

Supporting Information

Anisotropic Growth of TiO₂ onto Gold Nanorods for Plasmon-Enhanced Hydrogen Production from Water Reduction

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Experimental information

Materials. All of the syntheses were carried out using commercially available reagents.

Hexadecyltrimethylammonium bromide (C₁₆TAB, >95%), myristyltrimethylammonium bromide (C₁₄TAB, 99%), modecyl-trimethylammonium bromide (C₁₂TAB, 99%), sodium borohydride (NaBH₄, 99%), hydrogen tetrachloroaurate trihydrate (HAuCl₄•3H₂O, 99.9%), Sodium dodecyl sulfate (FlukaTM, SDS, 99%) and TiCl₃ (15% with 5-10% excess HCl, Riedel-de Haën) were purchased from Sigma-Aldrich. Silver nitrate (AgNO₃, >99.97%), L-ascorbic acid (AA, 99.9%), sodium bicarbonate (NaHCO₃, 99%), methanol (99%, BDHTM), absolute ethanol (Gold ShiledTM, 200 proof) and hydrochloric acid (HCl, 36.5-38% in water, EMDTM) were purchased from Fisher Scientific. Sodium oleate (NaOL, >95%) was purchased from TCI America. Methylene Blue (>98%, BAKER ANALYZED[®] Reagent) was purchased from Avantor Performance Materials. Ultrapure water obtained from a Milli-Q SimplicityTM 185 system with the resistivity no less than 18.2 MΩ•cm was used in all experiments. All glasswares and stir bars were cleaned in aqua regia and fully rinsed with ultrapure water. If not specified, all solutions in the following paragraphs refer to aqueous solutions. All were used as received without further purification.

Synthesis of Au nanorods (AuNRs). Very high quality AuNRs can be prepared in high yield by a simple synthesis procedure.^{S1}

The Au seed solution: 10 mL 0.1 M C₁₆TAB solution was mixed with 0.1 mL 25 mM HAuCl₄ in a 20 mL scintillation tube and stirred at 30 °C for 5 min. Afterwards, 0.6 mL freshly prepared 100 mM NaBH₄ solution (ice cooled) was injected rapidly into the solution mixture. The solution was stirred for 2 min and left to stand at 30 °C for 30 min before use.

Growth solution: The stock solution of surfactants was prepared by dissolving 9.0 g C₁₆TAB and 1.234 g NaOL into 250 mL water at 90 °C with vigorous stirring. The solution was then cooled to room temperature before use. In a typical gold nanorod synthesis, 20 mL of surfactant solution was mixed with 20 mL of water and 0.8 mL 25 mM HAuCl₄ solution (using vortex mixing or shaking). The solution was mixed thoroughly and kept in a 30 °C water bath for 90 min. Concentrated HCl solution (36.5-38%) was added to the solution to adjust its pH. After 15 min, a

small amount of 10 mM AgNO₃ solution was added, the solution was shaken, and 0.064 mL 0.1 M ascorbic acid was injected into the solution. Immediately, a small amount of seed solution was added to the growth solution. The solution was shaken for 30 seconds and then left undisturbed in the 30 °C water bath for 12-20 h. The final product was separated by centrifuging at 8000 rpm for 20 min with Eppendorf 5804 centrifuge (F34-6-38 rotor) followed by dispersion and the 2nd centrifuge with 5500rpm for 20 min. Finally, the gold nanorods were dispersed into 10 mL of H₂O as the stock solution. The concentration of C₁₆TAB in this solution should be lower than 0.89 mM (1st CMC of C₁₆TAB),^{S2} so that no stable foams are generated upon shaking.

