at a rate of 5.4 °C min⁻¹ to 300 °C, and then this temperature was maintained for 10 min. The reaction was quenched by placing the reactor in an ice-water bucket. The obtained mixture was centrifuged and washed with methanol; this procedure was repeated three times. The final suspended mixture was completely dried under vacuum and a powdery product was obtained.

Plasma treatment: The system consisted of a 15 cm glass tube and an external electrode in a cylindrical dielectric barrier discharge configuration.³ The nozzle exit was tapered from an inner diameter of 4 mm to 800 μm at the orifice. The emerging plasma jet was used to treat the catalysts. Helium gas was fed through the tube at a flow rate of 1.62 L min⁻¹. A sinusoidal high voltage of 10 kV at a fixed frequency of 50 kHz was applied to sustain the helium plasma. The length of the emerging plasma jet was 1 cm under the plasma operating conditions. Catalyst powder was placed downstream of the plasma jet. The working distance from the nozzle tip to the sample surface and the exposures time were varied.

Nanoassembly characterization: The morphologies of the obtained materials were observed using scanning electron microscopy (SEM, JEOL JSM-7300F) and transmission electron microscopy (TEM, JEOL JEM-2100F). The crystalline phase was identified by X-ray diffraction (XRD, Cu K α radiation, Rigaku SmartLab). Mass spectra were obtained using laser

desorption/ionization time-of-flight mass spectrometry (LDI-TOF MS, Bruker Autoflex speed TOF/TOF).

Evaluation of photocatalytic activity: The photocatalytic activities of the prepared and plasma-treated TiO₂ nanosphere assemblies were evaluated by methylene blue degradation. In these reactions, 5 mg of TiO₂ MARIMO assemblies were added to well-mixed aqueous solutions containing 10 mg L⁻¹ of methylene blue. The suspensions were stirred for 1 h in the dark to achieve an adsorption/desorption equilibrium. The suspensions were irradiated with UV light (300 W, Xenon Light Source MAX-301, Asahi Spectra Co., Ltd.) at room temperature. UV-Vis spectroscopy was used to measure the absorbance of the solution at given time intervals.⁴

Measurement of photocurrent: The photocurrent-time was measured using an electro-chemical analyzer (ECstat-300, EC Frontier Co., Ltd.) in a standard three-compartment cell consisting of a working electrode, a Pt-coil counter electrode, and a Ag/AgCl reference electrode. The working electrodes were made by drop casting TiO₂ MARIMO assemblies onto ITO glasses. Suspensions of 7 mg TiO₂ MARIMO assemblies in 1 mL methanol were prepared, and then 10 µL of these suspensions were dropped on-to 1 cm × 1 cm areas of the ITO glass electrodes (1 cm × 5 cm). The electrodes were soaked in an electrolyte containing 0.1 mol L⁻¹ KCl and 0.1 mol L⁻¹ triethylamine in water during the measurements, which were performed under UV light (300 W, Xenon Light Source MAX-301, Asahi Spectra Co., Ltd.) irradiation.

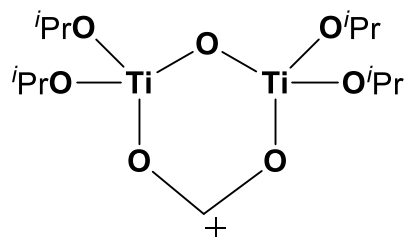


Fig. S1 A plausible structure of the contaminant.

