

Supporting information

**Nanoporous AuPt and AuPtAg alloy co-catalysts formed by
dewetting-dealloying on ordered TiO₂ nanotube surface lead to
significantly enhanced photocatalytic H₂ generation**

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Experimental section

➤ *Formation of TiO₂ tubes:* Titanium foils (Advent Research Materials, 0.125 mm thickness and 99.6+% purity) were cleaned by sonication in acetone, ethanol and deionized water for 10 minutes, followed by being dried under a N₂ gas stream. The spaced TiO₂ nanotubes were fabricated by anodizing cleaned titanium foils in triethylene glycol (TEG) electrolyte (consisting of 0.3 M NH₄F and 3 M H₂O) at 60 V for 1 h at 60 °C. The direct current potential was supported by a VLP 2403 pro, Voltcraft power supply. After anodization, the samples were immersed in ethanol for 2 h to remove organic remnants and then dried under a N₂ gas stream. These samples were annealed in air at 450 °C for 1 h (Rapid Thermal Annealer – Jipelec Jetfirst 100 – a heating and cooling rate of 30 °C min⁻¹).

➤ *Noble metal decoration:* Plasma sputtering deposition (Leica EM SCD500) was used to deposit Au, Pt and Ag on TiO₂ samples. The amount of sputtered metals was controlled by monitoring their nominal thickness using an automated quartz crystal film. The sputtering angle is 30°.

➤ *Thermal dewetting:* To form alloyed nanoparticles, metal-decorated TiO₂ tubes were annealed in Ar at 400 °C, 450 °C, 500 °C and 550 °C for 1 h.

➤ *Dealloying:* Dealloying was carried out in HNO₃ 63% at room temperature for 4 h.

➤ *Characterization of the structure:* Field-emission scanning electron microscope (FE-SEM Hitachi S4800) was employed to characterize the morphology of the TiO₂ samples. The chemical composition of the samples was examined by X-ray photoelectron spectroscopy (XPS, PHI 5600 US). X-ray diffraction (XRD) performed with a X'pert Philips MPD (equipped with a Panalytical X'celerator detector) using graphite monochromized Cu K α radiation ($\lambda=1.54056$ Å) was used to analyze the crystallographic properties of the samples. Transmission electron microscopy was carried out at a double-corrected FEI Titan³ Themis equipped with a SuperX detector. UV-Vis diffuse reflectance spectra (DRS) were recorded on

a LAMBDA 950 UV-vis spectrophotometer (Perkin Elmer, Beaconsfield, UK) with an integrating sphere (BaSO₄ standard white board was used as reference)

➤ *Photocatalytic measurements:* The photocatalytic H₂ generation experiments were carried out by irradiating with UV light (UV-LED smart Opsytec, 365 nm, 100 mW cm⁻²) for 2 h. The samples were immersed in an aqueous solution of ethanol (20 vol%) in a quartz tube cell which is sealed with a rubber septum. Before photocatalytic experiments, the quartz cell was bubbled with N₂ gas to purge O₂. 200 μL gas was extracted and analyzed by gas chromatography (GCMS-QO2010SE, Shimadzu) to examine the amount of photocatalytic H₂ production. The GC is equipped with a thermal conductivity detector (TCD), a Restek micropacked Shin Carbon ST column (2 m × 0.53 mm). GC measurements were conducted at a temperature of 45 °C (isothermal conditions) with the temperature of the injector setup at 280 °C and that of TCD at 260°C. The flow rate of the carrier gas (Argon) was 14.3 mL min⁻¹.

➤ *Photoelectrochemical measurements:* IPCE spectra were recorded at a constant potential of 0.5 V (vs. Ag/AgCl) with a potentiostat (Jaisle IMP83 PC-T-BC) in Na₂SO₄ aqueous solutions (0.1 M) under 200-800 nm light source (Oriol 6365 150 W Xe-lamp), while the wavelength was varied using a motor driven monochromator (Oriol Cornerstone 130 1/8 m). Incident photon to energy conversion (IPCE) values were calculated using $IPCE \% = (1240 * i_{ph}) / (\lambda * I_{light})$, where i_{ph} is the photocurrent density (mA cm⁻²), λ is the incident light wavelength (nm), and I_{light} is the intensity of the light source at each wavelength (mW cm⁻²).

Table S1. Atomic concentration (evaluated from EDS results) measured for samples decorated with Au (5 nm), Pt (5 nm) and Ag (30 nm) before and after dealloying in nitric acid.

	before dealloying (at%)	after dealloying (at%)	Loss of noble metals before and after dealloying (%)
Ti	64.90	59.63	
O	32.55	39.64	
Au	0.44	0.28	36.4
Pt	0.48	0.31	35.4
Ag	1.64	0.14	91.5

Table S2. Comparison of our porous AuPt/TiO₂ NTs photocatalyst with other promising TiO₂ photocatalysts

Catalyst	Amount	H ₂ generation rate	Light source	Scavenger
1 wt% PdAu/TiO ₂ NPs ¹	50 mg	19.6 mol kg ⁻¹ h ⁻¹	365 nm, 4×10 ⁷ photons/s	25 vol% glycerol
1 at% AuPt/TiO ₂ NTs ²	7 μm-long	21.26 mol kg ⁻¹ h ⁻¹	325 nm, 60 mW/cm ²	20 vol% ethanol
WO ₃ -Au-TiO ₂ NTs ³	200 nm-long	14.88 mol kg ⁻¹ h ⁻¹	325 nm, 40 mW/cm ²	20 vol% ethanol
Au-C ₃ N ₄ -TiO ₂ NPs ⁴	250 mg	0.35 mol kg ⁻¹ h ⁻¹	150 W Hg lamp	1 vol% methanol
0.15 at% Pt/TiO ₂ NPs ⁵	7 μm-long	18.71 mol kg ⁻¹ h ⁻¹	325 nm, 60 mW/cm ²	20 vol% ethanol
0.6 at% AuPt/TiO₂ NTs (this work)	3 μm-long (0.225 mg)*	27.38 mol kg⁻¹h⁻¹	365 nm, 100 mW/cm²	20 vol% ethanol

* The weight of TiO₂ nanotubular layers were calculated according to ⁶.

