

Supplementary Information

Fluorescence imaging of hydroxyl radicals at superhydrophobic gold flower-like surface in photocatalytic system

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1. Experimental

Chemicals and materials

1-Octadecanethiol (ODT) and sodium molybdenum oxide dihydrate were purchased from Alfa Aesar. Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%), homovanillic acid (3-methoxy-4-hydroxyphenylacetic acid, HVA), horseradish peroxidase (POD), 2,2-Azobis (2-amidinopropane) dihydrochloride (AAPH), and potassium superoxide (KO_2) were all purchased from Aldrich. Peroxynitrite was obtained from R&D Systems. An anatase TiO_2 sol (STS-21, 20 nm particle diameter) and TiO_2 nanoneedles (FT-2000, ~ 50 – 100 nm in width and ~ 3 – 5 μm in length) were obtained from Ishihara Sangyo Kaish. All other reagents were of analytical grade and used as received. All solutions were prepared with Milli-Q water. ITO-coated glass plates with a square resistance of ~ 10 – $20 \Omega \text{ cm}^{-2}$ were obtained from Nanbo (Shenzhen, China). Our experiments were operated at room temperature and the relative humidity was 60%, unless otherwise noted.

Preparation of gold flower-like nanostructures and TiO_2 -coated photomask

Gold flower-like nanostructures were electrodeposited onto an indium tin oxide (ITO)-coated glass plate ($1 \times 1 \text{ cm}^2$) from 40 mM HAuCl_4 solution at -0.08 V versus $\text{Ag}|\text{AgCl}$ (in saturated KCl) for 5 min. The TiO_2 -coated photomask was prepared as follows: the designed photomask ($1 \times 1 \text{ cm}^2$) was covered with TiO_2 sol by spin-coating method and then sintered at 723 K for 60 min, and the optimized thickness of TiO_2 film with high photocatalytic activity is $\sim 3 \mu\text{m}$.

Generation of free radicals

In selectivity test, superoxide anion (O_2^-) was chemically generated by ionization of potassium superoxide (KO_2) in aqueous solution.^{S1} Singlet oxygen (1O_2) was generated as a product of the disproportionation of H_2O_2 in basic aqueous solution catalyzed by molybdate ions.^{S2} Alkyl peroxy radical ($ROO\cdot$) was generated through thermolysis of 2,2-Azobis (2-amidinopropane) dihydrochloride (AAPH) in aqueous solution under elevated temperature (310 K).^{S3} Peroxynitrite ($ONOO^-$) was obtained by diluting commercially available peroxynitrite solution with a strongly basic solution (0.1 M NaOH). Hydroxyl radical ($HO\cdot$) was generated by the Fenton Chemistry. Their influences on the water contact angle of ODT-modified gold film were all obtained after 20 min reaction time.

Staining of the hydrophilic region by rhodamine B

The hydrophilic region of the obtained superhydrophobic|philic microband was stained by dropping 0.1 ml of 50 mM rhodamine B aqueous solution on gold film for 10 s and then fluorescence imaged after throwing off the droplet.

Apparatus and measurements

Fluorescence micrographs were acquired on a Nikon Model Eclipse TE300 inverted microscopy. Scanning electron microscopy (SEM) images were collected with a Hitachi Model S-4500 instrument. The X-ray diffraction (XRD) measurements were carried out via a BRUKER D8 diffractometer (Bruker, German), using $Cu\ K\alpha_1$ radiation ($\lambda = 1.54\ \text{\AA}$) over the 2θ range of 10° to 70° . X-ray photoelectron spectroscopy (XPS) (Model PHI 5000) was used to characterize the modification and decomposition of ODT. The water contact angle was measured by a contact angle meter (Model JC 2000A, Shanghai, China). Fluorescence spectrum was determined with a Perkin-Elmer LS-55

spectrophotometer, and the excitation and emission slits were both 5 nm. A home-made photocatalyst flow cell was prepared as follows: A TiO₂-coated ITO glass plate and a bare glass plate were faced to each other with a small intervening gap (~50 μm), and the sides were sealed with glass plates and silicone except for inlet and outlet tubes. The TiO₂ side was exposed to UV light (70 mW cm⁻²) with a cold mirror filter attached. The purified air passed through the photocatalyst cell (2 ml min⁻¹) and the out-flowing gas from the irradiated cell was flushed through a 3 ml optimized collecting solution containing 0.1 M tris buffer (pH 8.50), 2.5 mM homovanillic acid (3-methoxy-4-hydroxyphenylacetic acid, HVA), and 2.0 U ml⁻¹ horseradish peroxidase (POD) for a reaction time of 30 min at 298 K. The relative humidity was 60%, and the room temperature was 298 K, unless otherwise noted.