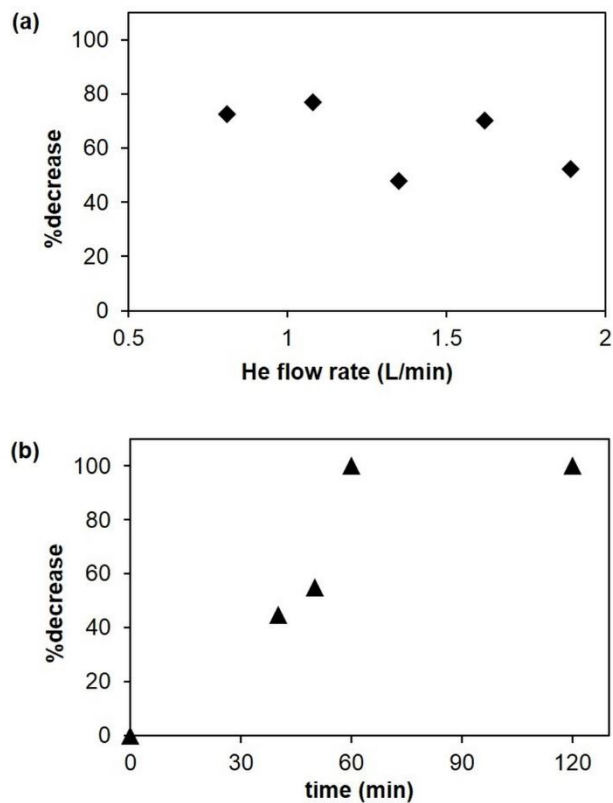


Fig. S2 Plots of percentage decrease in the intensity of the main peak ($m/z = 393$) against (a) helium flow rate and (b) treatment time.

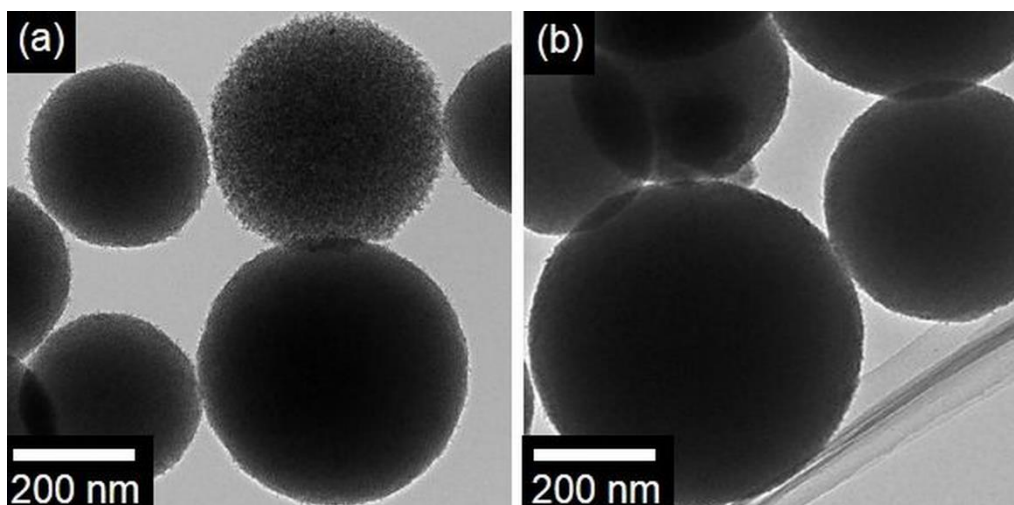


Fig. S3 TEM images of TiO_2 MARIMO assemblies (a) before APPJ treatment and (b) after APPJ treatment for 1 h at a helium flow rate of 1.62 L min^{-1} and a working distance of 2 cm.