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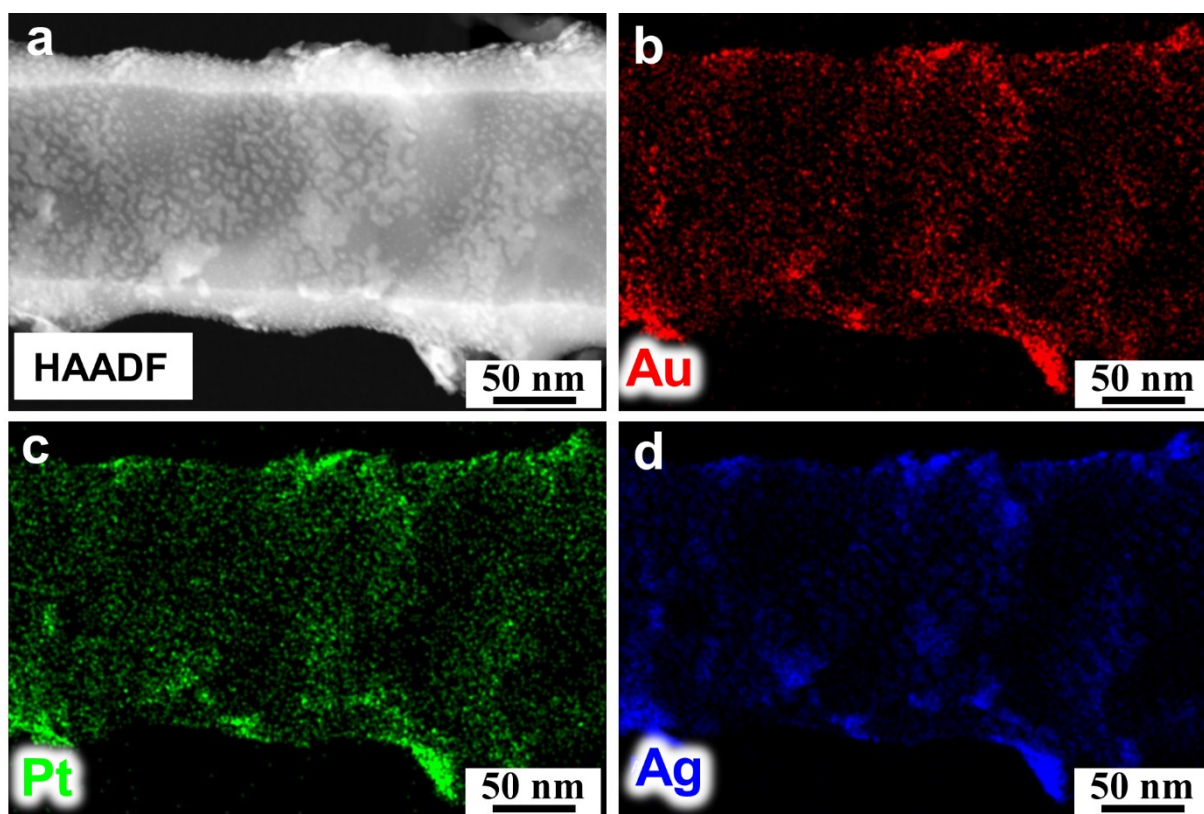


Figure S1. (a) HAADF image and (b-d) EDS mappings of TiO₂ nanotube after sputtering Au₁Pt₁Ag₆.

