

SUPPLEMENTARY INFORMATION

New insights into the influence of plasmonic and non-plasmonic nanostructures on the photocatalytic activity of titanium dioxide

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Experimental

Reagents:

Titanium dioxide – anatase (A-K-1, Tronox), anhydrous ethanol (POCh, 99,8%, pure for analysis), methanol (Sigma-Aldrich, for HPLC, >99.9%), terephthalic acid (Sigma-Aldrich, 98%), NaOH (POCh, pure), KNO₃ (Sigma-Aldrich, >99%), anhydrous LiClO₄ (Sigma-Aldrich, pure), acetonitrile ACN (Avantor, HPLC/MS grade), tetrabutylammonium perchlorate (TBAP) (Sigma-Aldrich), PdCl₂ (Aldrich, >99%), HAuCl₄ (Warchem, pure), HCl (POCh, ~37%) were used without further purification. Deionized water was obtained using Hydrolab HLP 10UV system (0.05 μS, t = 20°C).

Synthesis of TiO₂ with metallic nanostructures:

Metallic nanostructures were deposited on TiO₂ through photoreduction. Typically, 200 mg of titanium dioxide powder was added to the quartz reactor with 60 ml of deionized water and 0.8 ml of anhydrous ethanol under vigorous stirring. The reactor was placed in front of the Xe lamp (XBO 150 W, Instytut Fotonowy). Then, 20 ml of precursor solution (1 mmol/dm³) was added, and the suspension was irradiated for 60 s or 10 min. After irradiation, the suspension was washed several times with deionized water to remove possible residues of the precursor. Precursors of the metallic nanostructures were aqueous solutions of H₂[PdCl₄], HAuCl₄ or their mixture in a 1:1 volume ratio.

Characterization and spectroscopic analysis:

SEM analysis was performed on FEI HELIOS G4 (BSE, 5 kV) equipped with an EDS analyzer (Bruker). Silicon wafers were used as substrates for imaging.

Diffuse reflectance spectroscopy (DRS) spectra were recorded using Shimadzu UV-3600 UV–Vis–NIR spectrophotometer equipped with a 10 cm diameter integrating sphere. As the reference, BaSO₄ was used. Obtained spectra were subsequently normalized and transformed using the Kubelka-Munk and Tauc functions to visualize the changes in absorption spectra and determine the bandgap energy of the modified materials.

Photoelectrochemical and spectroelectrochemical measurements:

Photoelectrochemical measurements were conducted using a photoelectric spectrometer (Instytut Fotonowy) equipped with an XBO 150 W lamp as the light source. Three-electrode setup was applied with Ag/AgCl (in 3 mol/dm³ KCl) as the reference electrode, Pt wire as the counter electrode and ITO foil (Sigma-Aldrich, 60 Ω/sq) covered with a thin film of the examined material as the working electrode. The electrolyte was the aqueous KNO₃ solution (0.1 mol/dm³) deaerated with argon purged through the cell during the whole experiment. Potentials were changed from –200 to 800 mV with the 100 mV step, and wavelength was changed from 300 to 600 nm with the 10 nm step.

Spectroelectrochemical measurements were carried out using Shimadzu UV-3600 UV–Vis–NIR spectrophotometer and BioLogic SP-150 potentiostat in a three-electrode setup with the Ag/Ag⁺ reference electrode (0.01 mol/dm³ AgNO₃ and 0.1 mol/dm³ TBAP in ACN), Pt wire as the counter electrode and Pt foil covered with the examined material as the working electrode. A solution of LiClO₄ in ACN (0.1 mol/dm³) was used as the electrolyte. Potentials were applied in the range of 0 to –2.7 V vs. reference electrode with a step of 50 mV. The DRS spectrum of the sample before applying potential was the reference and new spectra were taken after 20 minutes of each potential application. The results were presented as the differences between the two last spectra ($\Delta(\Delta K M)$) at 780 nm *versus* potential.

Photocatalytic tests:

Tests with terephthalic acid:

Prepared materials were added to 14 ml of 3 mmol/dm³ solution of terephthalic acid in 0.1 mol/dm³ NaOH (1mg of photocatalyst per 1 ml of solution). Then the quartz cuvette with the suspension was irradiated with the XBO 150 W lamp equipped with an AM 1.5G filter for simulated solar light experiments or a cut-on filter ($\lambda > 420$ nm) for visible light. Then, the fluorescence of samples was measured at 5 min intervals. The maximum of the peak from generated hydroxyterephthalic acid was measured at 425 nm using a Perkin-Elmer LS-55 spectrofluorimeter.