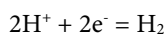
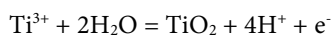
Table S1. Detailed Synthesis Recipe for Gold Nanorods with Geometric Parameters

Number	LSPR (nm)	HCl (μL)	AgNO ₃ (μL)	Seed (μL)	Diameter (nm)
1	789	168	400	32	15
2	718	230	290	32	17
3	690	168	290	64	22
4	682	168	290	32	27
5	678	168	290	16	32
6	850	156	768	16	32

Synthesis of AuNR/TiO₂ nanodumbbells and AuNR@TiO₂ core/shell nanoparticles

AuNR/TiO₂ nanodumbbells. In a typical synthesis, 0.2 mL of 15% TiCl₃ was diluted with 4 mL deaerated H₂O in a 10-mL centrifuge tube (for small-scale synthesis, starting from deaerated H₂O makes it easy to repeat, even when the latter reaction is done in air). 0.72 mL of 1 M NaHCO₃ was added to the diluted TiCl₃ solution dropwise under stirring. After the addition of last two or three drops of NaHCO₃, the mixture turned into a dark blue solution. The pH of this solution was about 2.5. (Note: the required amount of NaHCO₃ may vary for TiCl₃ from different vendors or batches; even when they are described as having the same TiCl₃ concentration.) Afterwards, a mixture (0.5 mL of AuNR stock solution+0.5 mL 0.2 M C₁₆TAB solution +1.3 mL deaerated H₂O) was added into the above dark blue solution. The dispersion was then gently kept stirring/shaking for 30-60 min. The product was collected by centrifuge at 6000 rpm for 10 min and washed with ethanol twice. Most of the surfactant C_nTAB and unreacted Ti³⁺ precursor can be washed away in this step. This recipe can be easily scaled up at least by 20 times.

The hydrolysis of Ti³⁺ follows this process:^{S3}



Note 1: The decreased tip area may dramatically reduce the ability of nucleating TiO₂ caps. For example, considering the hemisphere area on the tips of AuNRs and assuming the same TiO₂ coating length (10–20 nm, based on TEM

analysis) from the tips along the NRs, the coated surface area will be reduced by 20–30% when the AuNR diameter is reduced from 32 to 27 nm; this obviously changes the ability to form the TiO₂ caps on AuNRs and their stability. As shown in Figure 4a, the onset diameter of this change is ~20 nm. In addition, Au does not have strong chemical binding to amorphous TiO₂. From our observations, the overall effect of reducing the AuNR diameter is dominated by this stability aspect.

AuNR@TiO₂ core/shell nanoparticles. The deposition solution with TiCl₃ was prepared with the same protocol as described above, but the synthesis was performed in the absence of C₁₆TAB. Afterward, 0.5 mL aqueous solution of AuNRs with SDS exchanged surface was mixed with the TiCl₃-NaHCO₃ deposition solution and left for reacting 30 min. The SDS exchange of AuNRs was carried out by the following procedure: C₁₆TAB-capped AuNRs separated from their growth solution were first dispersed with a few drops of water and then mixed with 20 mL 0.1 M SDS solution; the suspension was left for 30min and AuNRs were then collected and washed once by centrifuge-dispersion with H₂O; Finally, the SDS-capped AuNRs were dispersed into 10 mL H₂O for homogeneous TiO₂ coating.

The Au-free amorphous TiO₂ sample was prepared by reacting the TiCl₃-NaHCO₃ deposition solution without metal nanoparticles at room temperature for 2-12 h. The product was collected by centrifugation and washed twice with ethanol and H₂O respectively.

Characterization

Transmission electron microscopy (TEM). Samples were prepared by dropping an ethanol or water dispersion onto 200-mesh carbon-coated copper grids and slowly evaporating the solvent. TEM (including high-resolution transmission electron microscopy, HRTEM) studies were performed on a FEI TECNAI™ T20 high-resolution transmission electron microscope operating at 200 kV. HAADF-STEM and elemental mapping were performed on a TECNAI™ Titan high-resolution transmission electron microscope operating at 300 kV. The calculations of sizes and numbers were based on more than 300 nanoparticles.

