Highly enhanced fluorescence of fluorophores inside a metallic nanocavity

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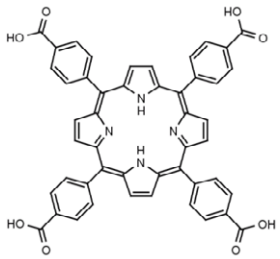
Supporting Information

Materials

All chemicals were obtained commercially and used without further purification. Titanium chloride ($TiCl_4$) was obtained from Fisher. Meso-tetra(4-carboxyphenyl) porphine (TCPP) was purchased from Frontier Scientific. Sodium citrate, sodium borohydride ($NaBH_4$) and hydrogen tetrachloroaurate ($HAuCl_4$, 99.99%) were obtained from Sigma-Aldrich. All chemicals, unless specified, were of reagent grade. Deionized water, with a resistivity greater than 18.0 MΩ·cm (Millipore Milli-Q system), was used in preparing the aqueous solutions. All glassware used in the experiments was washed with freshly prepared aqua regia (3:1 of HCl : HNO_3) and rinsed thoroughly in tap water first and then DI water prior to use.



TCPP

Figure S1. Molecular structure of TCPP.

Experimental

Preparation of colloidal TiO_2 nanoparticles

Stock solutions of TiO_2 colloidal were prepared by the hydrolysis of $TiCl_4$ as previously described.[S1,S2] In brief, 2.00 mL of 99.8% $TiCl_4$ at 0 °C was introduced under a stream of argon

into 300.0 mL of ice-chilled 0.10 M HCl solution under vigorous stirring. After 30 min stirring on a 0 °C ice-water bath, the solution was dialyzed against aqueous HCl (pH=2.3) using Spectra/Por membrane tubing of MW 6000–8000 cutoff pores. A transparent solution containing ~ 2.0 g/L TiO_2 at pH 2.3 was thus obtained. The solution was kept in the refrigerator around 4 °C and used within 3 months.

Preparation of colloidal TCPP-TiO_2 nanoparticles

TiO_2-TCPP nanoparticles were prepared by mixing 2.60 mg of TCPP with 10.00 mL of 0.20 g/L colloidal TiO_2 solution (pH=2.3) for 3 days under vigorous stirring, while kept in dark to avoid photocatalytic decomposition of TCPP. Excessive TCPP molecules were then separated from the aqueous phase as precipitate after centrifugation since they are not soluble in pH 2.3 solution.

Formation of Ag nanoshell onto TiO_2-TCPP

Sodium citrate-stabilized Ag nanoshell on the TiO_2-TCPP nanoparticle surface was prepared by $NaBH_4$ reduction of $AgNO_3$. Briefly, 1.0 mL of 25 mM aqueous sodium citrate solution was added to 10 mL of a 0.20 g/L TiO_2-TCPP. Next, 1.0 ml of 10 mM aqueous $AgNO_3$ solution was mixed thoroughly with the above solution. It is worthwhile to notice that Ag^+ could be adsorbed to TiO_2-TCPP surface due to the surface charge and extremely small Ag nanoparticles could form on the TiO_2-TCPP surface. Lastly, after one hour, a total of 0.20 mL of 0.05 M freshly prepared aqueous $NaBH_4$ solution was added dropwise under vigorous stirring, giving rise to a yellowish brown solution.

Determination of the concentration of colloidal TiO_2 nanoparticles

Colloidal TiO_2 nanoparticles prepared by our method usually result in an average diameter of less than 3 nm.[S2] Molecular TiO_2 concentration was determined by spectraphotometric measurement at 215 nm using molar extinction coefficient 6050 $M^{-1}cm^{-1}$.[S3] In these cases, TiO_2 concentrations are reported in terms of TiO_2 particles (C_{TiO2} particles, molarity) for better reflecting the experimental conditions. The nanoparticle concentration is calculated according to Equation (1) using a TiO_2 density (d_{TiO2}) of 4 g/cm^3 and an average diameter (ϕ_{TiO2}) of 3 nm.

$$C_{TiO_2\ particles,\ molarity} = \frac{\frac{C_{TiO_2,\ g/L}}{d_{TiO_2,\ g/cm^3}}}{\frac{4}{3}\pi(\frac{\phi_{TiO_2}}{2}\times 10^{-7}\ nm)^3} \Big/ 6.02\times 10^{23} \qquad (1)$$

Extinction spectra and fluorescence measurements

Extinction spectra were measured by a Shimadzu 2550 Spectrophotometer (Shimadzu Corporation Japan) using the quartz cuvette with a 1-cm optical path length in the range from 200 to 800 nm at room temperature. Fluorescence spectra were recorded with a fluorescence spectrophotometer from Photon Technology International in the range of 460 to 800 nm, and the samples were excited at 416 nm. The respective spectra are shown in Figures S2 and S3.