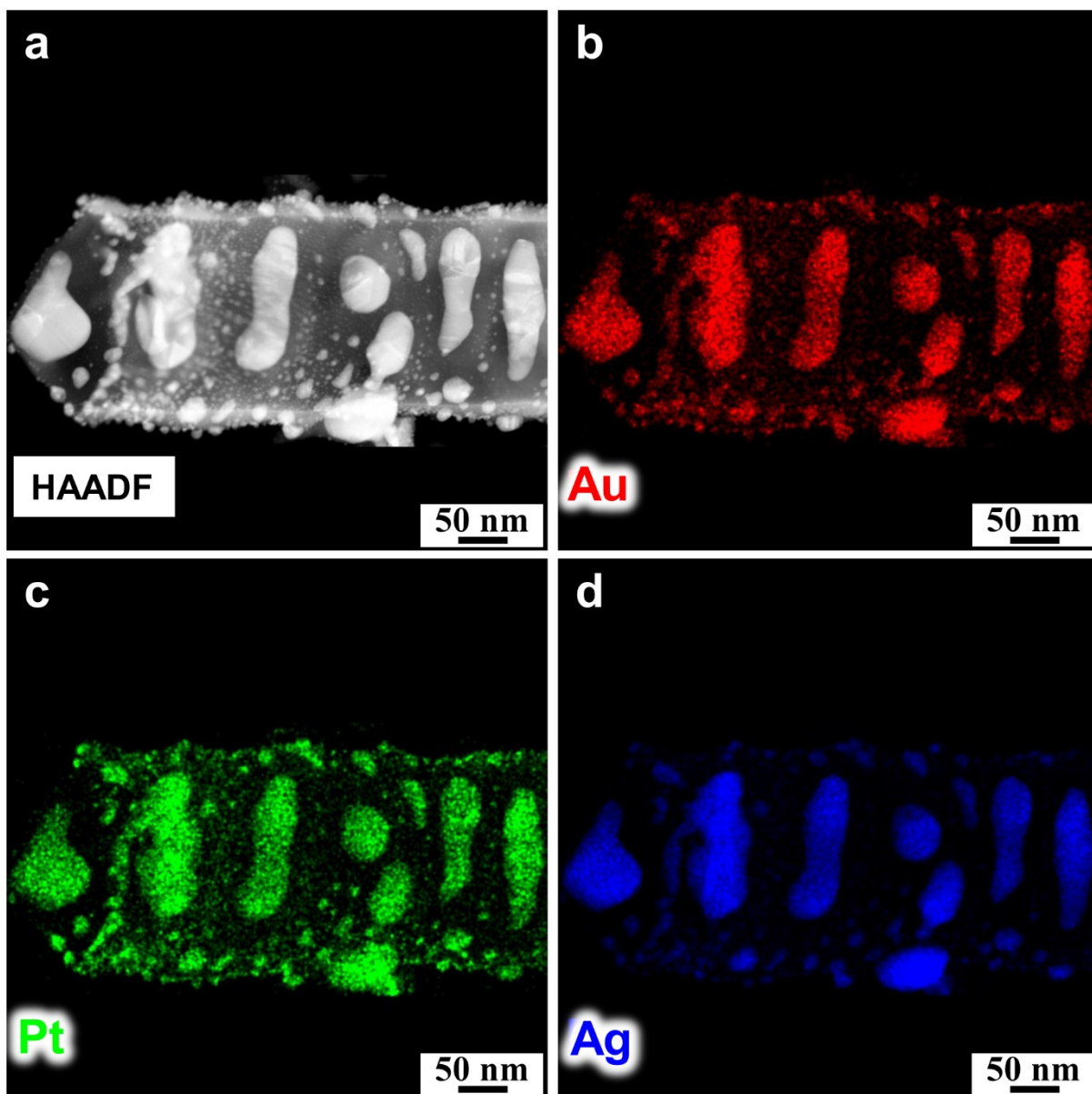


Figure S2. (a) HAADF image and (b-d) EDS mappings of TiO₂ nanotube after dewetting Au₁Pt₁Ag₆. Homogeneous AuPtAg alloyed nanoparticles are formed on the tube wall.

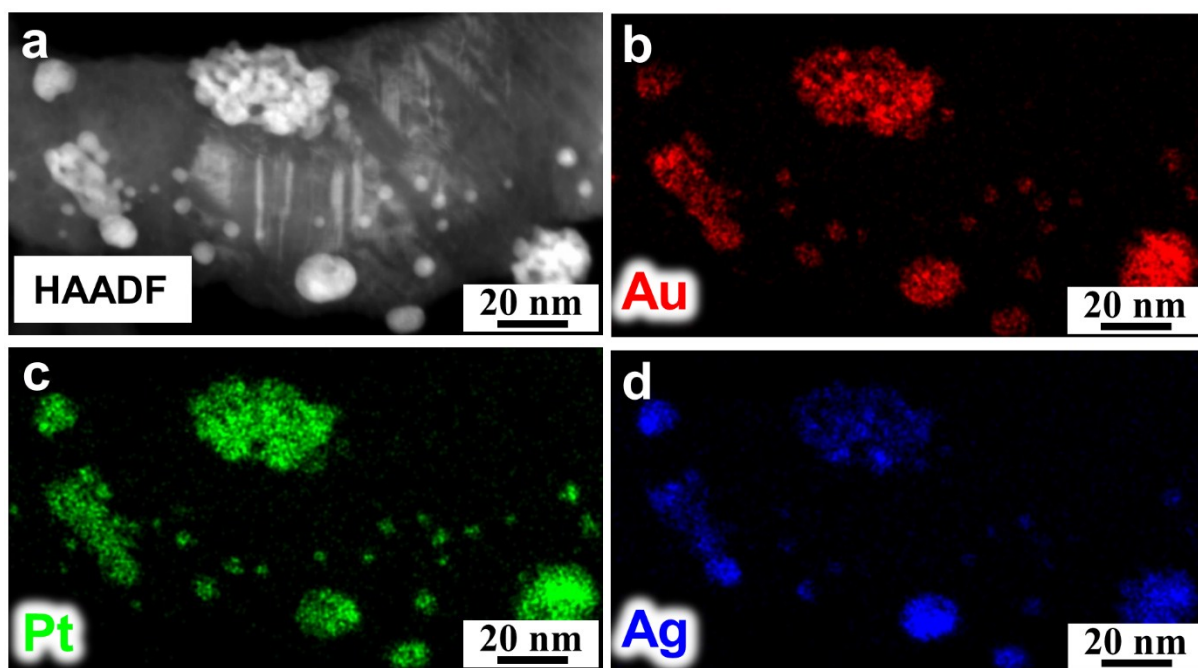


Figure S3. (a) HAADF image and (b-d) EDS mappings of TiO₂ nanotube after dealloying Au₁Pt₁Ag₆. Porous alloyed nanoparticles are formed on the tube wall.

