Electronic Supplementary Information

An Efficient Layer-by-Layer Self-Assembly of Metal-TiO_2 Nanoring/Nanotube Heterostructures, M/T-NRNT (M = Au, Ag, Pt), for Versatile Catalytic Applications

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Experimental

1.1 Preparation of citrate-stabilized noble-metal colloidal NPs

(a) Synthesis of citrate-stabilized Au NPs

Citrate-stabilized Au NPs were prepared by Dotzauer's method.[1] Briefly, all the glasswares were cleaned thoroughly with aqua regia (3 parts HCl, 1 part HNO_3) for 12 h and rinsed with deionized water. In a 100 mL Erlenmeyer flask, 25 mL of aqueous 1mM $HAuCl_4\cdot 3H_2O$ was heated to a rolling boil under vigorous stirring (2500 rpm). 2.5 mL of 38.8 mM aqueous sodium citrate dihydrate was also heated to a rolling boil and then added rapidly to the above gold solution. After 20 s, the mixture became dark and then burgundy, heating was continued with 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 ^{o}C in a dark area and used within two weeks.

(b) Synthesis of citrate-stabilized Ag NPs

Citrate-stabilized Ag NPs were prepared from the $NaBH_4$ reduction of $AgNO_3$ in aqueous solutions following the procedures of Lee's approach.[2] Briefly, 100 mL of a 1 mM aqueous $AgNO_3$ solution was mixed with 8 mL of a 40 mM aqueous sodium citrate solution used as stabilizer. 2 mL of 112 mM aqueous $NaBH_4$ solution was then added dropwise under vigorous stirring (2500 rpm) at ambient temperature, immediately yielding a yellowish brown Ag hydrosol. The Ag hydrosol was subsequently stocked in a refrigerator at 4 ^{o}C and aged for 24 h to decompose the residual $NaBH_4$ before it was used in subsequent steps.

(c) Synthesis of citrate-stabilized Pt NPs

The synthesis of citrate-stabilized Pt NPs was referred to the Elliott's method.[3] Briefly, 26 mL of 2.8 mM aqueous trisodium citrate dehydrate solution was added to 50 mL of 0.4 mM aqueous hydrogen hexachloro-platinate solution at room temperature. An amount of 5 mL of 12 mM $NaBH_4$ was then introduced dropwise with vigorous stirring (2500 rpm), and the pale yellow solution turned dark brown in 5 min. Finally, the dark brown colloidal solution was stirred for 4 h and stored in a refrigerator at 4 ^{o}C until ready for further use.

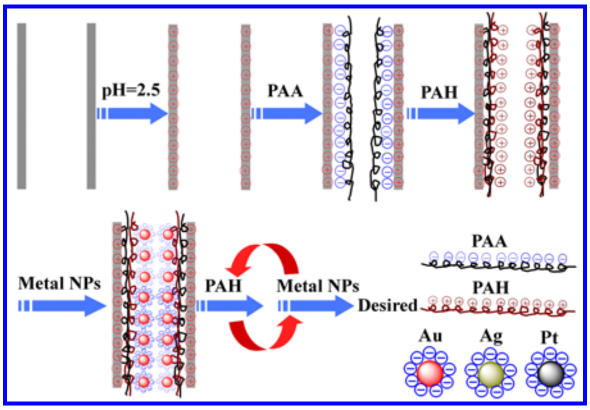
1.2 Electrochemical preparation of TNTAs and T-NRNT

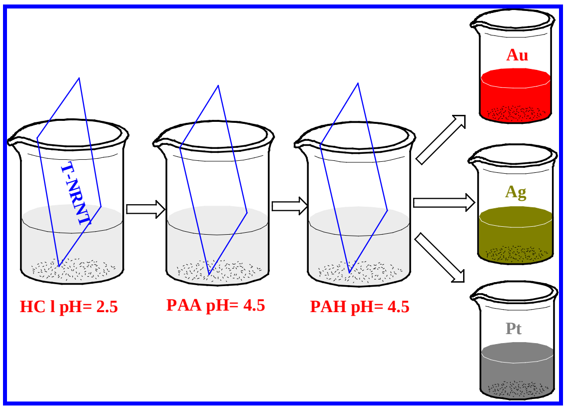
Titanium sheets (50 mm × 20 mm × 0.1 mm, 99.9 %, Xin RuiGe. Co. Beijing) were first polished by abrasive paper and ultrasonically washed by acetone, ethanol, and ddH_2O for 15 min, respectively. Afterward, the titanium sheets were immersed into a mixed solution of HF-HNO_3-H_2O with volume ratio of 1: 4: 5 for 30 s, washed by ddH_2O and dried in a N_2 stream. Anodization of Ti foil was conducted in an organic electrolyte of ethylene glycol containing 0.5 % (w/v) NH_4F and 2 % (v/v) H_2O, where the titanium sheet was used as a working electrode and graphite sheet as a counter electrode. The first-step anodization (1st anodization) was firstly carried out at 40 V for 2 h. After which, the samples were washed by ddH_2O five times and dried in a N_2 stream to attaine the TNTAs. TNTAs samples were subjected to sonication for 10 min to completely remove the surface layers, and second-step anodization (2nd anodization) was subsequently carried out under the same experimental conditions. Finally, the thus-obtained

T-NRNT and TNTAs samples were annealed at 450 ^{o}C in air for 3 h to transform the amorphous phase of TiO_2 to the anatase phase.

