Electronic Supplementary Information

A Novel Route for Self-Assembly of Gold Nanoparticles-TiO₂ Nanotube Arrays (Au/TNTs) Heterostructure for Versatile Catalytic Applications: Pinpoint Position *via* Hierarchically Dendritic Ligand

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1. Experimental

1.1 Preparation of DTDTPA ligand

Dithiolated diethylentriaminepentaacetic (DTDTPA) and Au@DTDTPA nanoparticles (NPs) were synthesized according to the Debouttiere's method. ^{1 - 3} In brief, 2 g of diethylenetriaminepentacetic acid bis-anhydride (DTPA) was dissolved in DMF (40 mL) and heated to 70 °C in a 250 mL round flask. In another flask, 1.1 g of aminoethanethiol was dissolved in a mixed solution consisting of DMF (30 mL) and triethylamine (1.74 mL). This solution was added to the round flask and stirred magnetically (2000 rpm) at 70 °C for 12 h. Subsequently, the solution was cooled to room temperature and put in an ice bath. A white powder precipitated was filtered and the acquired filtrate was concentrated at low pressure. White precipitate was collected by adding the concentrated solution into a chloroform solution. After filtration of the mixed solution, washed with 50 mL of chloroform, and dried under vacuum, DTDTPA was obtained as white power.

1.2 Preparation of Au@DTDTPA and Au@Citrate

All the glasswares used were cleaned thoroughly with aqua regia (3 parts HCl, 1 part HNO₃) for 12 h and rinsed completely with ddH₂O. 200 mg of HAuCl₄.4H₂O in 70 mL of methanol was mixed with a solution composing of 482 mg of DTDTPA, 50 mL of methanol, and 2 mL of acetic acid, and stirred magnetically (2000 rpm) for 1 h. Then a freshly prepared solution of 192 mg (NaBH₄) was added under vigorous stirring (2500 rpm) for another 1 h. The color of the mixture changed instantly from yellow to dark brown indicating the presence of Au NPs. The solution was filtered through nylon membrane (0.2 μ m) and washed with 100 mL of 0.01 N HCl, water, diethyl ether, respectively, to obtain the Au@DTDTPA.

Au@Citrate was prepared by the Dotzauer's method.⁴ Briefly, in a 100 mL Erlenmeyer flask, 25 mL of aqueous HAuCl₄ \cdot 3H₂O (1mM) solution was heated to a rolling boil under vigorous stirring (2500 rpm). 2.5 mL of 38.8 mM aqueous sodium citrate was also heated to a rolling boil and added rapidly to the above gold precursor solution. After 20 s, the mixture became dark and then burgundy, heating was continued with vigorous stirring for 10 min, and finally the mixture was stirred without heating for an additional 15 min to fulfill the synthesis. The as-prepared Au NPs were stored in a refrigerator at 4 °C in a dark area and used within two weeks.

1.3 Electrochemical anodization preparation of TNTs

Titanium sheets (50 mm×20 mm×0.1 mm, 99.9 %, Xin RuiGe. Co. Beijing) were polished by abrasive paper and ultrasonically washed by acetone, ethanol, and ddH₂O for 15 min, respectively. Afterward, titanium sheets were immersed into a mixed solution of HF-HNO₃-H₂O with volume ratio of 1: 4: 5 for 30 s, washed by ddH₂O and dried in a N₂ stream. Anodization of Ti foil was conducted in an organic electrolyte of ethylene glycol containing 0.5 % (w/v) NH₄F and 2 % (v/v) H₂O, where the titanium sheet was used as a working electrode with a graphite sheet as a counter electrode. The anodization of titanium foil was firstly carried out at 20 V for 2 h. After which, the thus obtained samples were washed by ddH₂O, dried in a N₂ stream, and subsequently sonicated for 5 min to remove the surface layer, the second anodization was subsequently carried out under the same experimental conditions. Finally, the TNTs samples were gently sonicated and annealed at 450 °C in air for 3 h to transform the amorphous phase of TiO₂ to the anatase phase.