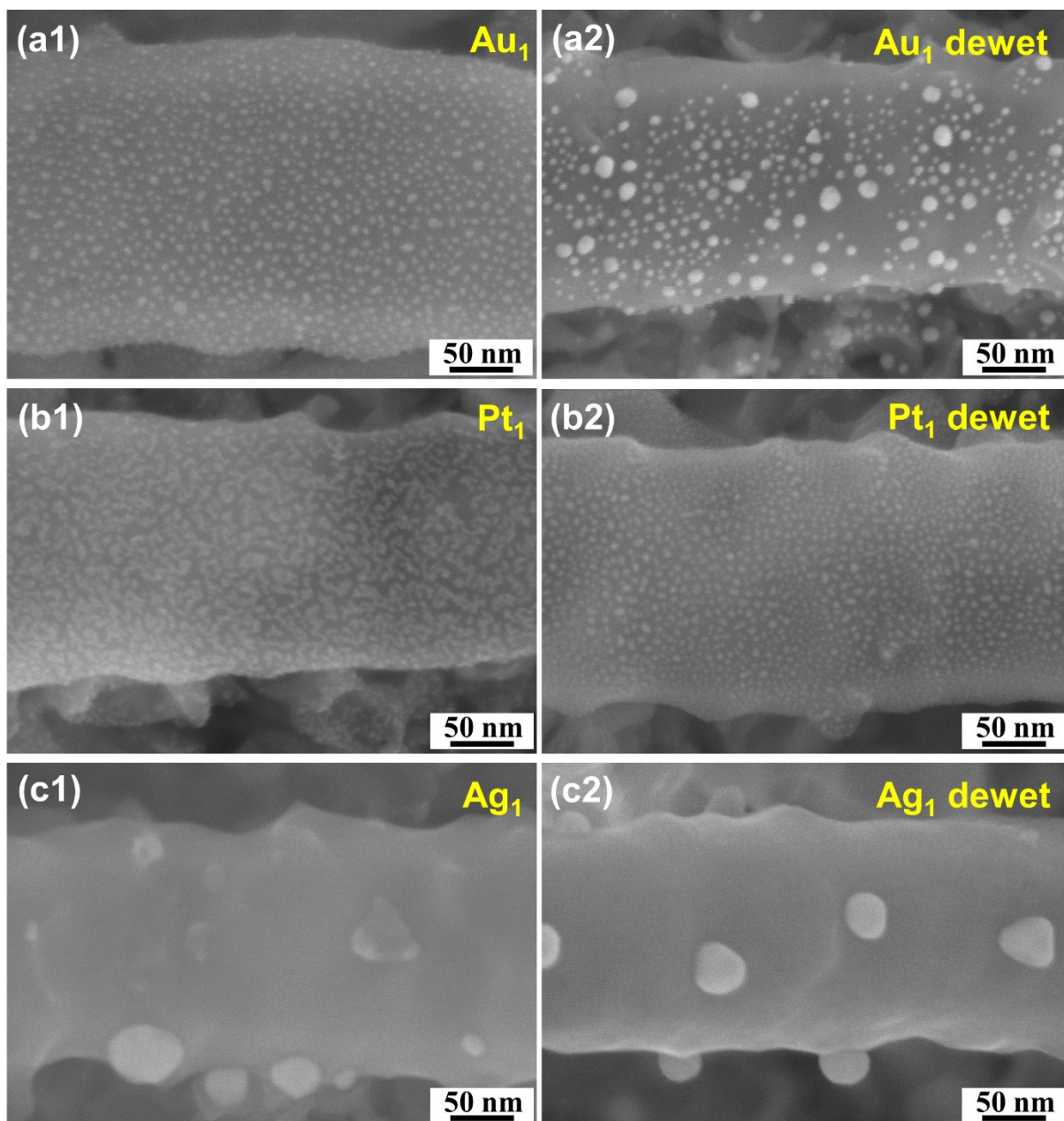


Figure S4. SEM images of TiO₂ nanotubes decorated with (a1,a2) 1 nm-thick Au; (b1,b2) 1 nm-thick Pt and (c1,c2) 1 nm-thick Ag. Samples (a2,b2,c2) were dewetted in Ar at 500 °C for 1 h.

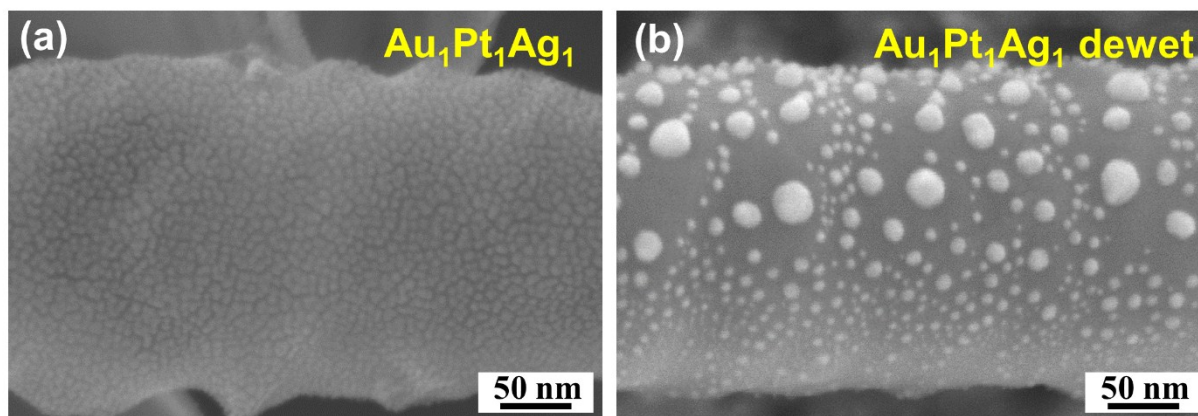


Figure S5. SEM images TiO₂ nanotubes decorated of 1 nm-thick Au, 1 nm-thick Pt and 1nm-thick Ag: (a) after sputtering and (b) after dewetting in Ar at 500 °C for 1 h.