1.3 LBL self-assembly of metal NPs (Au, Ag, Pt) on the framework of T-NRNT or TNTAs

Polyelectrolytes solutions, *i.e.* poly(acrylic acid) (PAA, 25 wt % soln. in water, M_w~240,000 g mol^{-1}, 1.0 mg mL^{-1}), poly(allylamine hydrochloride) (PAH, M_w ~15000 g mol^{-1}, 1.0 mg mL^{-1}) contain 0.5 M NaCl with pH value of 4.5. Firstly, T-NRNT was dipped in an aqueous HCl solution (pH = 2.5) for 20 min, washed three times by ddH_2O for 2 min, and followed by drying with a gentle stream of nitrogen, yielding positively charged T-NRNT ($T\text{-}NRNT^+$). Secondary, negatively charged PAA layer was deposited to the $T\text{-}NRNT^+$ substrate ($T\text{-}NRNT^+/PAA^-$) by the same washing and drying procedures. Thirdly, positively charged PAH layer was deposited on the $T\text{-}NRNT^+/PAA^-$ layer to acquire the positively charged layer ($T\text{-}NRNT^+/PAA^-/PAH^+$). Finally, the $T\text{-}NRNT^+/PAA^-/PAH^+$ multilayer films were dipped in the pre-synthesized metal NPs (Au, Ag, Pt), respectively, to obtain the well-defined T-NRNT/PAA/PAH/Au (or Ag, Pt) heterostructures, *i.e.* M/T-NRNT (M = Au, Ag, Pt). It should be mentioned that the outermost layer of the PE multilayer films fabricated were always PAH, a positively charged layer, thus, negatively charged metal NPs facilitate the periodic deposition to the PE multilayer films. The deposition cycle was repeated till the desired $T\text{-}NRNT/PAA/PAH/(Au/PAH)_n$, (n =1, 4, 6, 8, 10) multilayer thin films were attained. The protocol for preparation of M/TNTAs (M = Au, Ag, Pt) nanostructures is analogous to that for M/T-NRNT (M = Au, Ag, Pt) heterostructures except that the substrate of T-NRNT is replaced with TNTAs.





1.4 Characterization

The phase composition of the samples was determined by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. The UV-vis diffuse reflectance spectra (DRS) were recorded on a Varian Cary 500 Scan UV-vis-NIR spectrometer, in which $BaSO_4$ was used as the background between the 200 nm and 800 nm scope. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) using a monochromatic Al Kα X-ray beam (1486.60 eV). Binding energy of the elements was calibrated to that for carbon (284.60 eV). The morphologies of the samples were measured by field emission scanning electron microscopy (FESEM/EDX, FEI Nova NanoSEM 230).

1.5 Photocatalytic activity

Photocatalytic activity was evaluated by using methyl orange (MO) as a model organic dye pollutant compound. In a typical test, TNTAs, T-NRNT, M/T-NRNT (M = Au, Ag, Pt), or Au/ T-NRNT with different deposition cycles (n = 4, 6, 8, 10) sample with the same area of 2 cm^2 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 used as the UV light source. The temperature of the reaction system was controlled to be around 25 ^{o}C by a commercial electric fan. The irradiation time ranged from 5 min to 2.5 h. Under ambient conditions, 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/cm^2. 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.

1.6 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 Na_2SO_4 electrolyte (30 mL), and a potentiostat. A platinum black sheet was used as a counter electrode and $Hg/Hg_2Cl_2/KCl$ as a reference electrode. A thin film of TNTAs, T-NRNT, or M/T-NRNT (M = Au, Ag, Pt) sample (20 mm × 10 mm) with an area of 2 cm^2 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.

1.7 Catalytic reduction activities of the M/T-NRNT (M = Au, Ag, Pt) nanostructures

The catalytic properties of the hierarchically ordered M/T-NRNT (M = Au, Ag, Pt) nanostructures were evaluated by employing the reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$ as a model reaction. In a typical reaction, T-NRNT, M/T-NRNT (M = Au, Ag, Pt), or $T\text{-}NRNT/PAA/PAH/(Au/PAH)_n$, (n =1, 4, 6, 8, 10) sample (20 mm × 10 mm) with an area of 2 cm^2 was dipped into an aqueous solution in a quartz cuvette containing 2 mM (40 μL) 4-nitrophenol, 100 mM (400 μL) $NaBH_4$, and 2 mL of ddH_2O. Afterward, the mixture was stirred at room temperature for 30 min to generate uniform aqueous solution (200 rpm). The use of a high excess of $NaBH_4$ 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.[4, 5] Samples of the reaction mixture were collected at specific time interval (10 min) for UV-vis spectroscopy analysis.