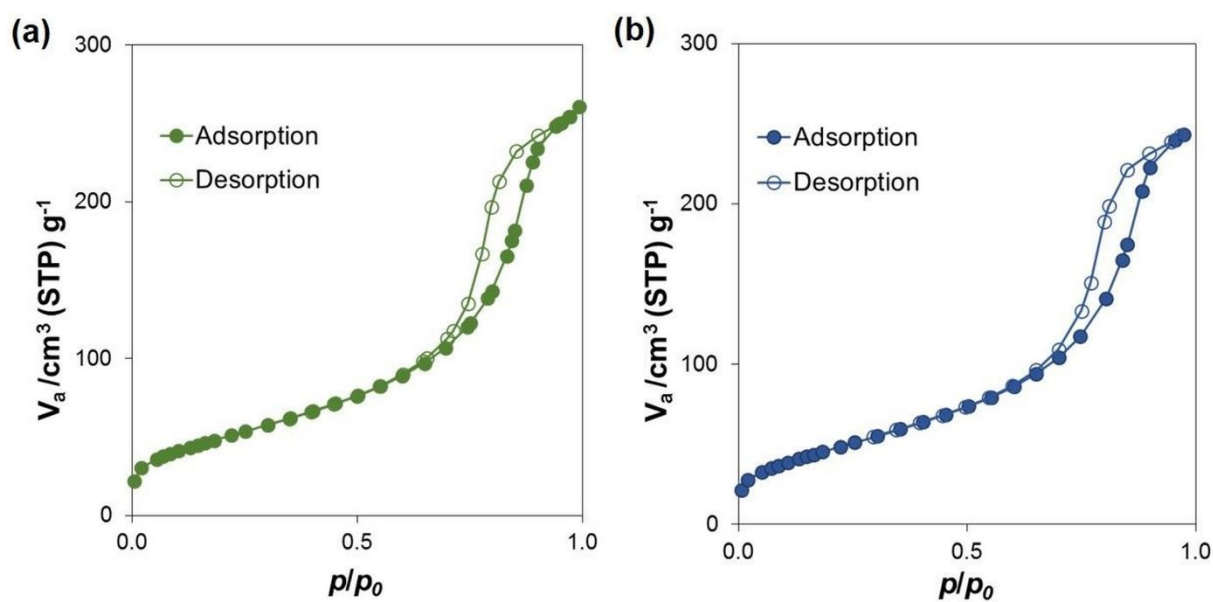


Fig. S4 N_2 adsorption/desorption isotherms of solid TiO_2 MARIMO assemblies (a) before APPJ treatment and (b) after APPJ treatment for 1 h at a helium flow rate of 1.62 L min^{-1} and a working distance of 2 cm.

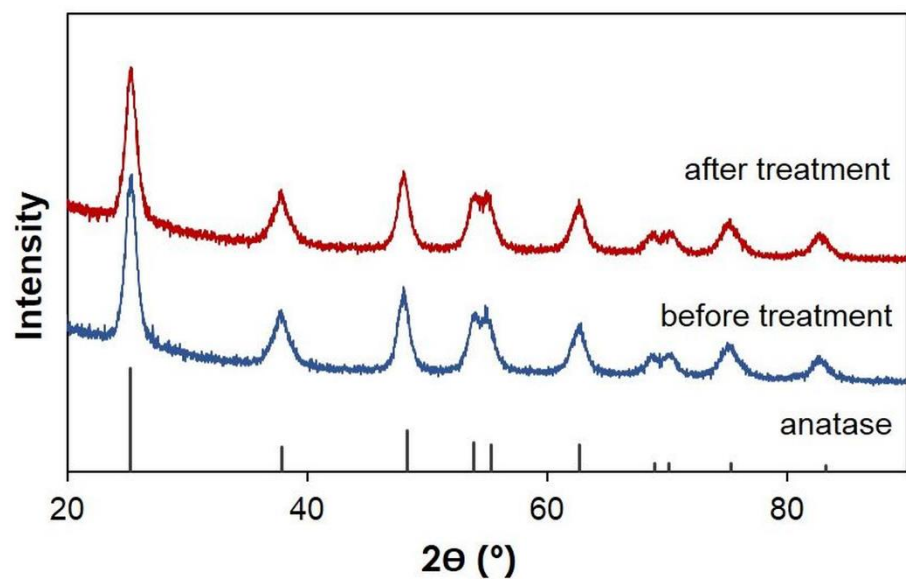


Fig. S5 XRD patterns of solid TiO₂ MARIMO assemblies before and after APPJ treatment for 1 h at helium flow rate of 1.62 L min⁻¹ and a working distance of 2 cm.