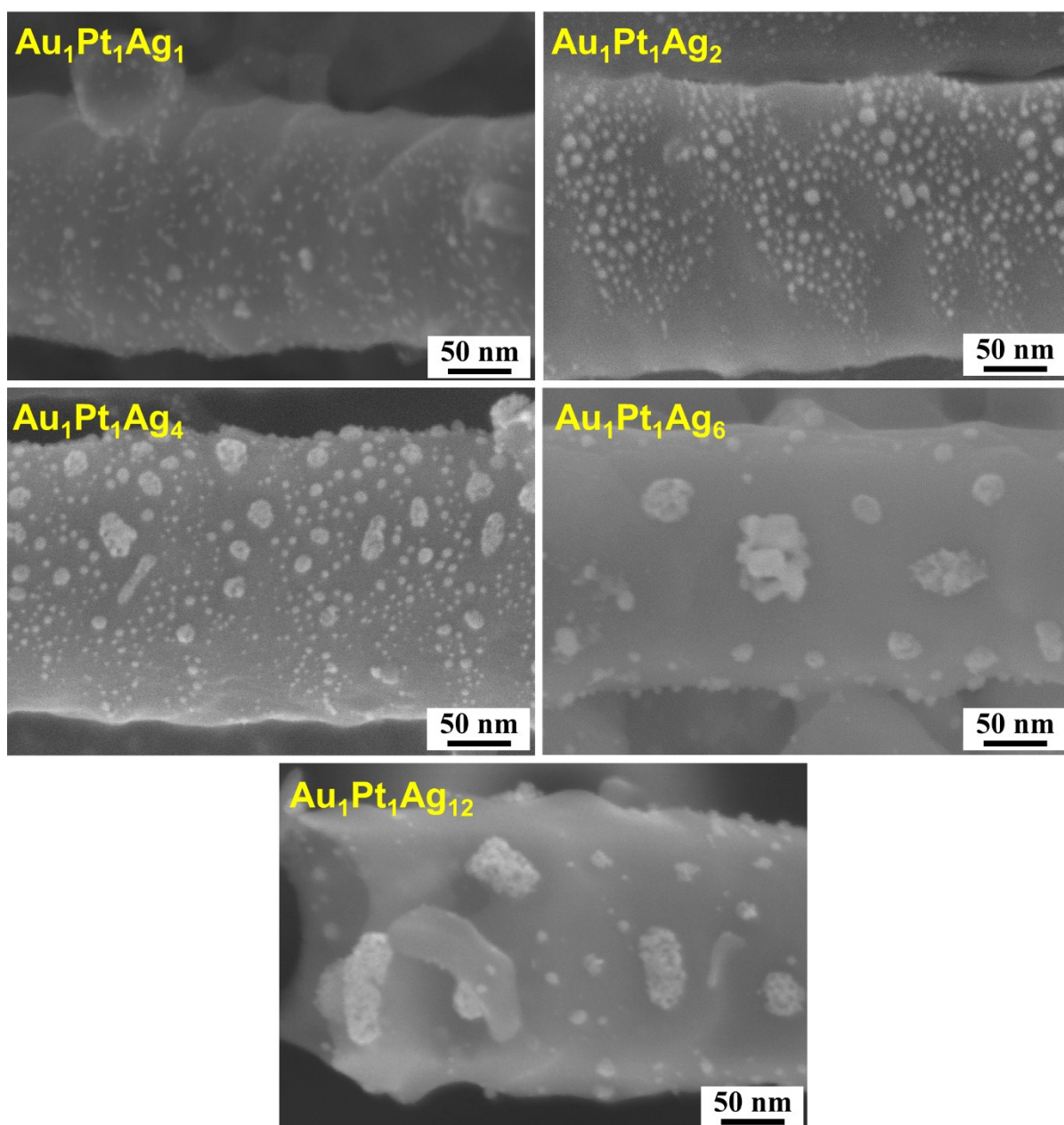


Figure S6. SEM images of porous AuPt alloy-nanoparticle-decorated TiO_2 nanotubes. All samples were sputtered with 1 nm-thick Au, 1 nm-thick Pt and different amounts of Ag (1, 2, 4, 6 and 12 nm-thick). The samples then were dewetted in Ar at 500 °C for 1 h, followed by a dealloying step in HNO_3 at 25 °C for 4 h.