Reference

1. D. M. Dotzauer, J. H. Dai, L. Sun and M. L. Bruening, *Nano letters.*, 2006, **6**, 2268.
2. J. Yang, J. Y. Lee and H. P. Too, *J. Phys. Chem. B*, 2005, **109**, 19208.
3. C. J. Jiang, J. M. Elliott, D. J. Cardin and S. C. Tsang, *Langmuir*, 2008, **25**, 534.
4. K. Esumi, R. Isono and T. Yoshimura, *Langmuir*, 2004, **20,** 237.
5. K. Hayakawa, T. Yoshimura and K. Esumi, *Langmuir*, 2003, **19**, 5517.

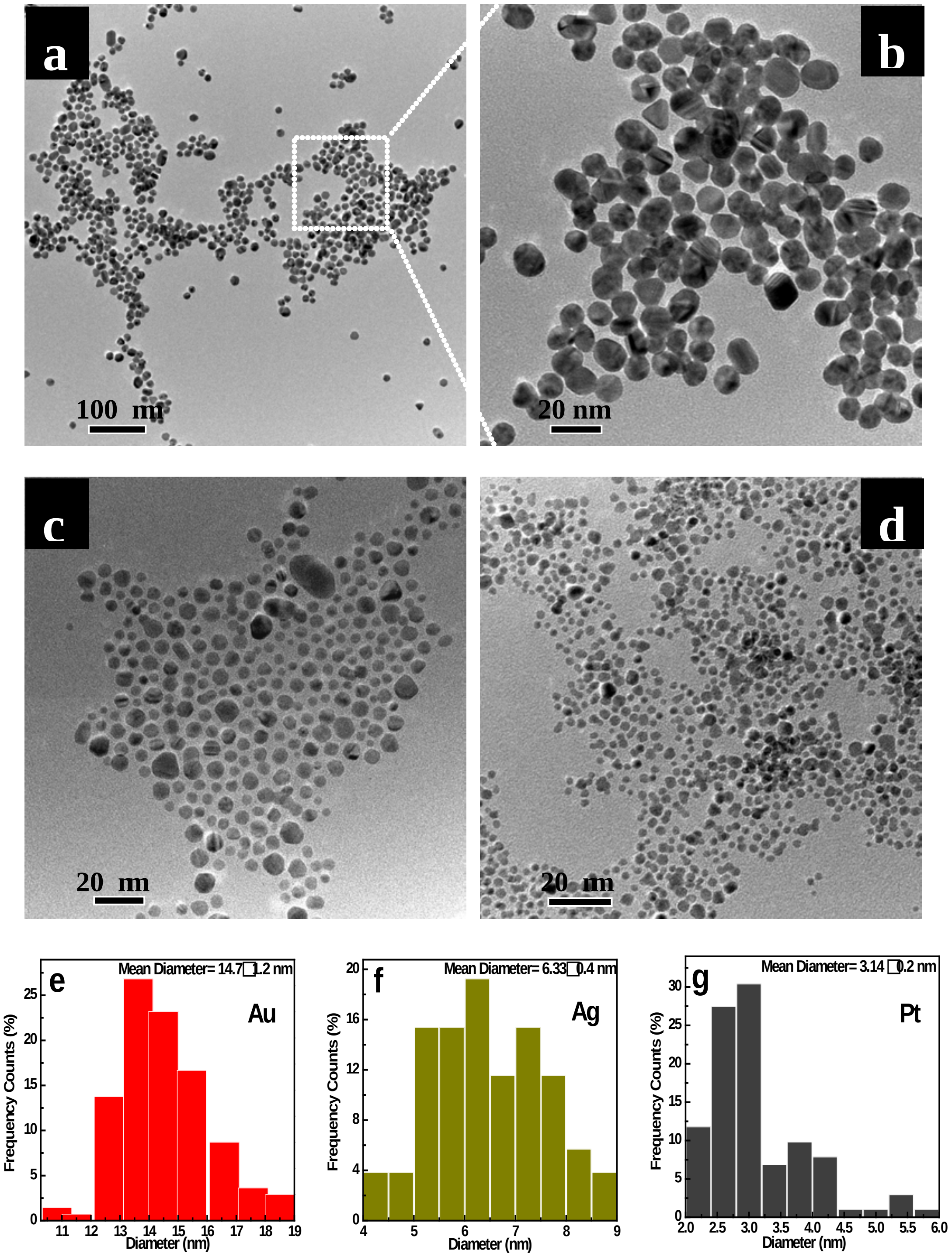


Fig. S1 TEM images of citrate-stabilized (a-b) Au, (c) Ag, (d) Pt NPs, and mean diameter histogram of as-prepared (e) Au, (f) Ag, (g) Pt NPs.

