

Electronic Supplementary Information

Active Control of Plasmon Coupling via Simple Electrochemical Surface Oxidation/Reduction of Au Nanoparticle Agglomerates

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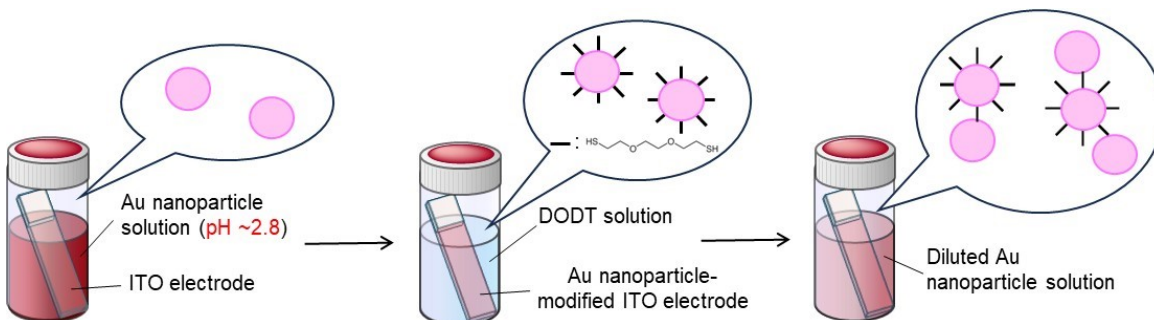
Experimental details

Materials

Tetrachloroaurate(III) tetrahydrate was purchased from Kishida Chemical. Trisodium citrate, concentrated sulfuric acid and potassium nitrate were commercially available from Fujifilm Wako Pure Chemical Corporation. 3,6-Dioxa-1,8-octanedithiol (DODT) was obtained from Tokyo Chemical Industry. All reagents were used without further purification. Water was purified with a Milli-Q system. ITO (thickness: 150 nm)-coated glass plates were purchased from Geomatec and washed in a detergent solution before use.

Preparation of Au nanoparticle-modified ITO electrode.

An aqueous solution (50 mL) of trisodium citrate (120 mg) was added quickly to a boiling aqueous solution (100 mL) containing tetrachloroaurate(III) tetrahydrate (40 mg). The mixed solution was refluxed for 30 min and cooled to room temperature. After adjusting the pH of the nanoparticle solution to ca. 2.8 by dilute sulfuric acid, a cleaned ITO electrode (4.0×1.2 cm) was immersed into the solution for 5 or 20 min.



Scheme S1. Schematic illustration showing fabrication processes of the electrodes modified with Au nanoparticle agglomerates.

Characterization and spectroelectrochemical measurements

Extinction (absorption + scattering) spectra were obtained by using a Jasco V-770 spectrophotometer. Scanning electron microscopy (SEM) images were obtained using a

JEOL JSM-6700F. Spectroelectrochemical measurements were carried out using the spectrophotometer and a Meiden Hokuto HSV-110 automatic polarization system. The Au nanoparticle-modified ITO electrode, a Ag|AgCl (sat. KCl) electrode and a bare ITO electrode were used as the working, reference and counter electrodes, respectively, and immersed in an electrolyte containing 0.01 M KNO₃ in A glass cuvette (4.0 × 1.0 × 4.5 cm). The electrochemical cell was set in the light path of the spectrophotometer to obtain the λ - E -ext plot shown in Fig. 2 and 3. The extinction spectrum was measured after applying a potential for 50 s.

Spectral simulation

Extinction spectra were simulated by a finite-difference time-domain (FDTD) method by using Ansys Lumerical FDTD software. The entire simulation domain was 65 × 55 × 65 nm, composed of 1 nm cubic cells and the nanogap region was further meshed with 0.2 nm cubic cells. Data for dielectric functions for Au was obtained from the literature.^{S1}

S1. P. B. Johnson and R. W. Christy, *Phys. Rev. B*, 1972, **6**, 4370.