1.4 Self-assembly of the Au/TNTs heterostructure

TNTs (30 mm \times 10 mm \times 0.1 mm) was first vertically exposed to UV light ($\lambda = 365 \pm 15$ nm) for 4 h to facilitate hydroxylation of the TiO₂ surface,⁵⁻⁸ which could promote chemical bonding with 3-aminopropyl-trimethoxysilane (APS). TNTs were subsequently immersed in ethanol (50 mL) by gentle ultrasonication for 1 h, and 500 µL of APS was added and refluxed for 4 h. The APS-treated TNTs were sufficiently rinsed with ethanol to wash away residual APS and dried by a N₂ flow. 20 mg of Au@DTDTPA was dissolved in 10 mL of deionized water and sonicated for 10 min to attain a Au@DTDTPA aqueous solution of 2 g L⁻¹, the pH of which was carefully mediated by 1 N NaOH at pH value of 6. The APS-treated positive charged TNTs was immediately immersed in the negative charged Au@DTDTPA solution (2.5 mL, 2 g L^{-1} , pH = 6) in a quartz cuvette with gentle stirring (200 rpm). After mixing for 1 h, the obtained mixture was washed by deionized water (20 mL) for three times to remove any remaining Au@DTDTPA solution and dried at 80 °C under vacuum for 12 h, thus giving rise to the Au@DTDTPA/TNTs hybrid heterostructure. Subsequently, calcination at 300 °C for 4 h in O₂ atmosphere to remove organic component was performed to obtain the Au/TNTs heterostructure.^{1, 9} For comparison, in order to highlight the significant role of APS, the same experiments without using APS were also carried out under analogous conditions.

1.5 Characterization

The phase composition of the sample was determined by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. Transmission electron microscopy (TEM), energy-dispersive X-ray spectrometer (EDX), and high-resolution transmission electron microscopy (HRTEM) images were obtained by a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The UV-vis diffuse reflectance spectra (DRS) were recorded on a Varian Cary 500 Scan UV-vis-NIR spectrometer, in which BaSO₄ was used as the background between the 200 nm and 800 nm regime. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) at 2.4×10^{-10} mbar using a monochromatic Al K α X-ray beam (1486.60 eV). Binding energy (BE) of the element was calibrated to the carbon BE of 284.60 eV. The morphologies of the samples were measured by field emission scanning electron microscopy (FESEM/EDX, FEI Nova NanoSEM 230).

1.6 Photocatalytic activity

Photocatalytic activities of the samples were evaluated by using methyl orange (MO) as a model organic dye pollutant compound. In a typical test, TNTs, Au@DTDTPA/TNTs, or Au/TNTs sample with the same area of 3 cm² was soaked into 3 mL of MO solution (5 mg/L) at pH value of 7 in a quartz cuvette. Before irradiation, the mixtures were kept in the dark for 1 h to reach the equilibrium of adsorption-desorption at room temperature. A 300 W Xe arc lamp (PLS-SXE 300C) equipped with a cutoff filter ($\lambda = 365 \pm 15$ nm) was applied as the UV light source. The temperature of the reaction system was controlled to be around 25 °C by a commercial electric fan at ambient conditions. The irradiation time ranged from 5 min to 2.5 h. All the samples in the quartz cuvette were placed *ca*. 21 cm away from the UV source with the same light intensity of *ca*. 5 mW/cm². At each time interval of 30 min, light absorption of the reaction solution was measured by a Cary 500 scan UV-Vis spectrophotometer. The concentration of MO was determined by the absorption of MO at 464 nm. The degradation ratio of MO at each time

interval was calculated from the difference of the light absorbance of irradiated to the non-irradiated solution.