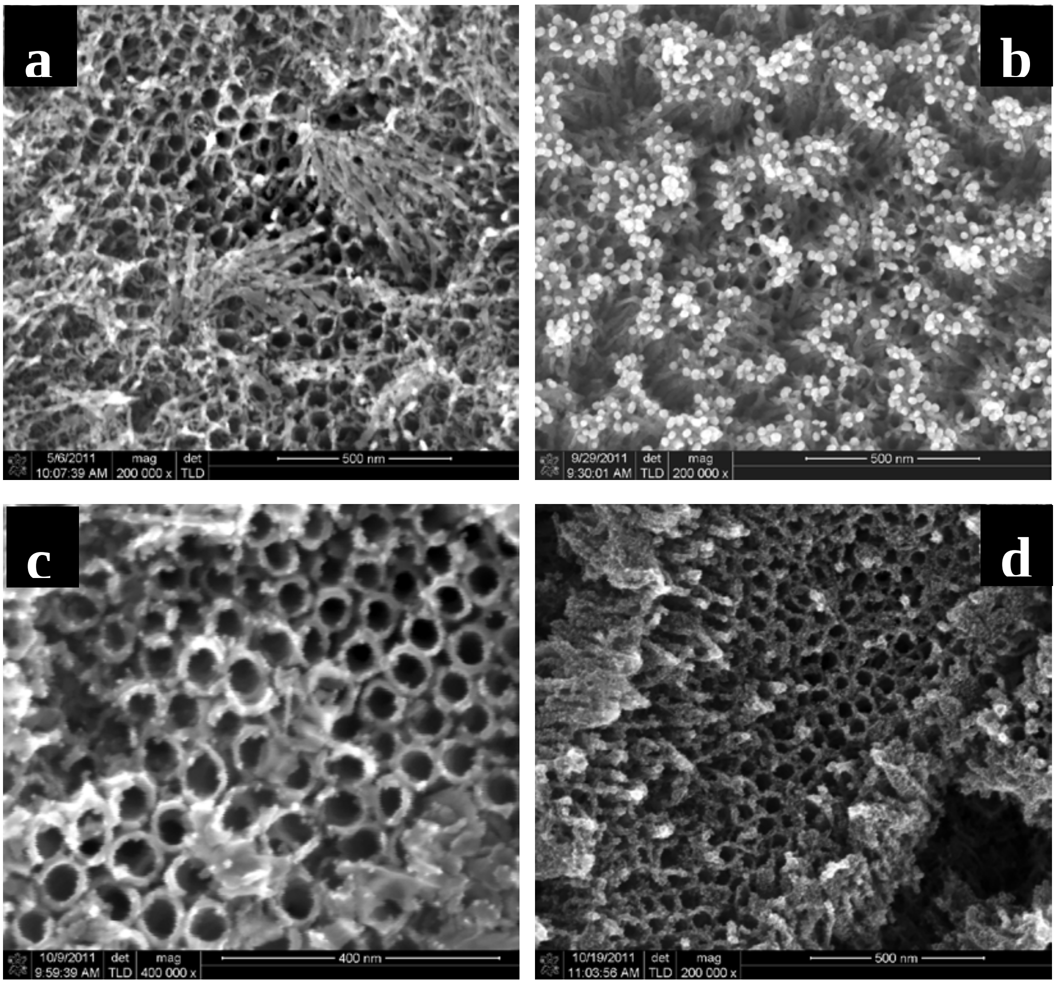


Fig. S2 (a) TNTAs obtained *via* the 1st anodization, (b) Au/TNTAs, (c) Ag/TNTAs, and (d) Pt/TNATs nanostructures *via* the same LBL self-assembly approach.