Determination of the concentration of TCPP in TiO_2-TCPP complex

The as-prepared TiO_2-TCPP solutions are very stable at pH 2.3. The extinction coefficient of TiO_2-TCPP at 416 nm in pH 2.3 aqueous solution was determined by spectraphotometric measurement at 416 nm using molar extinction coefficient $6.8\text{x}10^4$ M^{-1} cm^{-1}.[S2] The amount of

TCPP chemisorbed on TiO_2 surface is therefore determined at 416 nm according to Beer's law using $\varepsilon_{416\ nm} = 6.8x10^4\ M^{-1}\ cm^{-1}$. By adjusting the ratio of TiO_2 to TCPP in the formation of TiO_2-TCPP complex, we can control the average number of TCPP molecules per TiO_2 particle.

TEM, EDX and PSA characterizations of TiO_2-TCPP/Ag-shell nanoparticles

TEM and EDX results are the other evidences to support the formation of TiO_2-TCPP /Ag-shell nanostructures. A drop of well-sonicated solution containing the nanoparticles was deposited on a Formvar-covered carbon-coated copper grid (Electron Microscopy Sciences, PA). The samples were allowed to dry at room temperature overnight. A JEOL 2010 high-resolution transmission electron microscope (HRTEM) was used to obtain the TEM images and EDX spectra at 200 kV.

Particle size analysis measurements were carried out with a Nanotrac particle size analyzer (PSA) from Microtrac Inc based on dynamic light scattering. The average values of the particle size and polydispersity, defined as a relative width of the size distribution, were determined from the PSA measurements. Figure S4 shows the typical TEM images and PSA histograms of the (a, b) TiO_2, (c, d) TiO_2-TCPP, (e, f) Ag-TiO_2-TCPP and (g, h) Ag-TiO_2-TCPP. It can be seen that the colloidal TiO_2 nanoparticles are rather uniform, with particle size about 3.2 nm. After the adsorption of TCPP and coating with extra TiO_2 layer, the particle sizes increase to 7.0 nm. Next, with the coating of Ag nanoshells, the particle sizes increase to ~12 nm and 20.1 nm. PSA results show the particle sizes and their distributions of TiO_2, TiO_2-TCPP, and Ag-TiO_2-TCPP, all consistent with the TEM results.

EDX data collected on the nanoparticles in respective samples (Figure S5) clearly indicate the presence of the major elements expected in the final TiO_2-TCPP/Ag-shell nanoparticles.

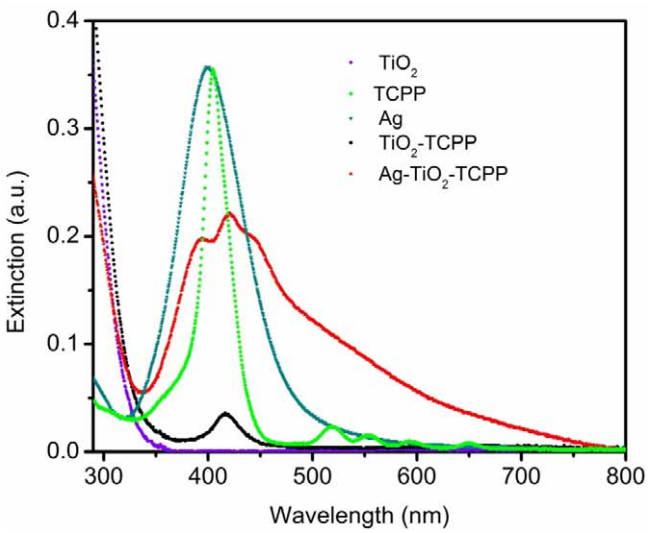


Figure S2. Extinction spectra of TiO_2, TCPP, Ag, TiO_2-TCPP and Ag-TiO_2-TCPP.