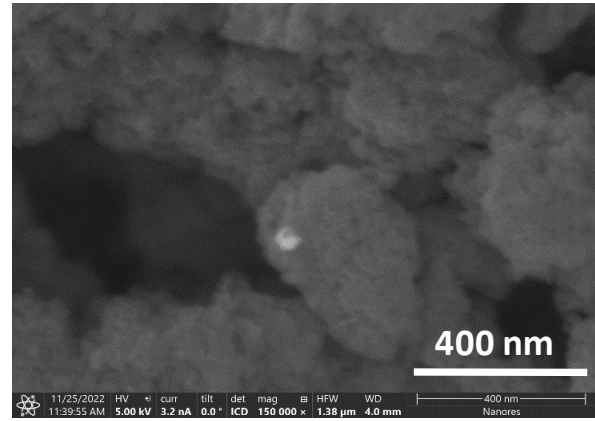
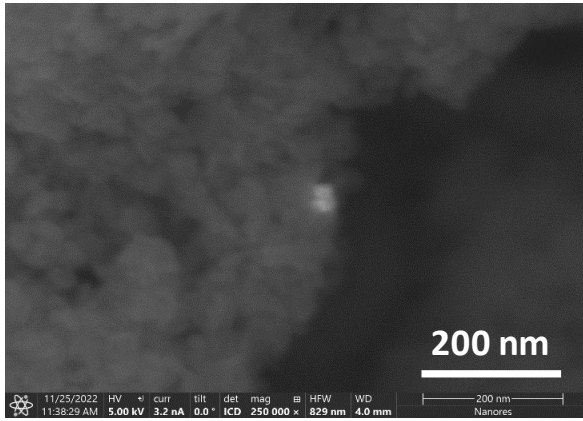
Tests of hydrogen evolution:

Photocatalysts were added to 10 ml of deionized water (1 mg of photocatalyst per 1 ml of solution). Subsequently, the suspension was deaerated by the stream of argon for 30 min and sealed tightly. Then the vial with the suspension was irradiated with the XBO 150 W lamp equipped with an AM 1.5G filter or a cut-on filter ($\lambda > 420$ nm). The hydrogen amount was detected with the gas chromatograph Thermo TRACE-1300 (Thermo-Scientific).

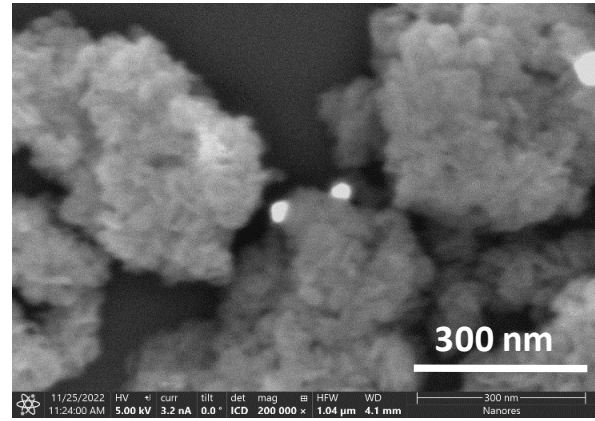
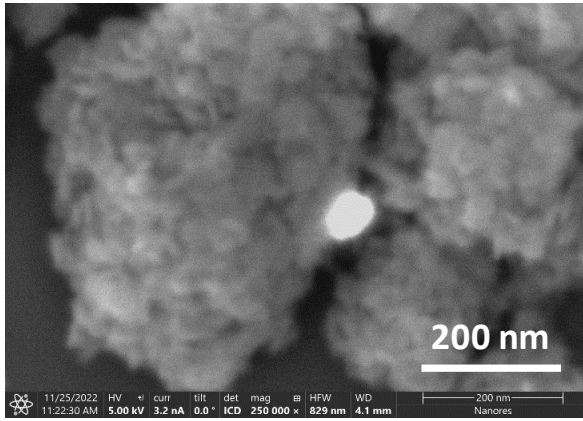
Tests with methanol were performed in the same way, but additionally, 100 μ l of methanol was added to the suspension and then the mixture was deaerated.