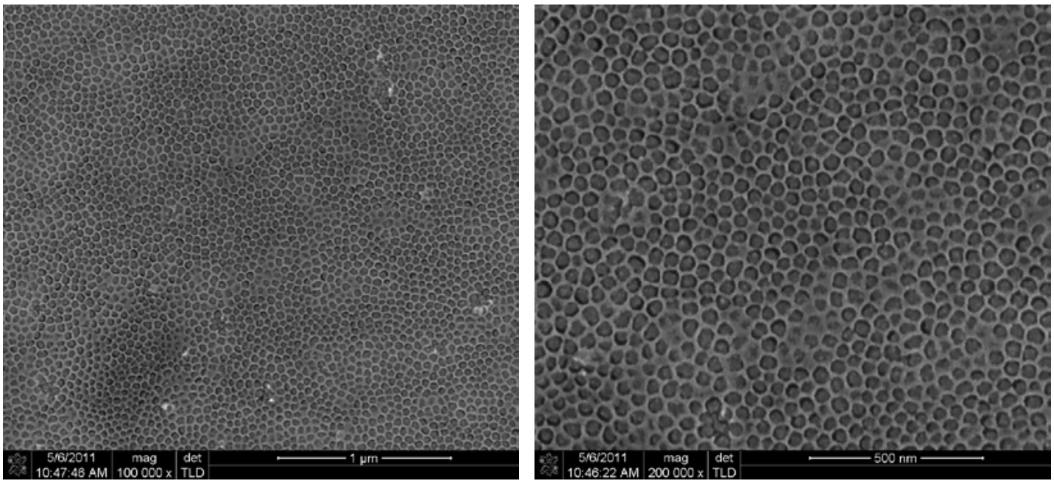


Fig. S3 Exposed surface of Ti foil after removal of the bundled nanotubes inherited from the 1st anodization.

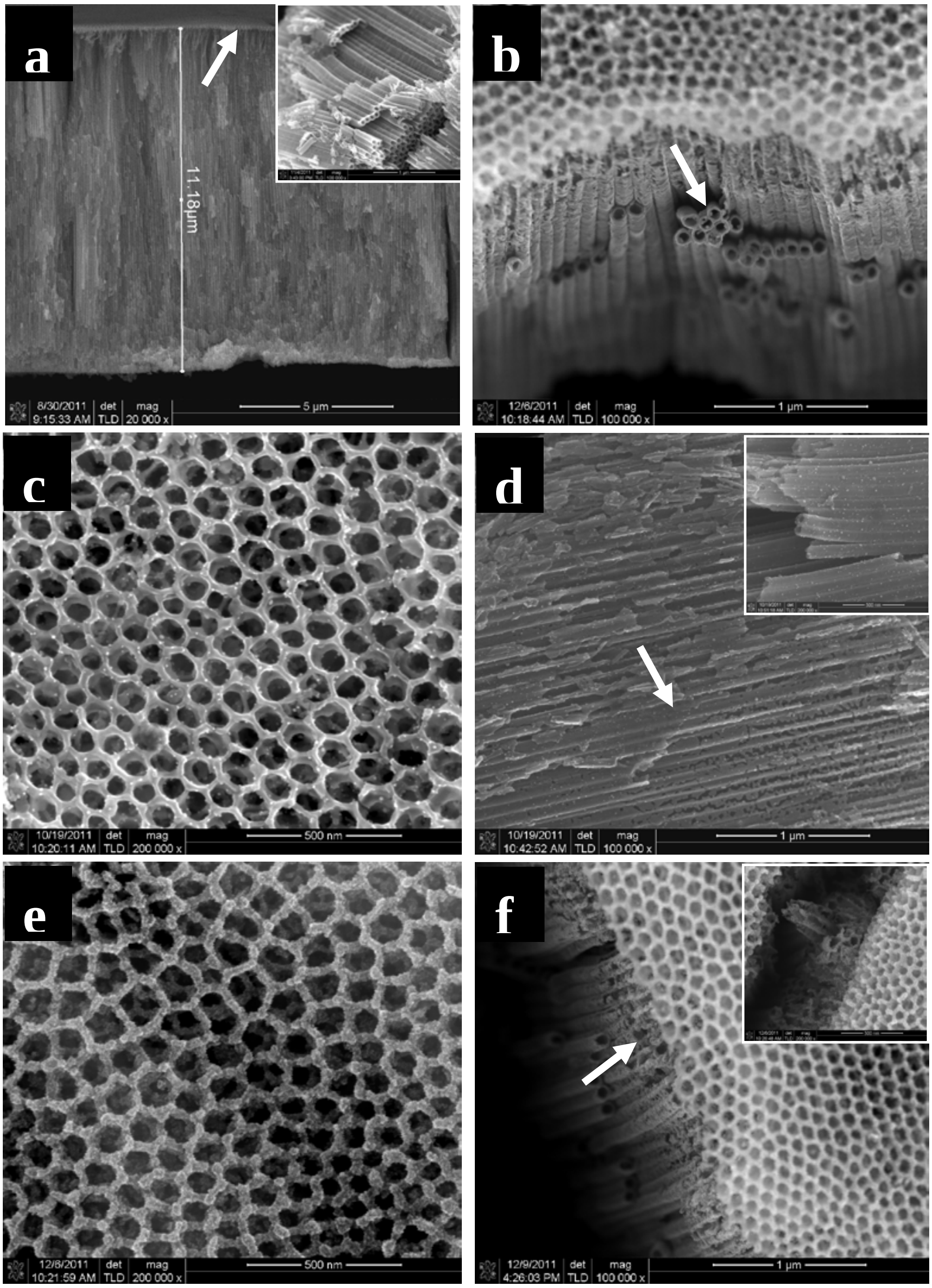


Fig. S4 (a) Cross-sectional image of T-NRNT obtained *via* the 2nd anodization with amplified image in the inset. SEM images of (b) Au/T-NRNT, (c-d) Ag/T-NRNT and (e-f) Pt/T-NRNT with enlarged views in the inset of (d) and (f), respectively.