2. Dependence of the width of fluorescence microbands on irradiation time

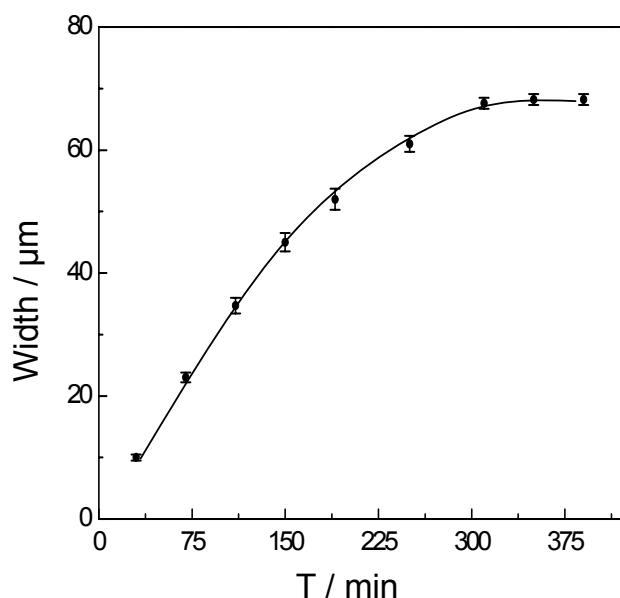


Fig. S1 Dependence of the average width of fluorescence microbands on time of exposure of the ODT-modified gold flower-like film to UV light (70 mW cm⁻²). The error bars were obtained from a set of ODT-modified gold films.

3. Selectivity of the present assaying method

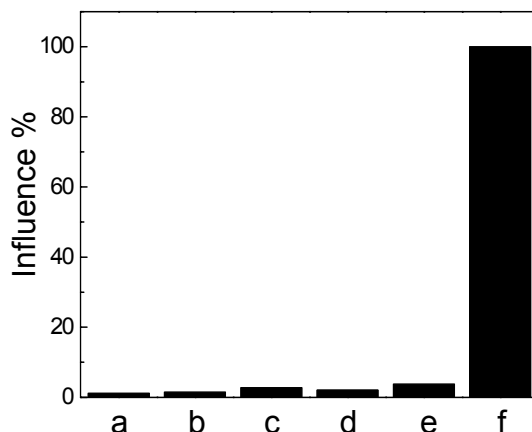
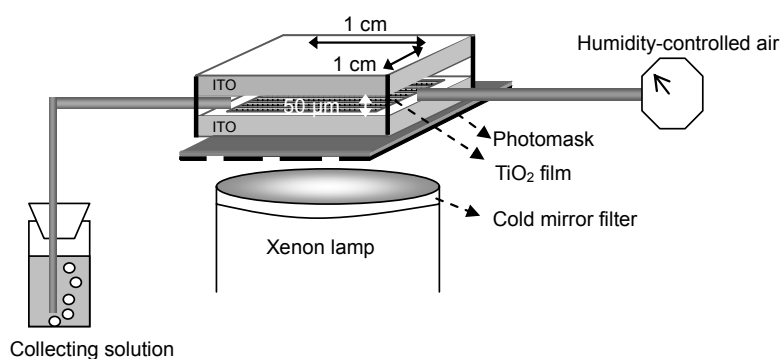


Fig. S2 Influence on the water contact angle decrease obtained at the ODT modified gold flower-like film imposed by (a) H_2O_2 , (b) O_2^- , (c) $^1\text{O}_2$, (d) ONOO^- , (e) ROO^\cdot , and (f) HO^\cdot . The influence by each species was the average value obtained from three independent experiments.

4. Home-made photocatalyst flow cell for the determination of H_2O_2

Scheme S1. Schematic illustration of the experimental device for the detection of H_2O_2 released from TiO_2 to air.



References

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