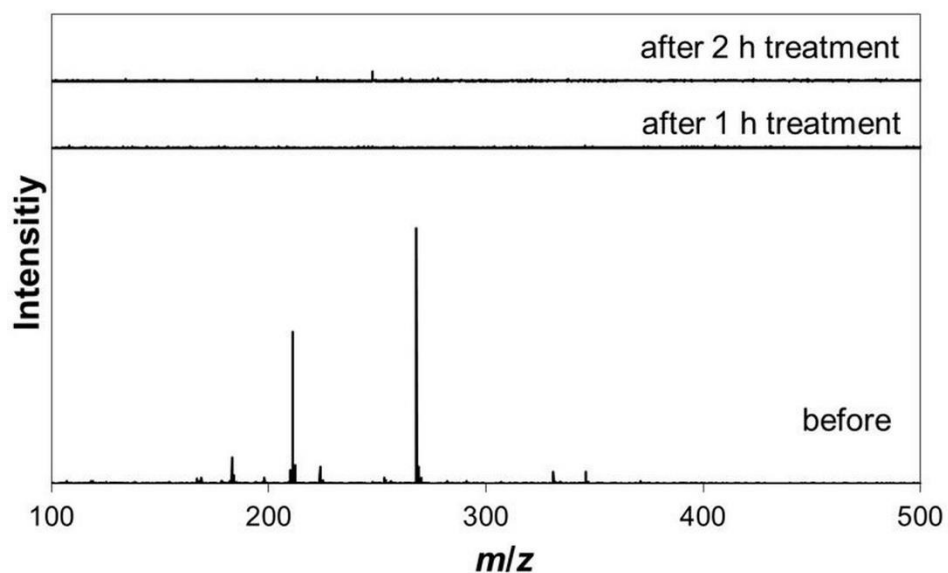


Fig. S6 Mass spectrum of commercial SiO₂ nanoparticles before APPJ treatment compared with those obtained after APPJ treatment for 1 h and 2 h.

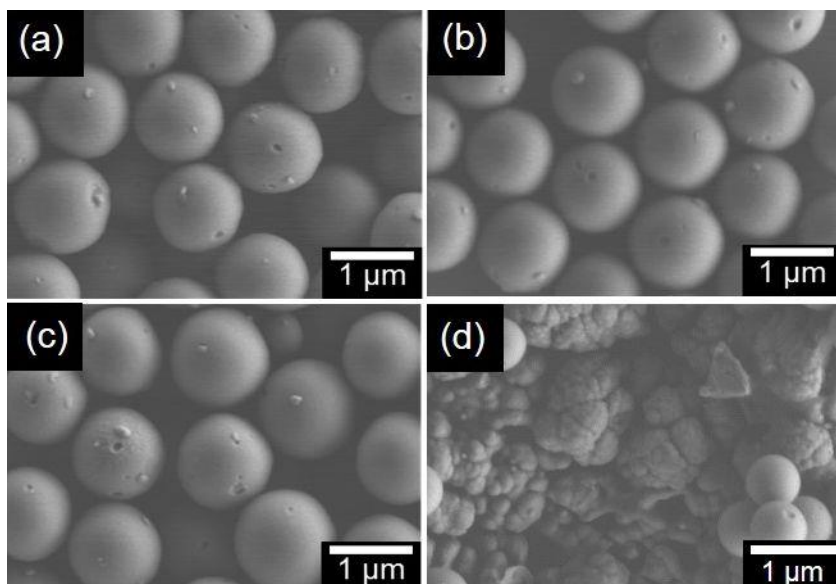


Fig. S7 SEM images of commercial SiO₂ nanoparticles (a) before APPJ treatment, after APPJ treatment at a helium flow rate of 1.62 L min⁻¹ and a 2 cm for (b) 1 h and (c) 2 h, and (d) with a working distance of 1 cm for 1 h.