1.7 Photoelectrochemical measurement

Photoelectrochemical measurements were performed on a CHI 600D electrochemical system (Chenhua Instruments Co. Shanghai). The system consisted of three electrodes, a single-compartment quartz cell, which was filled with 0.1 M Na₂SO₄ electrolyte (30 mL), and a potentiostat. A platinum black sheet was used as a counter electrode with Hg/Hg₂Cl₂/KCl as a reference electrode. A thin film of TNTs or Au/TNTs (30 mm \times 10 mm) with impregnated area of 3 cm² was employed as a working electrode. A 300 W Xe arc lamp (PLS-SXE 300C) equipped with a band-pass light filter ($\lambda = 365 \pm 15$ nm) was used as the exciting light source for UV light irradiation. The intensity of light was controlled to be around 5 mW/cm².

1.8 Catalytic reduction activity

In a typical reaction, blank TNTs, Au@DTDTPA/TNTs, or Au/TNTs sample (30 mm×10 mm× 0.1 mm) with an area of 3 cm² was dipped into a mixed aqueous solution in a quartz cuvette consisting of 2 mM (40 μ L) 4-nitrophenol, 100 mM (400 μ L) NaBH₄, and 2 mL of ddH₂O. Afterward, the mixture was stirred (200 rpm) at room temperature for 30 min to generate uniform aqueous solution. The use of a high excess of NaBH₄ ensure that its concentration remains essentially constant during the whole reaction, which allows the assumption of pseudo-first-order kinetics with respect to the nitro compound. Samples of the reaction mixture were collected at specific time interval (10 min) for UV-vis spectroscopy analysis. The light absorbance of the characteristic peak of 4-nitrophenol at 400 nm was monitored.



Fig. S1 TEM image and mean diameter histogram of the Au@DTDTPA.



Fig. S2 Chemical structure of DTDTPA profile and Au@DTDTPA.



Fig. S3 TEM images of Au/TNTs directly assembled of Au@DTDTPA to the TNTs framework without APS.



Fig. S4 Schematic view of the self-assembly of Au NPs on the framework of TNTs.



Fig. S5 HRTEM image of single Au NP without the interference of TNTs.



Fig. S6 EDX patterns of (a) TNTs and (b) Au/TNTs heterostructure obtained from the SEM measurement.



Fig. S7 Survey XPS spectra of (a) Au@DTDTPA, (b) TNTs, (c) Au@DTDTPA/TNTs heterostructure, and high-resolution spectra of (d) C 1s, (e) O 1s, (f) Ti 2p, and (g) A u 4f of the Au@DTDTPA/TNTs heterostructure.

Element	TNTs (eV)	Au@DTDTPA/TNTs (eV)	Chemical Bond Species
C 1s A	284.62	284.60	C-C/C-H
C 1s B	286.18	286.21	C-OH/C-O-C
C 1s C	288.56	289.00	Carboxylate (CO_3^{2-})
O 1s A	529.84	529.90	Lattice oxygen
O 1s B	531.40	531.04	Ti-OH
O 1s C	532.30	531.83	C-OH/C-O-C
O 1s D		533.07	СООН
Ti 2p _{3/2}	458.56	458.65	Anatase (4+)
Ti 2p _{1/2}	464.25	464.47	
Au 4f _{7/2}		83.96	Au (0)

Table S1. Chemical bond species *versus* binding energy for TNTs and Au@DTDTPA/TNTs heterostructure.



Fig. S8 TEM images of the Au@Citrate/TNTs nanostructure.



Fig. S9 UV-vis diffuse reflectance spectra (DRS) of TNTs and Au@DTDTPA/TNTs heterostructure.



Fig. S10 FTIR results of TNTs and Au@DTDTPA/TNTs heterostructure.



Fig. S11 XRD patterns of TNTs (a) before and (b) after heat treatment at 450 $^{\circ}$ C in air for 3 h, (c) Au/TNTs heterostructure, and (d) magnified diffraction peak of Au (200) marked in c.



Fig. S12 Enlarged view of Fig. 2 in the manuscript for clear view.

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