Scanning electron microscopy (SEM). Sample dispersions were dropped on a surface-polished Si<100> wafer by slow evaporation. SEM studies were performed on an FEI XL40 Scanning Electron Microscope equipped with a high stability Schottky field emission gun. The calculations of sizes and numbers were based on more than 300 nanoparticles.

UV-Vis spectrometry. UV-Vis spectra for water dispersion of AuNRs, AuNR/TiO₂ nanodumbbells and AuNR@TiO₂ nanoparticles were acquired on an Agilent 8453 UV-Vis spectrophotometer equipped with a cuvette holder. All spectra were recorded under ambient conditions with 1 cm light-path.

Powder X-ray Diffraction (XRD). XRD measurements were made on a Bruker Proteum diffractometer with a Microstar Cu rotating anode, operating at 35 kV and 25 mA. The samples in ethanol were first dried at 60 °C overnight, and then the colloidal monoliths condensed at the bottom of the container. A small monolith was adhered to a nylon ring for further single-crystal X-ray analysis.

Visible-light Photocatalysis. The photocatalytic H₂-production experiments were performed in a 55-mL cylinder-shape quartz reactor. The temperature was controlled to about 28 to 33 °C by a cooling fan. A Newport solar simulator (Housing part model#: 66902) equipped with a 300 W Xe arc lamp was used as light source (40 cm between the housing box and the reactor). In a typical photocatalytic experiment, the AuNR/TiO₂ nanodumbbell photocatalysts (all containing 1 mg AuNRs with 32 nm in diameter) were dispersed in 20 mL of aqueous solution of v/v 20% methanol and 10 mM NaHCO₃ by sonicating for 10 min. For the Au-free TiO₂, 5 mg of dry sample was used. Prior to the irradiation using a 420nm long pass filter, the reactor with a catalyst suspension was bubbled with Ar for 40 min to completely remove the dissolved O₂ to assure the anaerobic condition. Magnetic stirring (500-800 rpm) was applied in order to keep the photocatalyst particles suspended in the solution throughout the experiment. The reaction process was monitored by measuring the H₂ concentration with a gas chromatograph (HP 5890 equipped with TCD detector and 5Å molecular sieve column, Ar carrier gas). Sampling was processed with 0.1 mL gas intermittently through the septum. All glassware was rinsed thoroughly with Milli-Q water prior to use.

Experiments on the direct photocatalytic reduction of a model acceptor molecule, methylene blue (MB), were performed under conditions similar to those above, but in addition 1 mL 0.6 mM aqueous MB solution was injected into the quartz reactor before photocatalysis was initiated. A SamplePro FlexFilm bag (SKC Inc.) was filled with pure Ar gas, and then connected to the quartz reactor in order to balance the inner pressure for later liquid sampling. The reaction process was monitored by measuring the MB concentration/absorbance using an Agilent 8453 UV-Vis spectrophotometer. Liquid sampling was carefully processed with 0.8 mL liquid mixture intermittently through the septum to prevent air leakage.

Note 2: As pointed out by Yates (Ref. 24), metal/TiO₂ contact induces band bending in TiO₂ which can be used for either electron or hole transfer, depending on whether that band bends upward or downward, which, in turn, depends on the relative ordering of the semiconductor's and metal's Fermi levels. The Fermi level of TiO₂ is higher than that of Au, causing the bands of the TiO₂ to bend upward at the interface between these two materials (at which a Schottky junction is formed). At the interface, electrons would flow “down” and holes “up” in the bent conduction band and valence band, respectively, as shown in energy band diagrams. Holes generated in AuNRs under visible light are thus unlikely to transfer to TiO₂. In contrast, hot electrons generated in AuNRs under visible light that overcome the Schottky barrier are likely to flow from AuNRs to TiO₂ and be available for photoreduction with TiO₂ acting as the electron-transfer medium.”