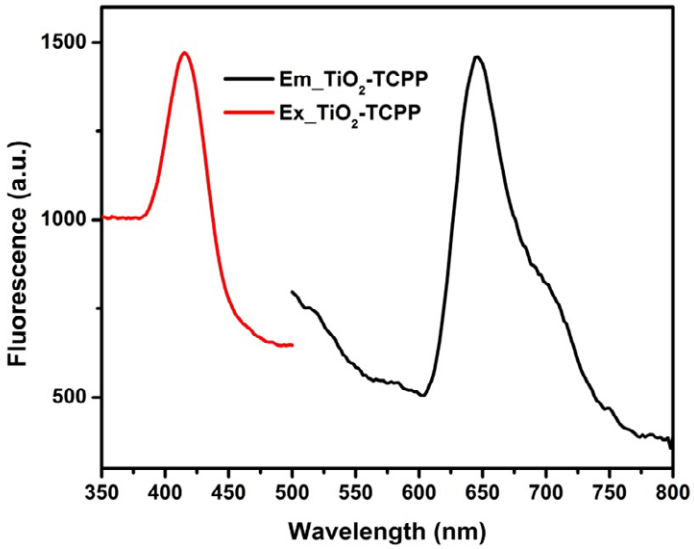


Figure S3. Fluorescence excitation and emission spectra of TiO_2-TCPP aqueous solution.

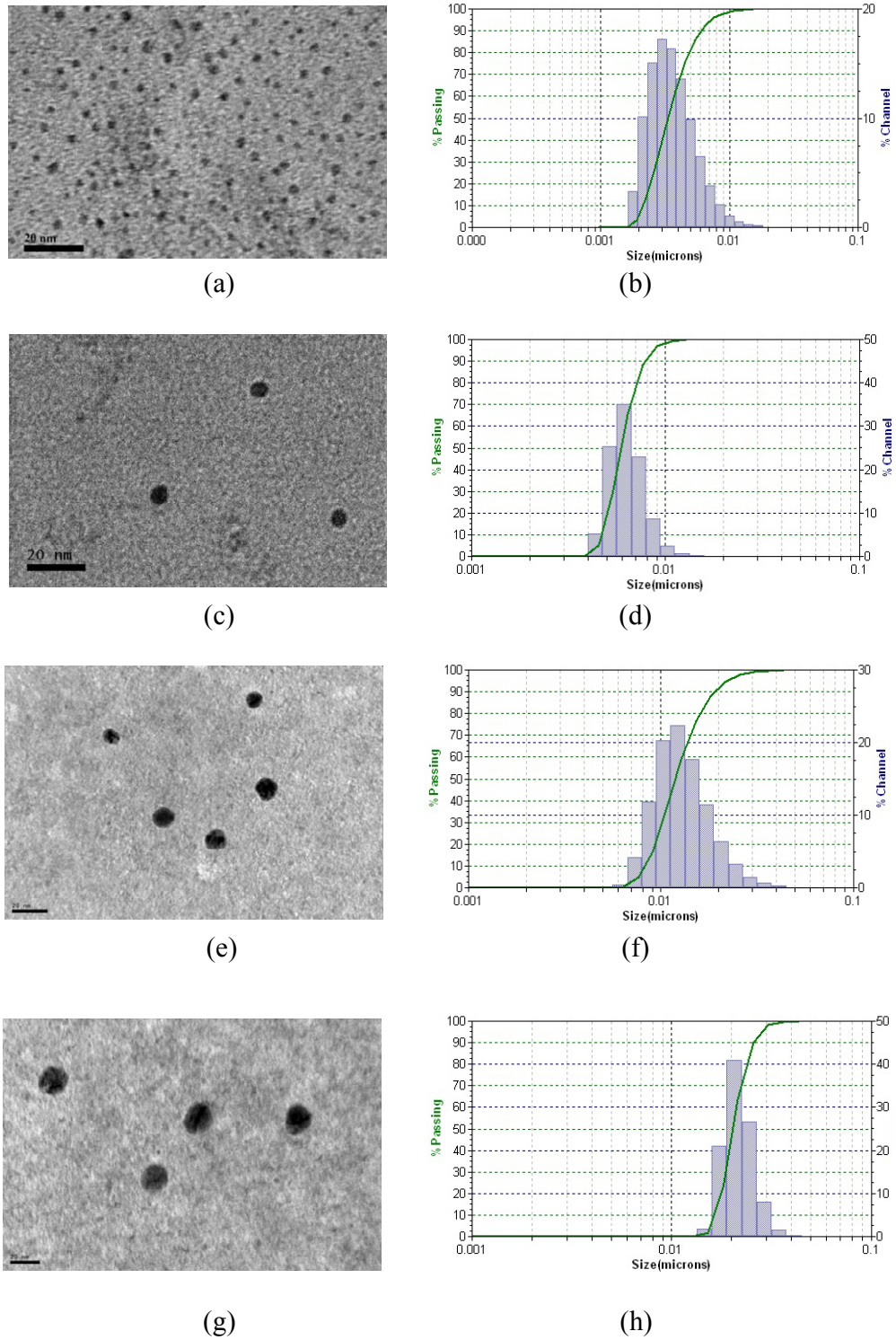
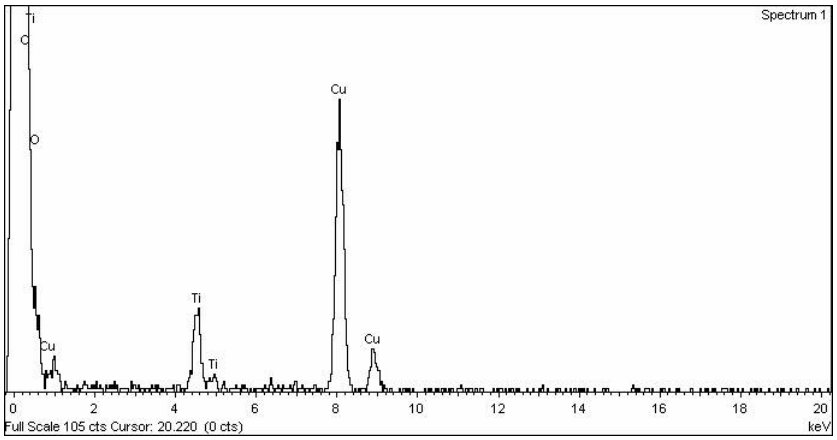
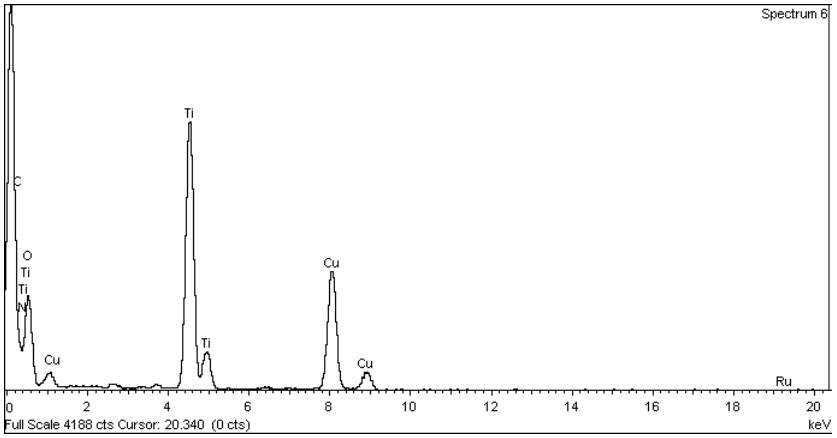