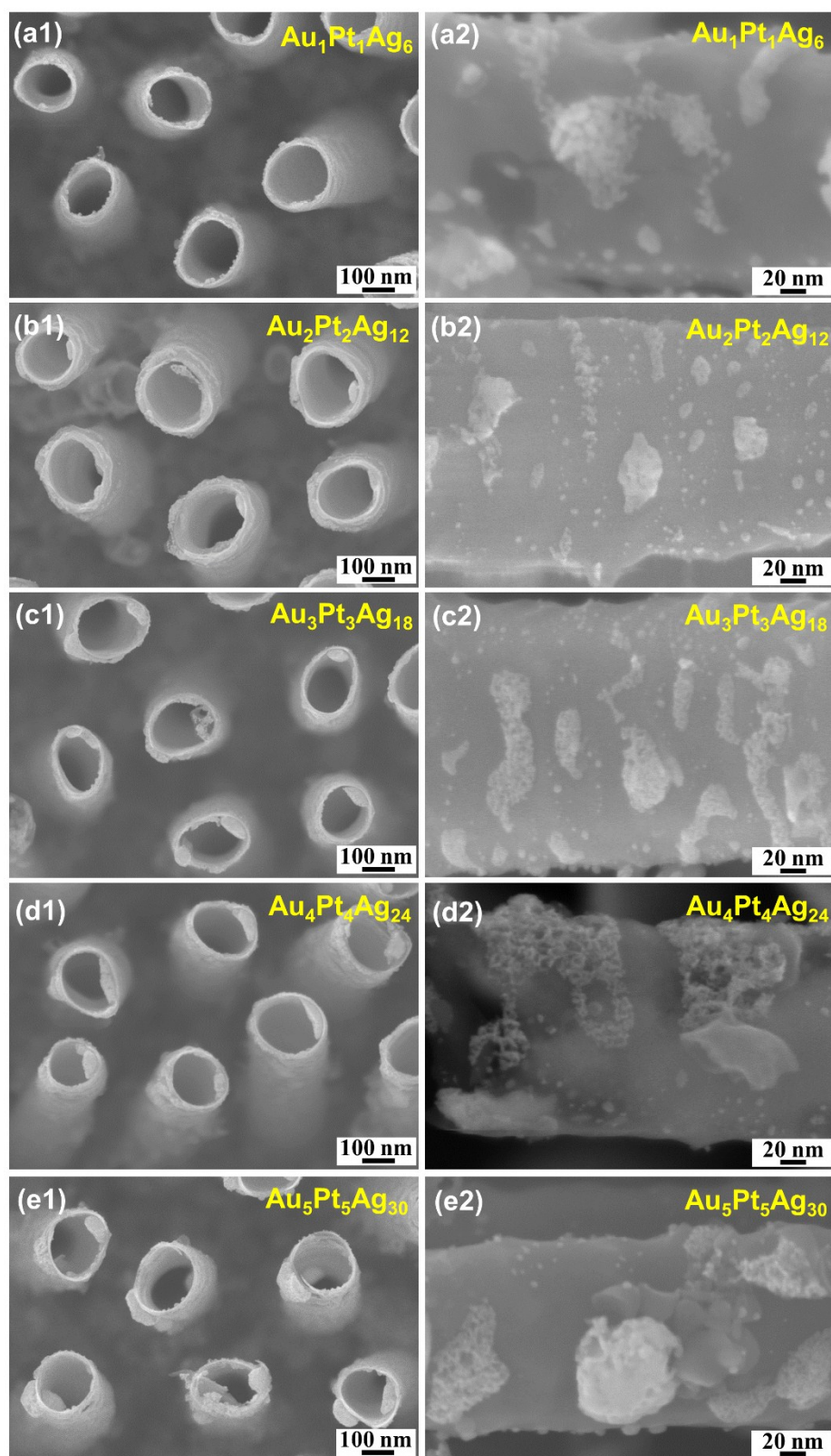


Figure S7. SEM images of porous AuPt alloy-nanoparticle-decorated TiO_2 nanotubes: (a1,a2) 1 nm-thick Au, 1 nm-thick Pt and 6 nm-thick Ag; (b1,b2) 2 nm-thick Au, 2 nm-thick Pt and 12 nm-thick Ag; (c1,c2) 3 nm-thick Au, 3 nm-thick Pt and 18 nm-thick Ag; (d1,d2) 4 nm-thick Au, 4 nm-thick Pt and 24 nm-thick Ag; (e1,e2) 5 nm-thick Au, 5 nm-thick Pt and 30 nm-thick Ag. All samples were dewetted in Ar at 500 °C for 1 h, followed by a dealloying step in HNO_3 at 25 °C for 4 h.

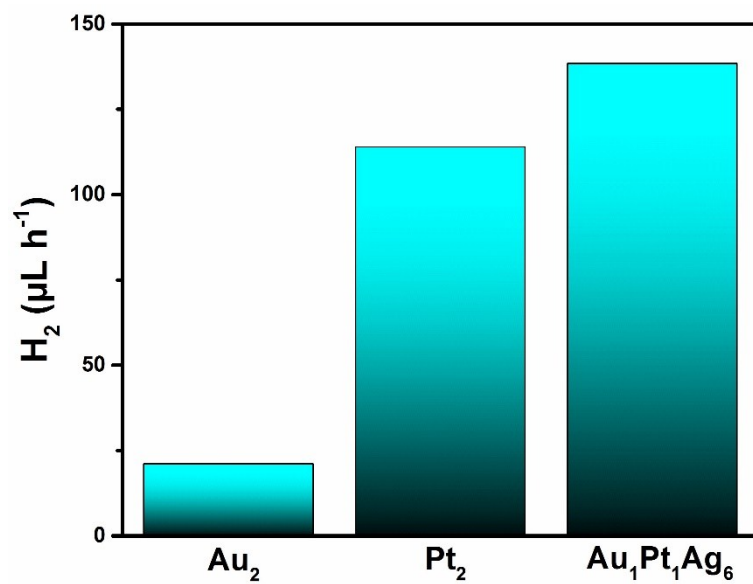


Figure S8. Photocatalytic H₂ generation of TiO₂ NTs decorated with 2 nm Au (Au₂), 2 nm Pt (Pt₂) and porous AuPt alloy particles (Au₁Pt₁Ag₆). After sputtering, plain Au and Pt decorated TiO₂ tubes were annealed at 500 °C in Ar to induce dewetting.