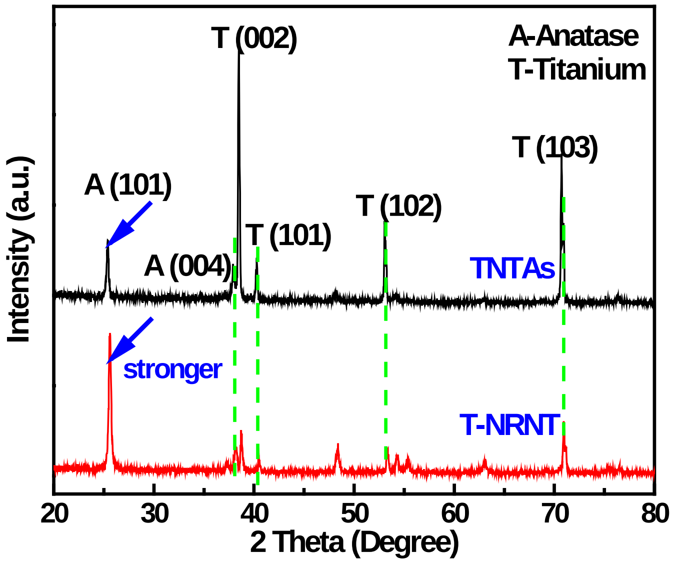


Fig. S5 XRD patterns of TNTAs and T-NRNT.

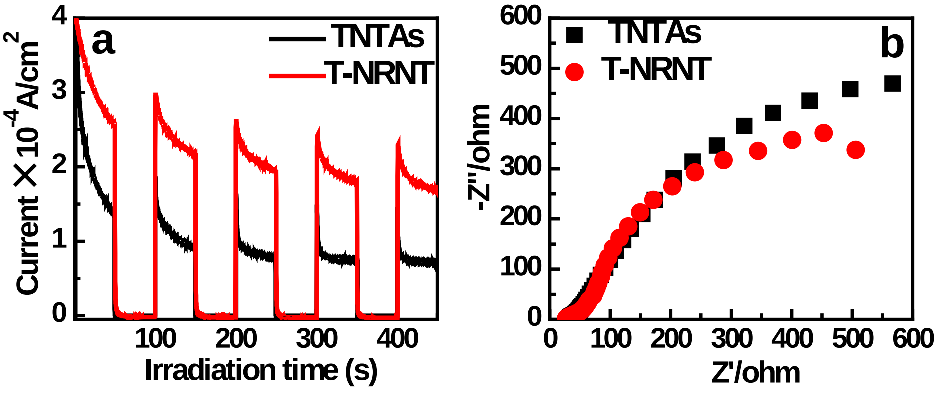


Fig. S6 (a) Transient photocurrent responses and (b) Electrochemical impedance spectroscopy (EIS) Nynquist plots of TNTAs and T-NRNT in 0.1 M Na_2SO_4 aqueous solution under UV light irradiation (365 ± 15 nm). The potential of the working electrode was set at 0.0 V *versus* the Pt counter electrode. The amplitude of the sinusoidal wave was set at 10 mV and the frequency varied from 100 kHz to 0.05 Hz for EIS measurement.

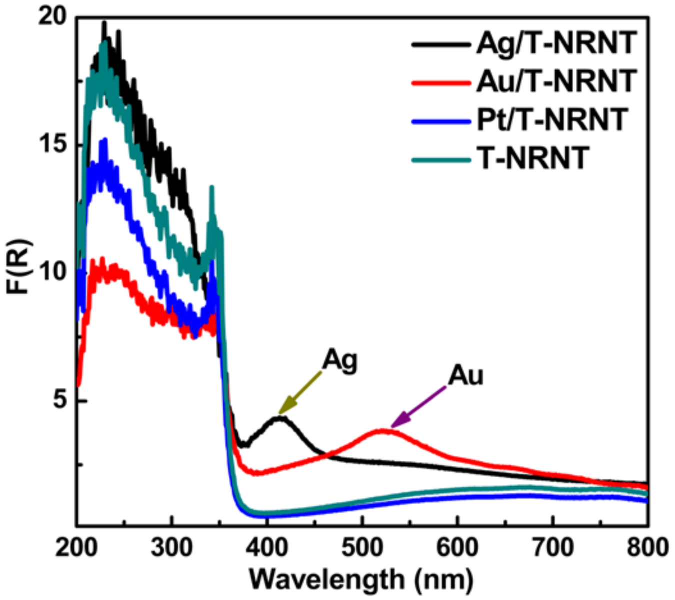


Fig. S7 UV-vis diffuse reflectance spectra (DRS) of T-NRNT and M/T-NRNT (M = Au, Ag, Pt) nanostructures.