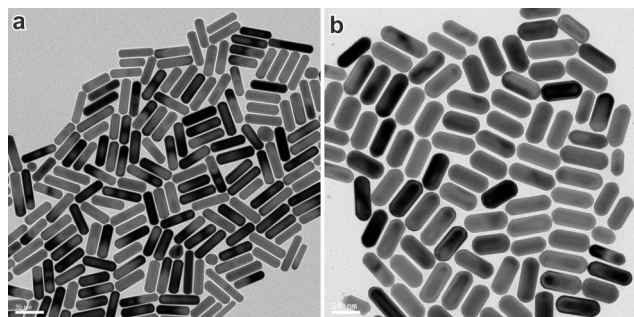


Figure S1. Typical TEM images of Au nanorods of (a) 15 nm (AuNR#1) and (b) 32 nm (AuNR#5) in diameter used in this research. Scale bars: 50 nm.

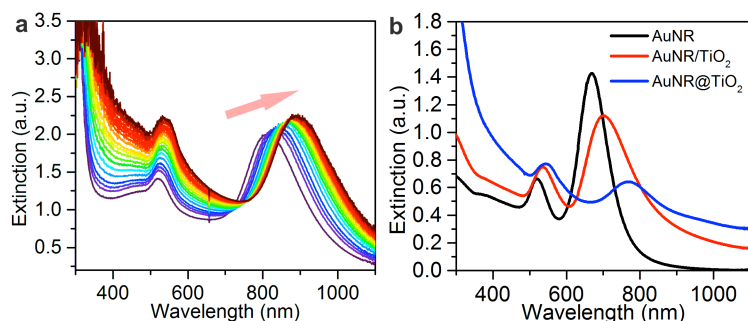


Figure S2. UV-Vis spectra: (a) Real-time monitoring of AuNRs (32nm in diameter, AuNR#6) reacting with the $\text{TiCl}_3\text{-NaHCO}_3$ deposition solution (including 13.9mM C_{16}TAB in the default procedure for nanodumbbell synthesis) from 30 seconds to 1800 seconds (peak red shifts along with increasing reaction time as indicated by the arrow, with evenly distributed time interval). Note that most of the absorption in <400 nm range is from the Ti species. (b) Aqueous solution of AuNR/ TiO_2 nanodumbbells and AuNR@ TiO_2 nanoparticles after cleaning and their corresponding AuNR seeds (AuNRs: 32 nm in diameter, AuNR#5).

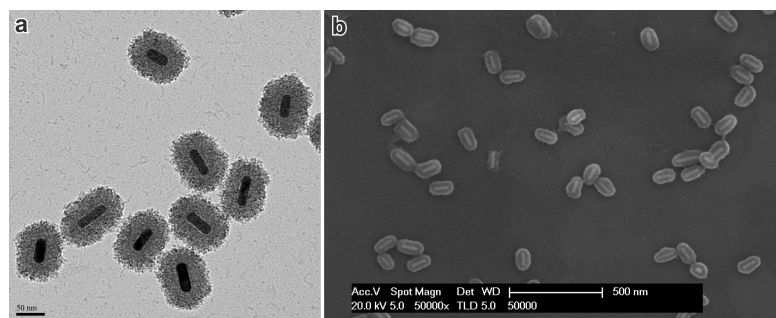


Figure S3. Typical (a) TEM and (b) SEM images of AuNR@ TiO_2 core/shell nanoparticles using SDS-capped AuNRs after exchanging C_{16}TAB with SDS. Scale bar in a: 50 nm.

