

In-Situ Room Temperature Synthesis of Polyaniline-Gold-Titanium(IV) Dioxide Heteronanojunction System

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Experimental details

Aniline polymerization on Au/TiO₂

A paste containing anatase TiO₂ particles (PST-18NR, Nikki Syokubai Kasei) was coated on ITO film-coated glass substrates (< 10 Ω/□, Geomatec) by a squeegee method, and the sample was heated in air at 773 K for 1 h to form mp-TiO₂ film-coated electrode. Au particles were loaded on anatase TiO₂ particles (A-100, Ishihara Sangyo) or mp-TiO₂ (Au/mp-TiO₂) by the DP method using HAuCl₄ as a starting material.^[16] Au/TiO₂ (1 g) or Au/mp-TiO₂ (25 mm × 30 mm) was added to a 0.5 mol dm⁻³ H₂SO₄ solution of 0.1 mol dm⁻³ aniline and H₂O₂ (250 mL for Au/TiO₂ or 100 mL for Au/mp-TiO₂), and the suspension was stirred at 298 K in the dark. After reaction, the

particles were recovered by centrifugation, and the resulting particles were washed with H₂O three times to be dried under vacuum.

Sample characterization

TEM observation was carried out at an applied voltage of 300 kV (JEM-3010, JEOL). The loading amount of Au was quantified by inductively coupled plasma spectroscopy (ICPS-7500, Shimadzu). The amount of PANI was determined by TG-DTA (DTG-60, Shimadzu), in which the samples were heated up to 1073 K at a rate of 20 K min⁻¹ in air. UV-Vis diffuse reflectance spectra were recorded on a Hitachi U-4000 spectrophotometer. The spectra were converted to the absorption spectra by using the Kubelka-Munk function. X-ray photoelectron spectroscopic (XPS) measurements were performed using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al K_α X-ray source ($h\nu = 1486.6$ eV) operated at 15 kV and 10 mA. The take-off angle was 90°, and multiplex spectra were obtained for Au4f, C1s, N1s, and S2p photopeaks. All the binding energies were referenced with respect to the C_{1s} at 284.6 eV. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the samples were obtained with a JASCO FT/IR-470Plus spectrometer equipped with a diffuse reflectance attachment.

Photoluminescence measurements

One hundred mL of a solution of terephthalic acid (1×10^{-4} mol dm⁻³) and H₂SO₄ (0.5 mol dm⁻³) was prepared by diluting a mixture of a dimethylformamide solution of terephthalic acid and a H₂SO₄ solution with water. After 0.1 mL of H₂O₂ (10 mol dm⁻³), and then Au/TiO₂ (0.4 g) were added the solution, the suspension was stirred at 298 K. Photoluminescence spectra of the solutions were measured with an excitation wavelength of 315 nm at room temperature using a JASCO FP-6000 spectrofluorometer. For comparison, the spectra of the same solutions without Au/TiO₂ were also measured.

Electrochemical measurements

Cyclic voltammograms were measured in a $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution under deaerated conditions using PANI/Au/mpTiO₂ as working electrode in a regular three-electrode electrochemical cell using a galvanostat/potentiostat (HZ-5000, Hokuto Denko). Glassy carbon and Ag/AgCl were used as counter electrode and reference electrode, respectively.

Quantum chemical calculations

The quantum chemical calculations were performed based on density functional theory (DFT) at the B3LYP/6-31+G level as implemented in Gaussian09.

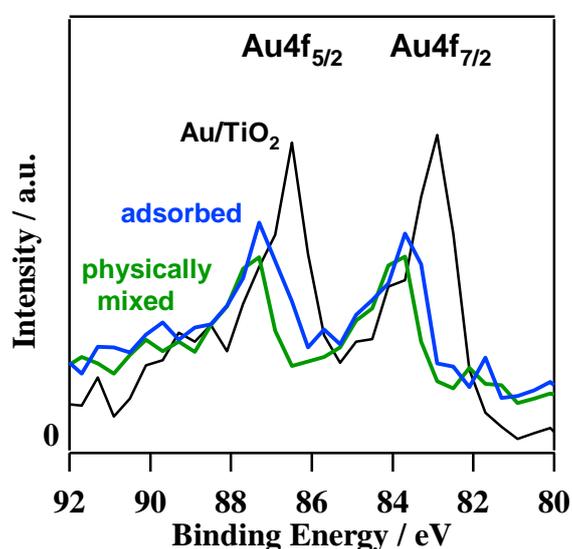


Fig. S1 XPS spectra of Au 4f of Au/TiO₂ samples with physically mixed (green) and adsorbed (blue) with authentic PANI and Au/TiO₂ (black).