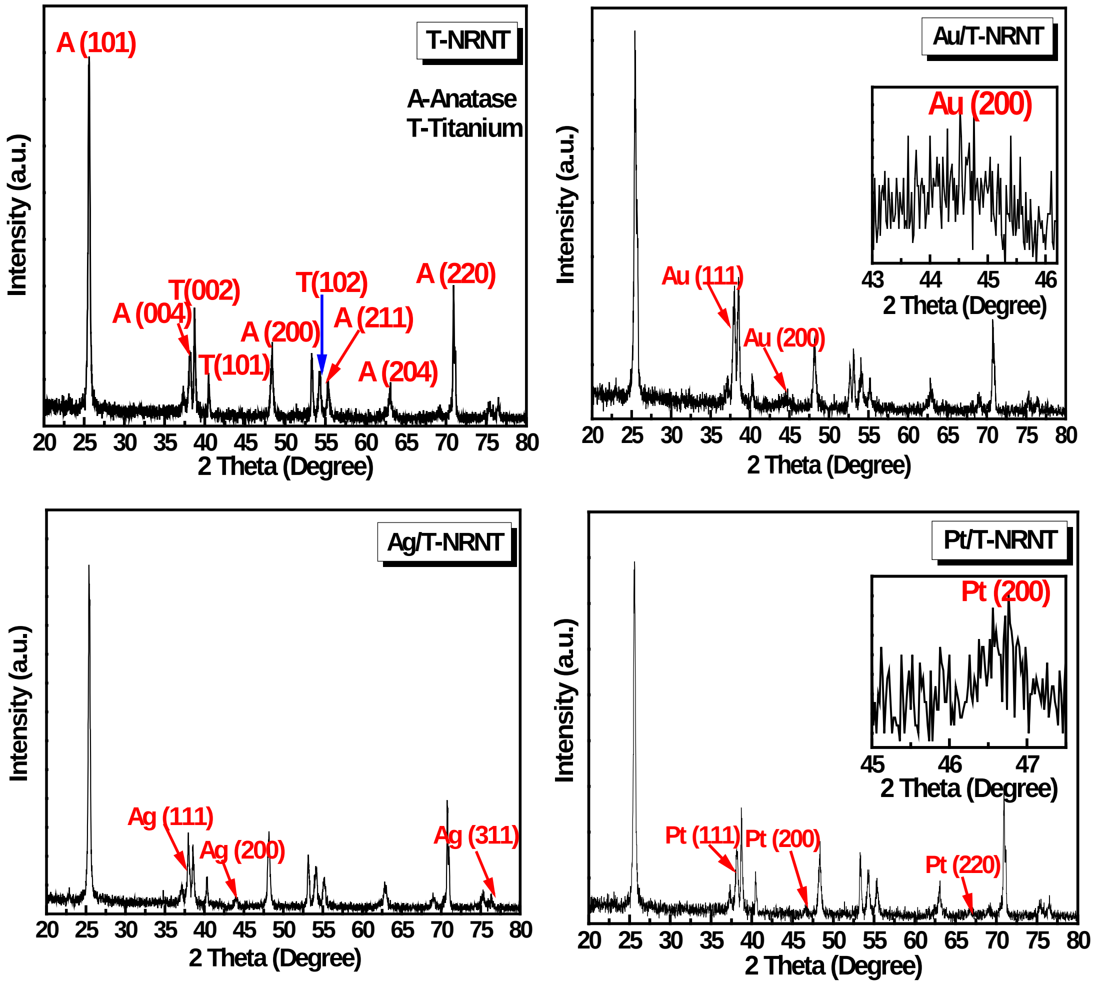


Fig. S8 XRD patterns of T-NRNT and M/T-NRNT (M = Au, Ag, Pt) nanostructures.