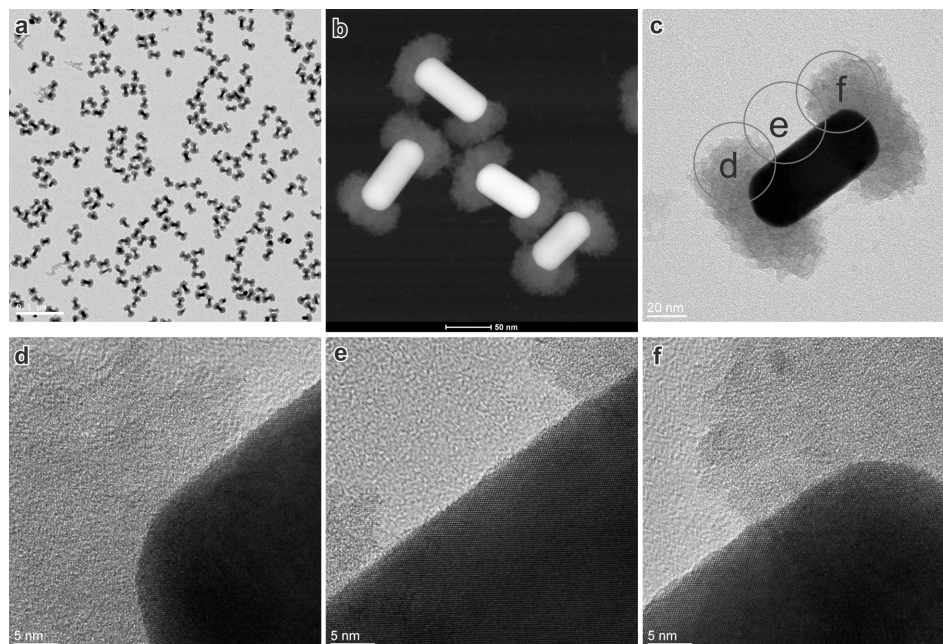


Figure S4. Extended (a,c) TEM, (b) STEM and (d-f) HRTEM images of AuNR/TiO₂ nanodumbbells shown in Figure 2 (AuNR: 32 nm in diameter, AuNR#5). (d-f) show corresponding HRTEM images from parts indicated in (c). Scale bars: a, 0.5 μm; b, 50 nm.

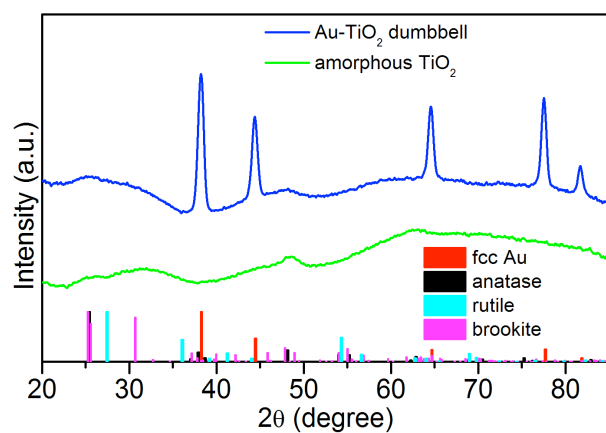


Figure S5. The XRD patterns of AuNR/TiO₂ nanodumbbells and AuNR-free amorphous TiO₂ samples. Both samples were obtained from similar hydrolysis process of TiCl₃. Amorphous TiO₂ was clearly observed in both cases, consistent with the similar preparation procedures.^{S3-5}