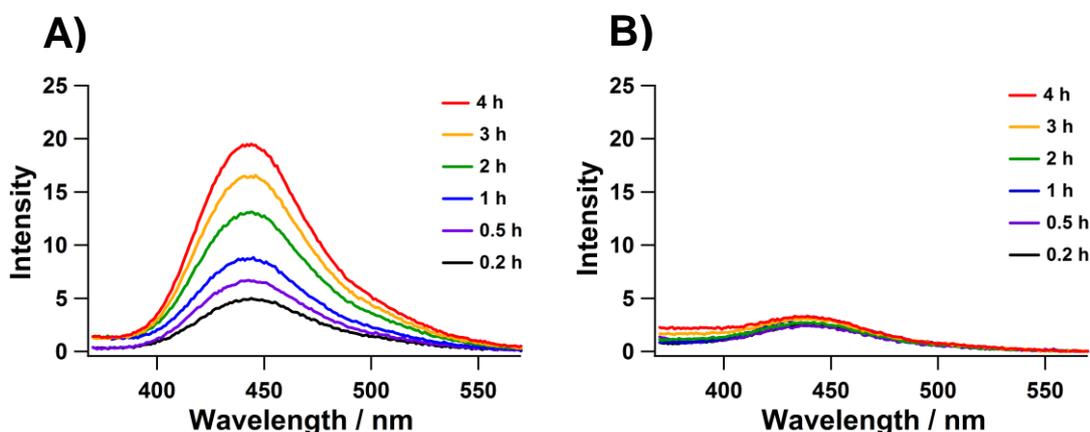


Fig. S2 Photoluminescence spectra of a H₂SO₄ solution containing H₂O₂ and terephthalic acid ($\sim 1 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence (A) and absence (B) of Au/TiO₂.

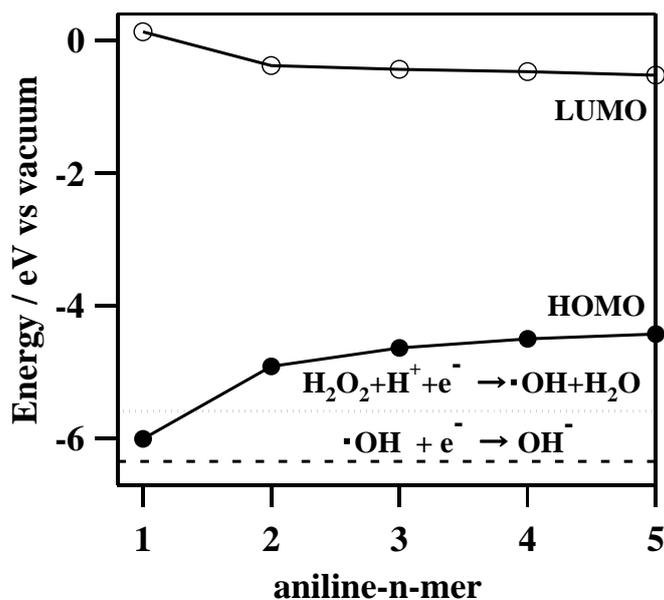


Fig. S3 HOMO energy of aniline n -mers as a function of n . The reduction potentials of H_2O_2 ($\text{H}_2\text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow \cdot\text{OH} + \text{H}_2\text{O}$) and $\cdot\text{OH}$ radical ($\cdot\text{OH} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$) were cited from Refs. 1 and 2, respectively. The standard hydrogen electrode potential was set -4.5 eV with respect to the vacuum level (Ref. 3)

References

- 1 *Denki Kagaku Binran*, Electrochemistry of Japan, Maruzen, Tokyo, 2000.
- 2 Y. Nosaka and A. Nosaka, *Nyumon Hikarisyokubai (Introduction to Photocatalysts)*, Tokyo Tosyo, Tokyo, 2004.
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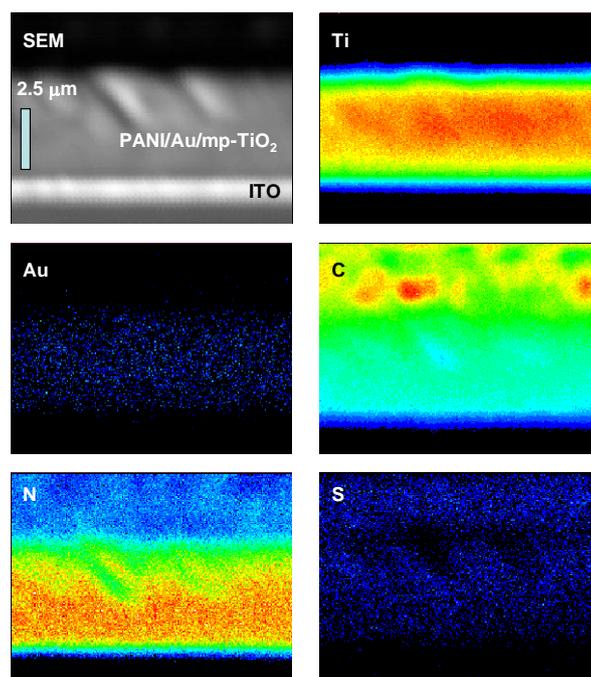


Fig. S4 SEM image, Ti, Au, C, N, S-elemental depth profiles for the cross-section for in-situ PANI/Au/mp-TiO₂.