A)

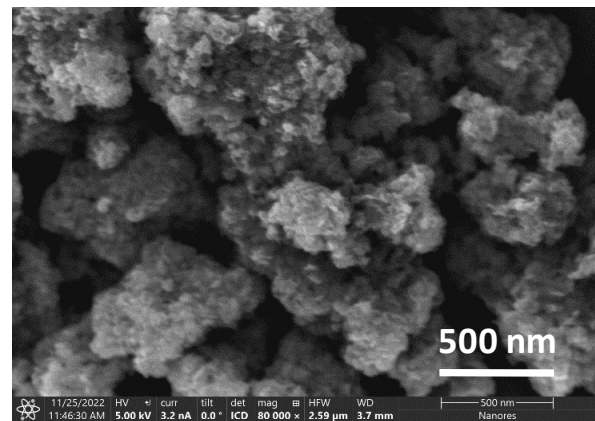
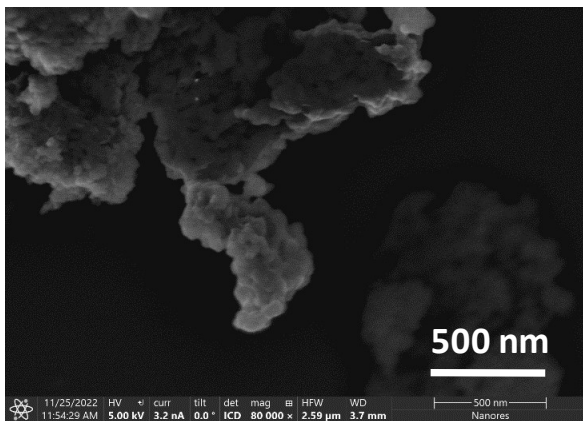
A60sPd



A60sAu



A60sAuPd



B)