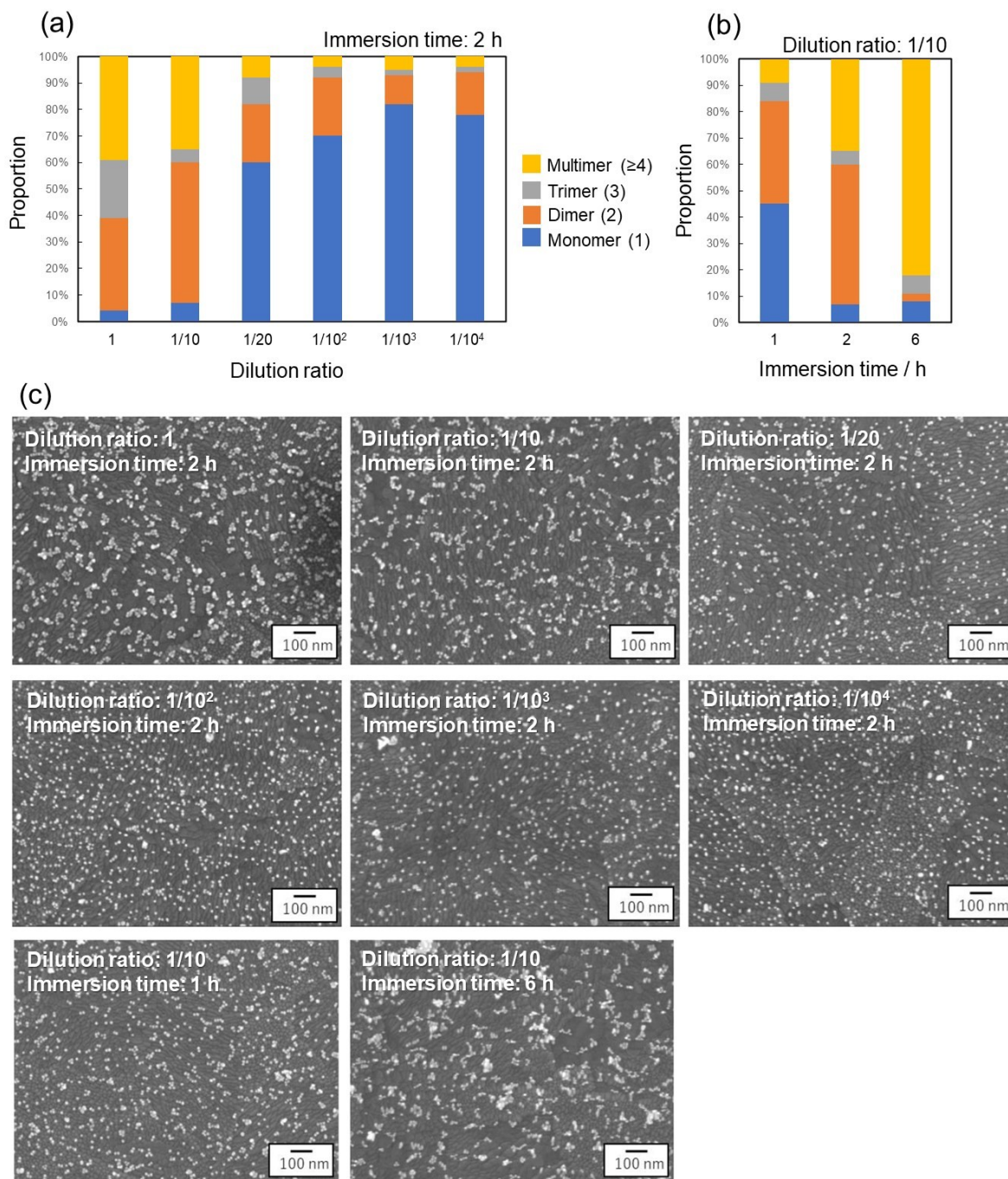


Fig. S1 (a) Relationship between the dilution ratio of the AuNP solution used and the proportion of AuNP monomer, dimer, trimer and multimer with more than four particles observed on the ITO electrode. (b) Relationship between immersion time in the AuNP solution (dilution ratio: 1/10) and the proportion. (c) Corresponding SEM images of the AuNP agglomerates prepared under each condition.