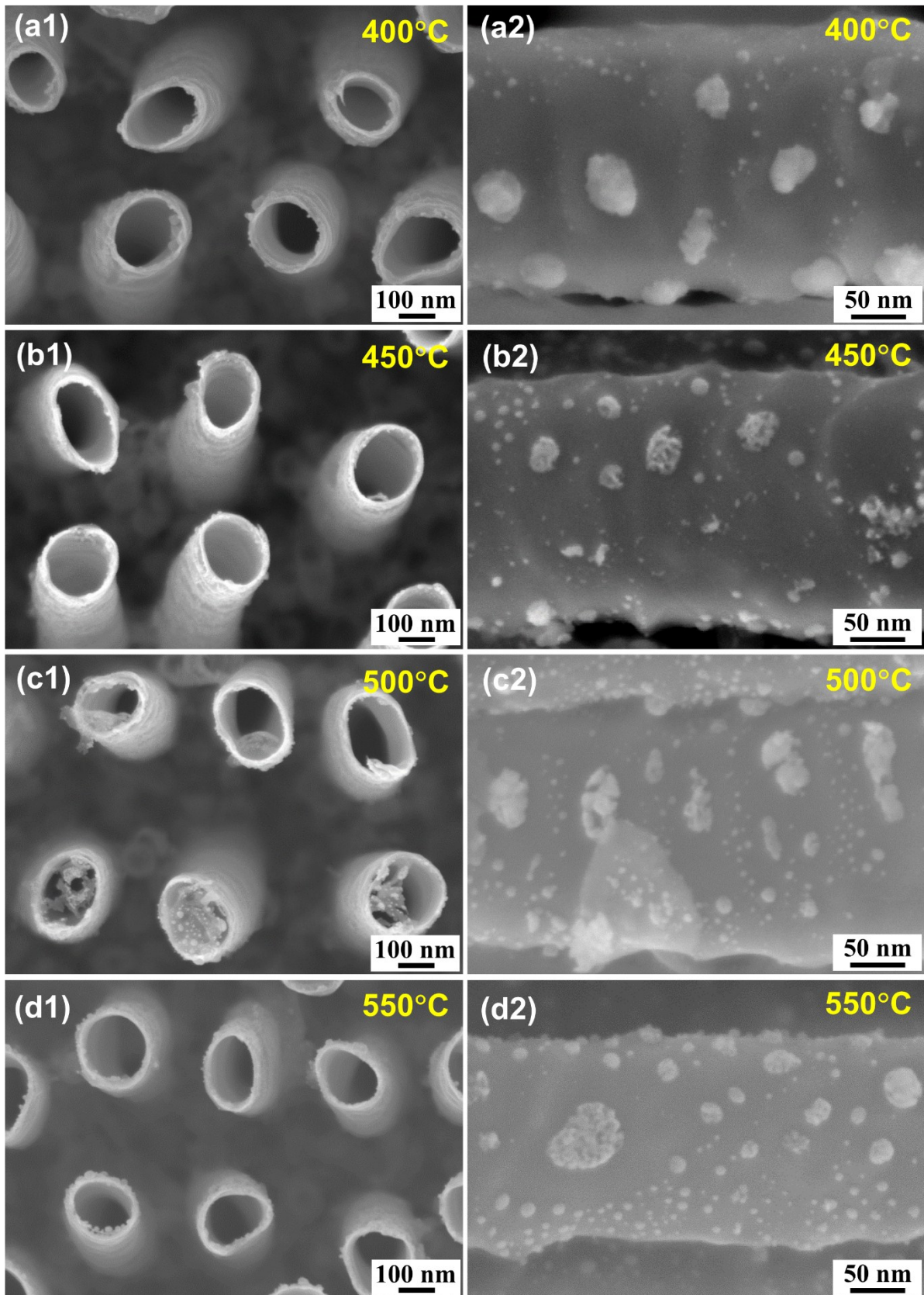


Figure S9. SEM images of TiO₂ nanotubes decorated with 1 nm-thick Au, 1 nm-thick Pt and 6 nm-thick Ag followed by a thermal dewetting in Ar for 1 h at different temperatures (a1,a2) 400 °C, (b1,b2) 450 °C, (c1,c2) 500 °C and (d1,d2) 550 °C. All samples were dealloyed in HNO₃ at 25 °C for 4 h.