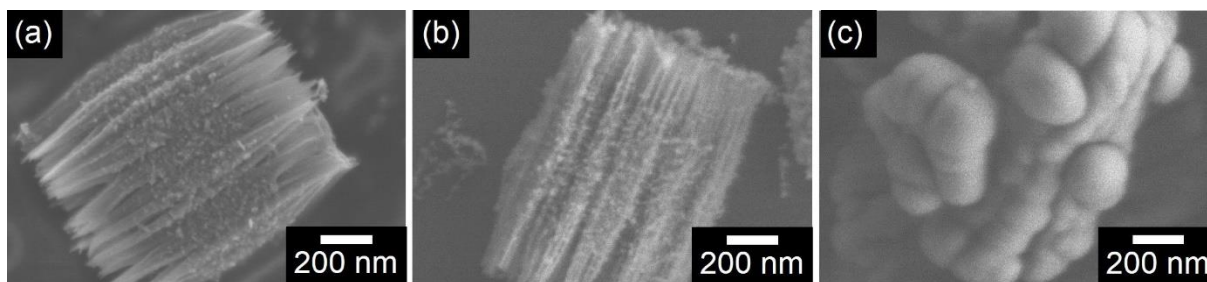


Fig. S8 SEM images of cheek-brush TiO₂ assemblies (a) without APPJ treatment and after APPJ treatment at a helium flow rate of 1.62 L min⁻¹ for (b) 1 h at a working distance of 2 cm and (c) 20 min at a working distance of 1 cm.

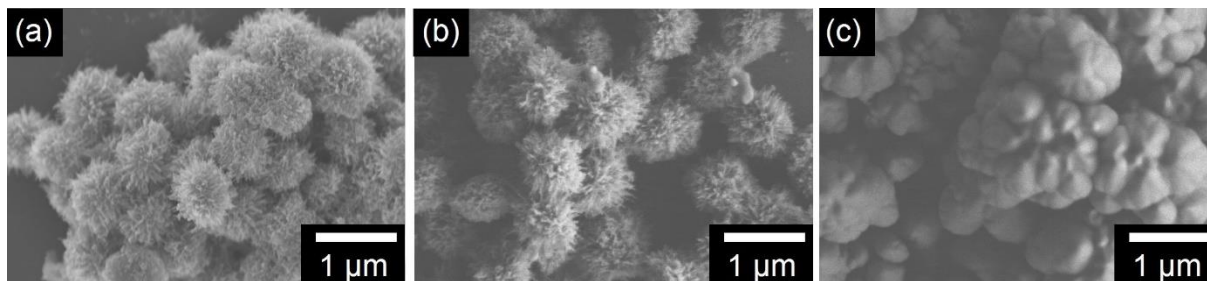


Fig. S9 SEM images of urchin-like TiO₂ assemblies (a) without APPJ treatment and after APPJ treatment at a helium flow rate of 1.62 L min⁻¹ for (b) 1 h at a working distance of 2 cm and (c) 20 min at a working distance of 1 cm.

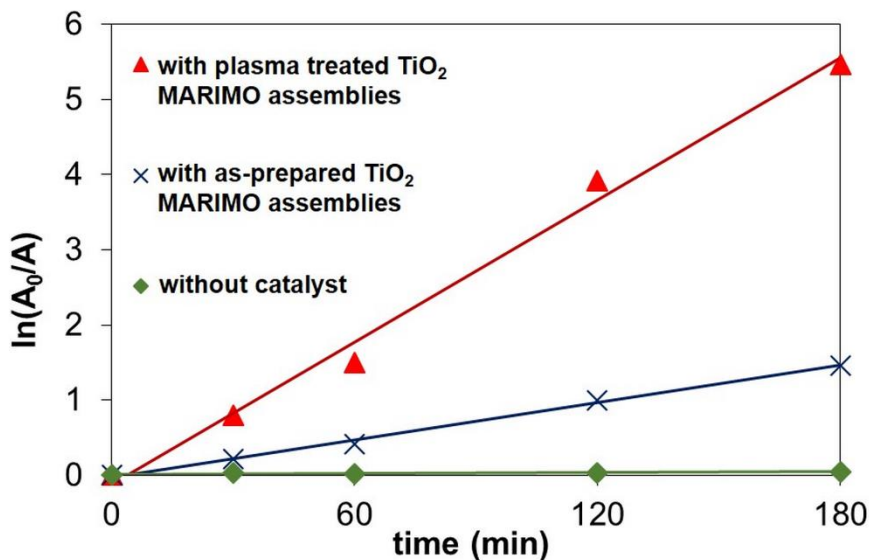


Fig. S10 A logarithmic plot of the photodegradation of methylene blue using as-prepared and APPJ-treated TiO₂ MARIMO assemblies.

References

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