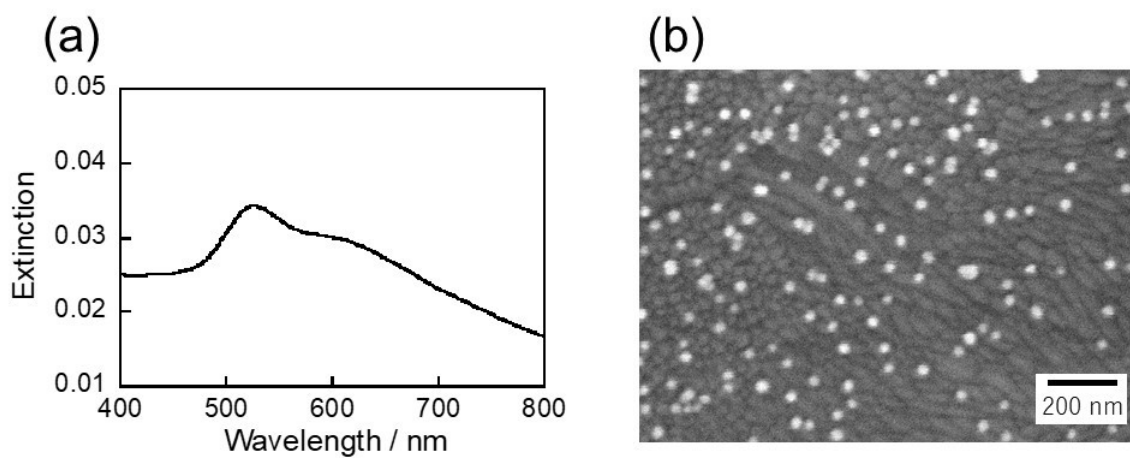


Fig. S2 (a) Extinction spectrum and (b) SEM image of AuNPs on ITO after immersion in diluted AuNP solution without DODT treatment.

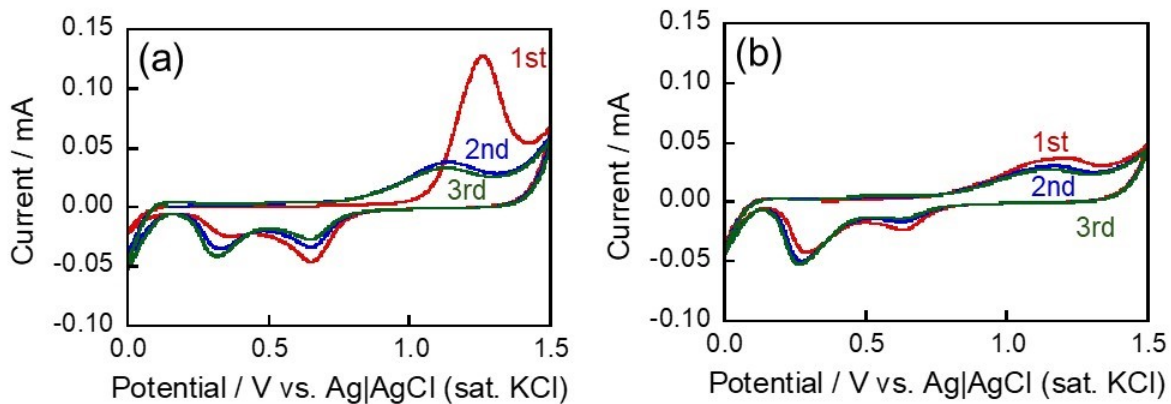


Fig. S3 Cyclic voltammograms of AuNP-modified ITO electrodes (a) with and (b) without DODT treatment measured in 0.01 M KNO_3 . Anodic current in the first cycle in panel a is assignable to oxidative desorption of DODT. The scan rate was set to