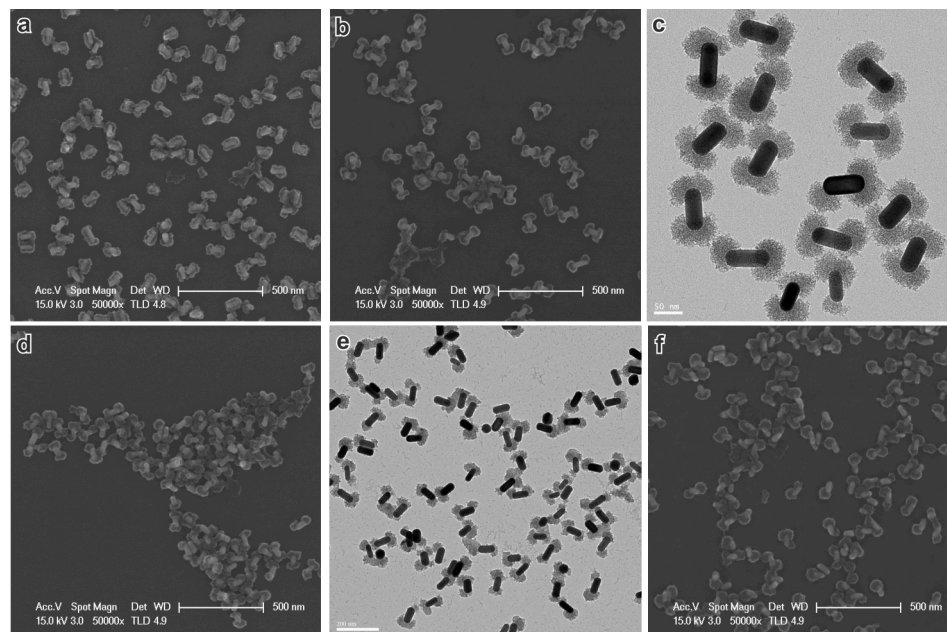


Figure S6. $C_{16}TAB$ concentration effect on TiO_2 caps of AuNR/ TiO_2 products synthesized with the same AuNR diameter (32 nm, AuNR#5), but different $C_{16}TAB$ concentrations: (a) no additional $C_{16}TAB$, (b) 5.54 mM, (c) 13.9 mM, (d) 27.7mM, (f) 49.9 mM, (e) 83.1 mM. Scale bars in c and e: 50 nm, 200nm, respectively.

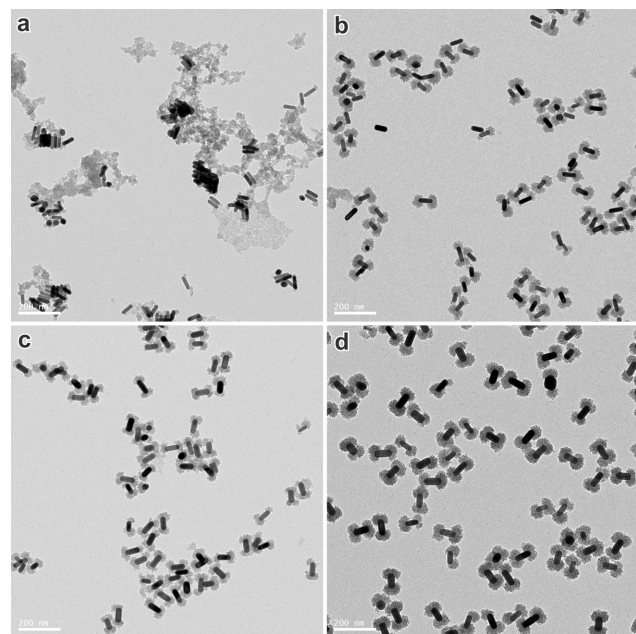


Figure S7. TEM images of AuNR/ TiO_2 products synthesized under similar conditions, with the same concentration of $C_{16}TAB$ (13.9 mM), but different AuNR diameters: (a) 15 nm (AuNR#1), (b) 22 nm (AuNR#3), (c) 27 (AuNR#4), (d) 32 nm (AuNR#5). All scale bars: 200 nm.