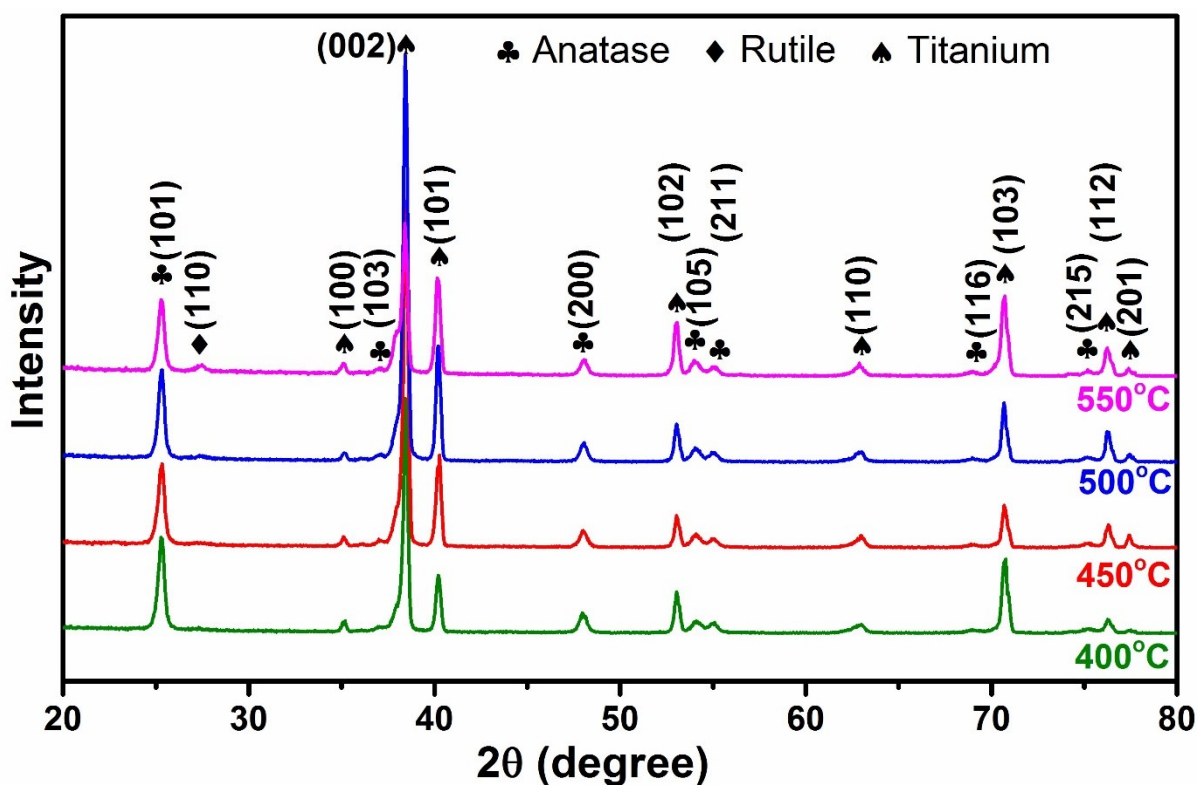


Figure S10. XRD patterns of TiO₂ nanotubes decorated with 1 nm-thick Au, 1 nm-thick Pt and 6 nm-thick Ag followed by a thermal dewetting process in Ar for 1 h at different temperatures: 400 °C, 450 °C, 500 °C and 550 °C. All samples were dealloyed in HNO₃ at 25 °C for 4 h.

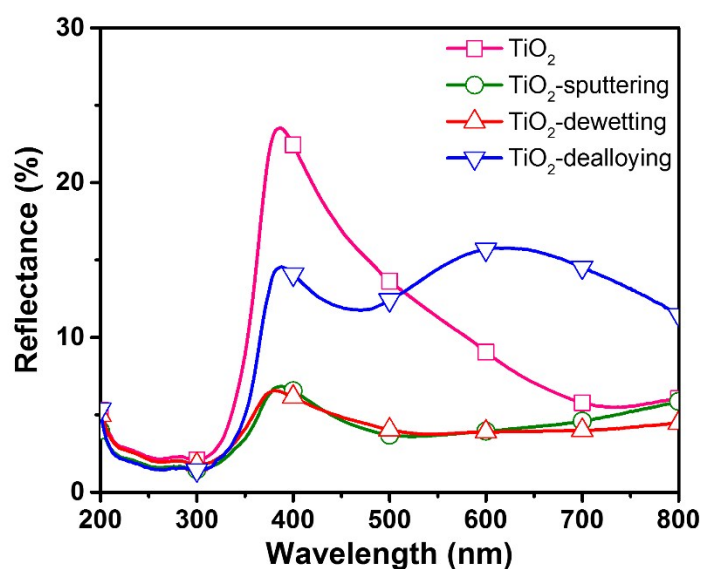


Figure S11. Reflectance measurements of TiO₂ NTs and Au₁Pt₁Ag₆-decorated TiO₂ NTs.

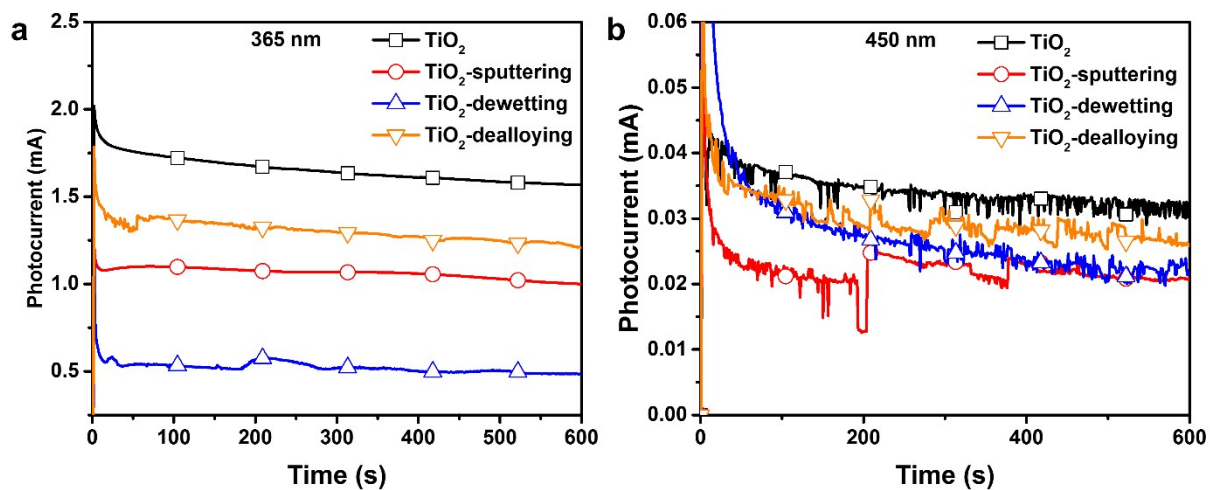


Figure S12. Photocurrent measurements of TiO_2 nanotubes and $\text{Au}_1\text{Pt}_1\text{Ag}_6$ -decorated TiO_2 NTs using a light source of: (a) 365 nm and (b) 450 nm.