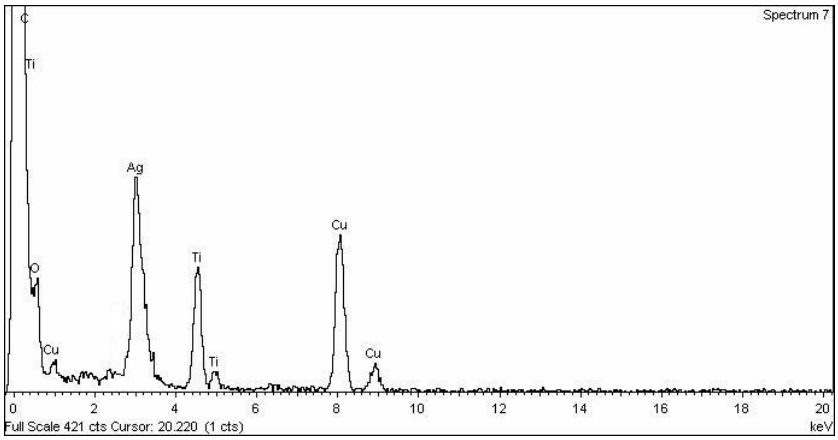
Figure S4. Typical TEM images and PSA histogram of (a, b) TiO_2, (c, d) TiO_2-TCPP, (e, f) Ag-TiO_2-TCPP and (g, h) Ag-TiO_2-TCPP. Scale bars: 20 nm.



(a)



(b)



(c)

Figure S5. EDX spectra of (a) TiO_2, (b) TiO_2- TCPP, (c) Ag-TiO_2-TCPP. Cu peaks are due to the TEM grid.

References:

[S1] Li, W.; Guo, Y.; Zhang, P. *J. Phys. Chem. C* **2010**, *114*, 7263.

[S2] Li, W.; Gandra, N.; Ellis, E,; Courtney, S.; Li, S,; Bulter, El; Gao, R. *ACS Appl. Mater. Interfaces*. **2009**, *1*, 1778.

[S3] Gao, R.; Safrany, A.; Rabani, J. *Radiat. Phy.s Chem.* **2002**, *65*, 599.