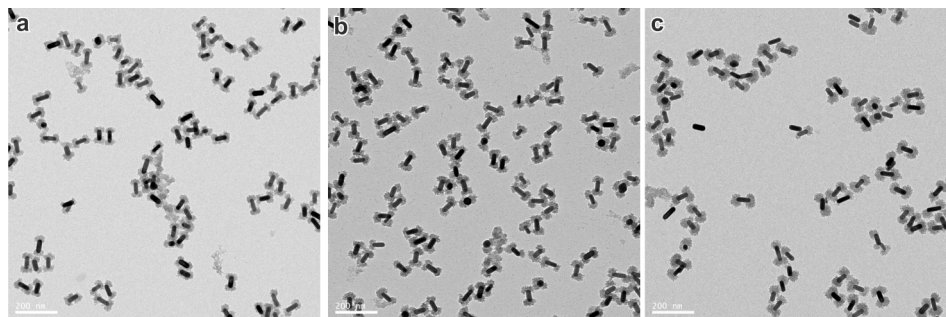


Figure S8. TEM images of AuNR/TiO₂ products using the same AuNRs (22 nm in diameter, AuNR#3) but different C_nTAB: (a) C₁₂TAB, (b) C₁₄TAB, (c) C₁₆TAB. Note that all C_nTAB mixtures have the same concentration (13.9 mM). All scale bars: 200 nm.

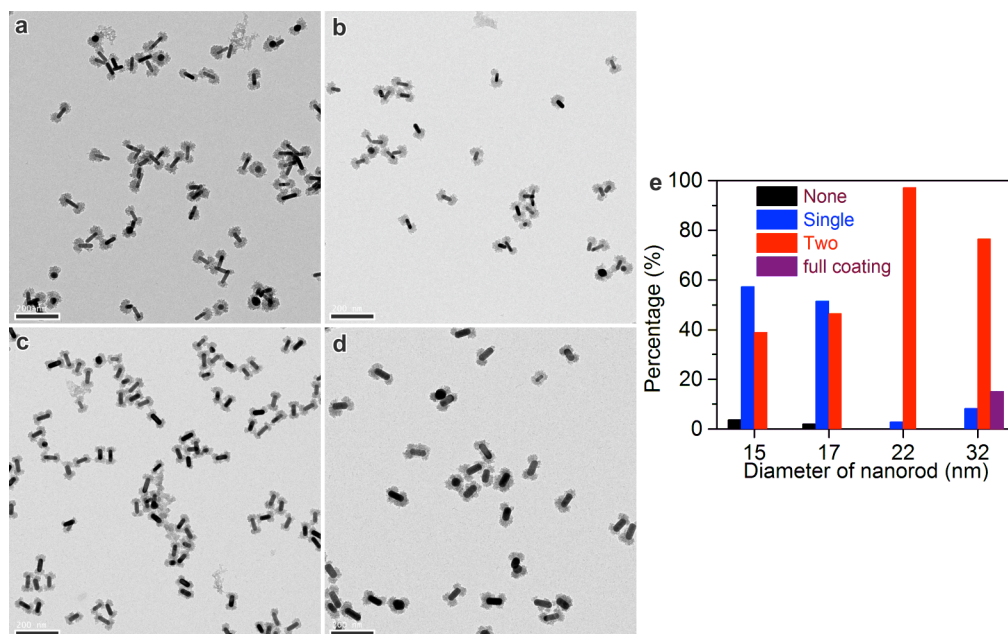


Figure S9. AuNR/TiO₂ products synthesized under similar conditions, with the same concentration of C₁₂TAB (13.9 mM), but different AuNR diameters: (a) 15 nm (AuNR#1), (b) 17 nm (AuNR#2), (c) 22 (AuNR#3), (d) 32 nm (AuNR#5). All scale bars: 200 nm.

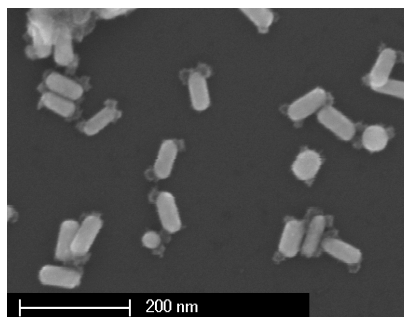


Figure S10. AuNR/TiO₂ product with TiO₂ on sharp corners of AuNR tips, prepared by using 1:1 mixed C₁₂TAB/C₁₆TAB (total concentration: 13.9 mM) in the default procedure for nanodumbbell synthesis. (AuNR: 32 nm in diameter, AuNR#5).

References

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