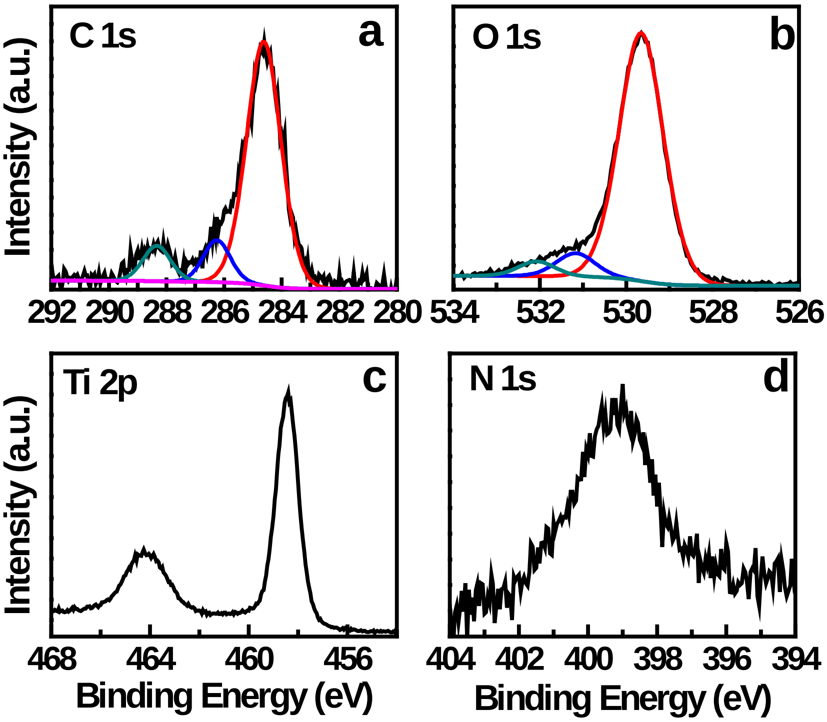


Fig. S9 High-resolution XPS spectra of (a) C 1s, (b) O 1s, (c) Ti 2p, and (d) N 1s for the Au/T-NRNT nanostructures.

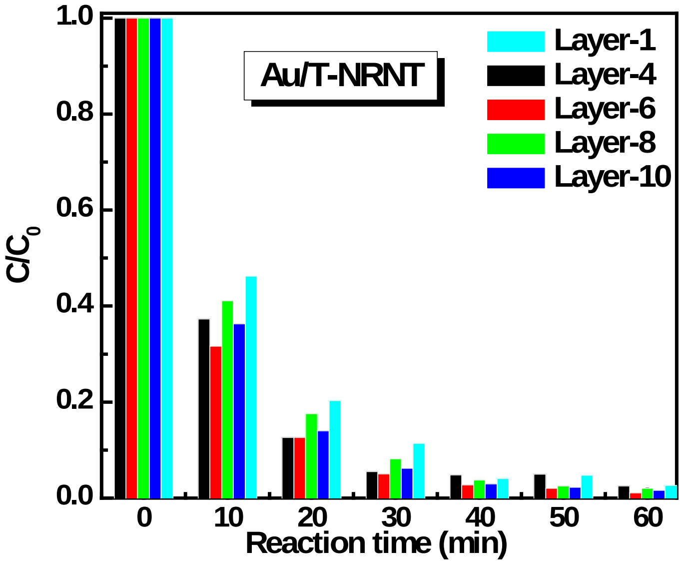


Fig. S10 Catalytic reduction of 4-nitrophenol (4-NP) toward 4-aminophenol (4-AP) over the Au/T-NRNT nanostructures with varied deposition cycles (n = 1, 4, 6, 8, 10).

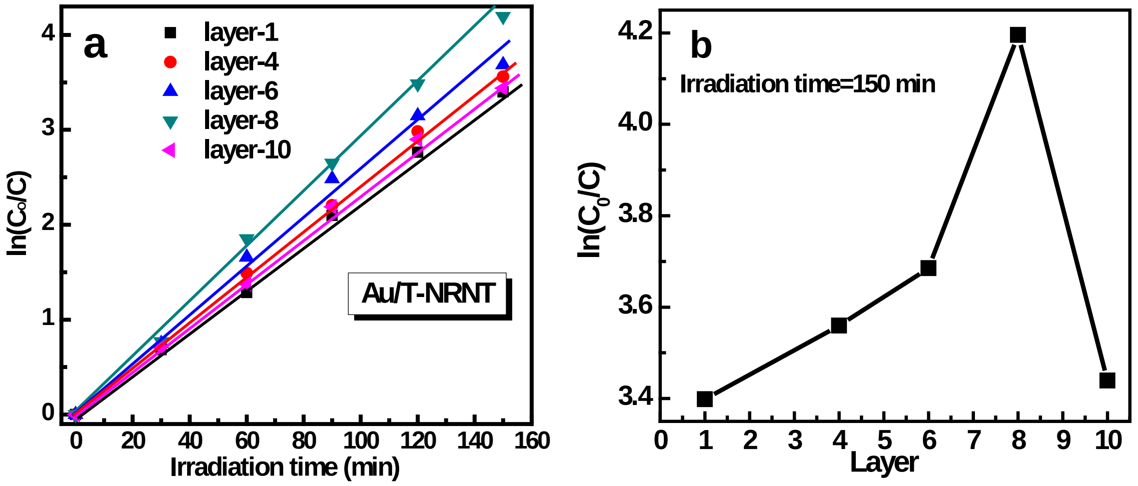


Fig. S11 (a) Photocatalytic performances of the Au/T-NRNT nanostructures with different deposition cycles (n = 1, 4, 6, 8, 10) under the irradiation of UV light (365±15 nm), and (b) photocatalytic activities at the irradiation time of 150 min for Au/T-NRNT nanostructures with varied deposition layers.