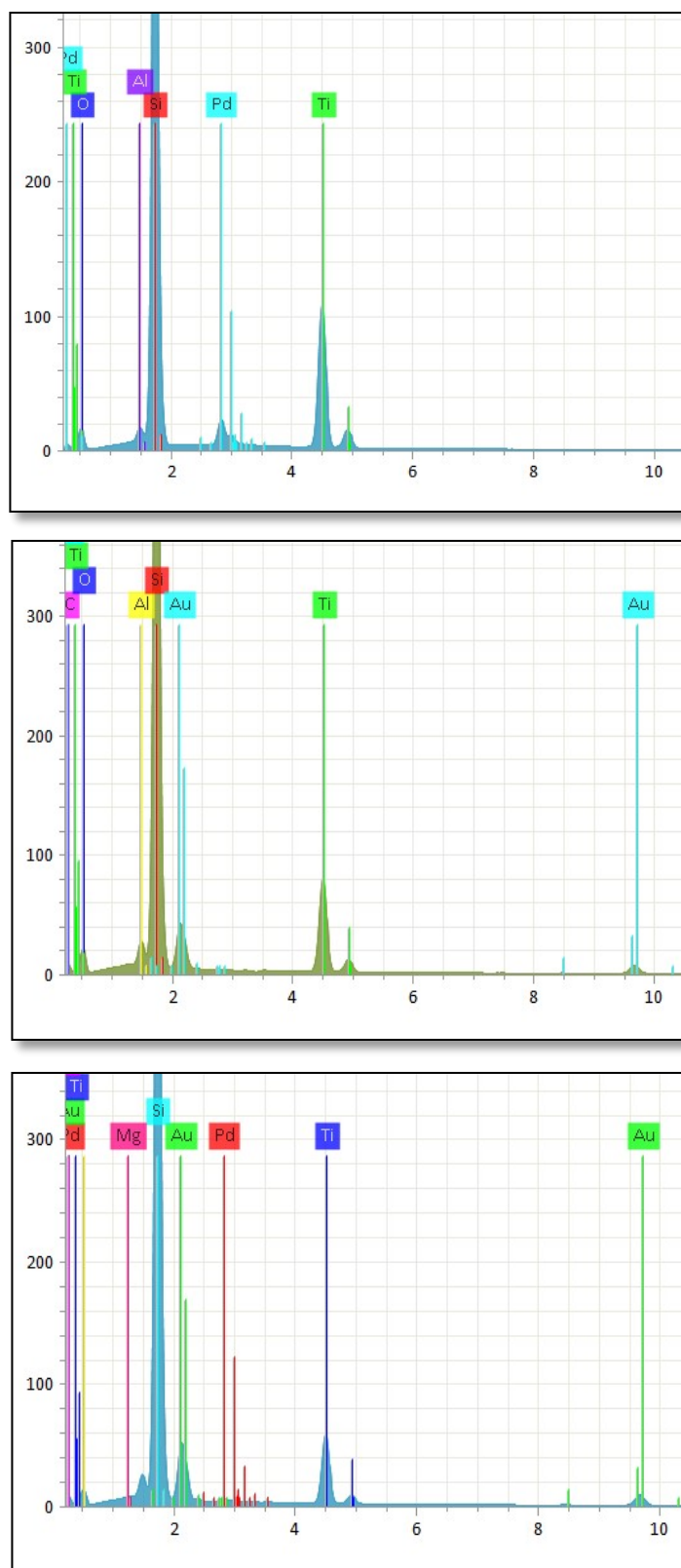


Fig. S1. SEM images of the TiO_2 with noble metals after 60 s photodeposition (A). EDS spectra taken for the modified samples (B).

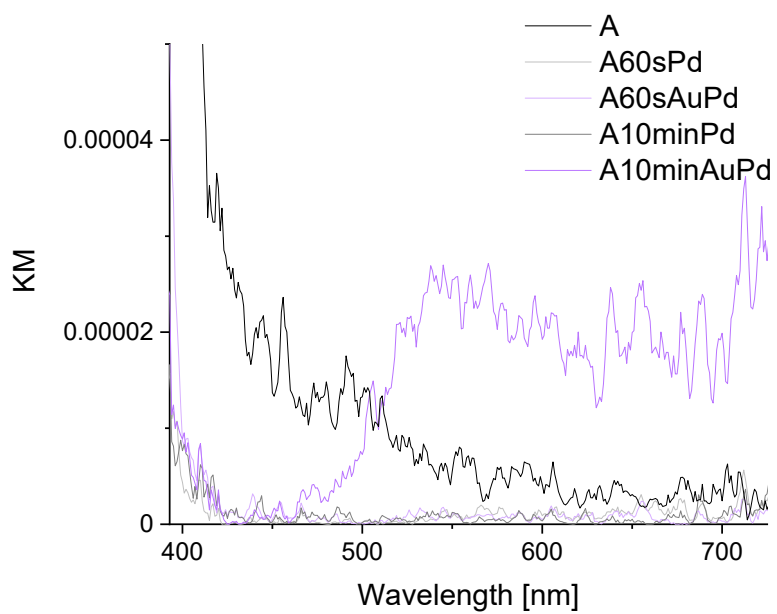
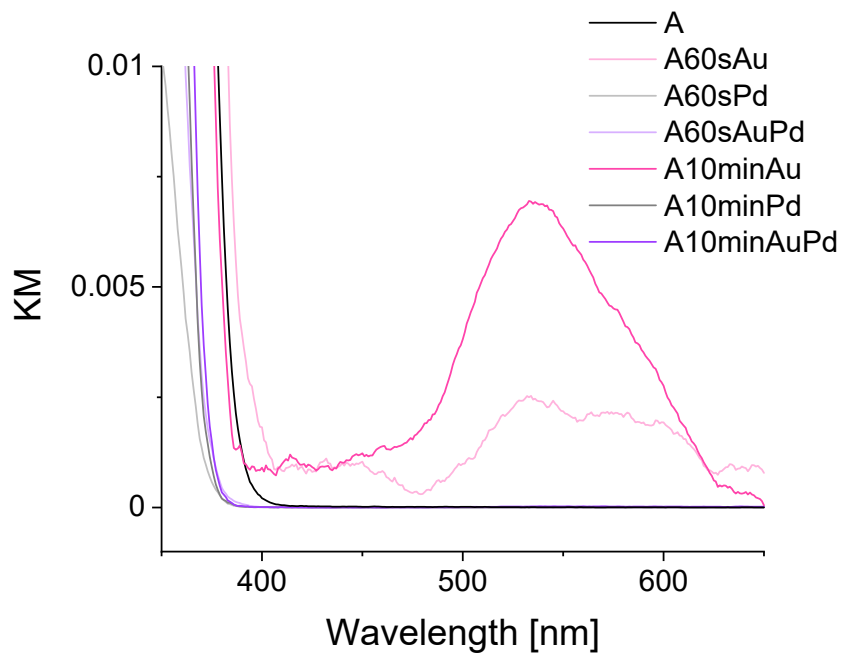


Fig. S2. Magnifications of DRS spectra of modified composites presenting SPR bands.

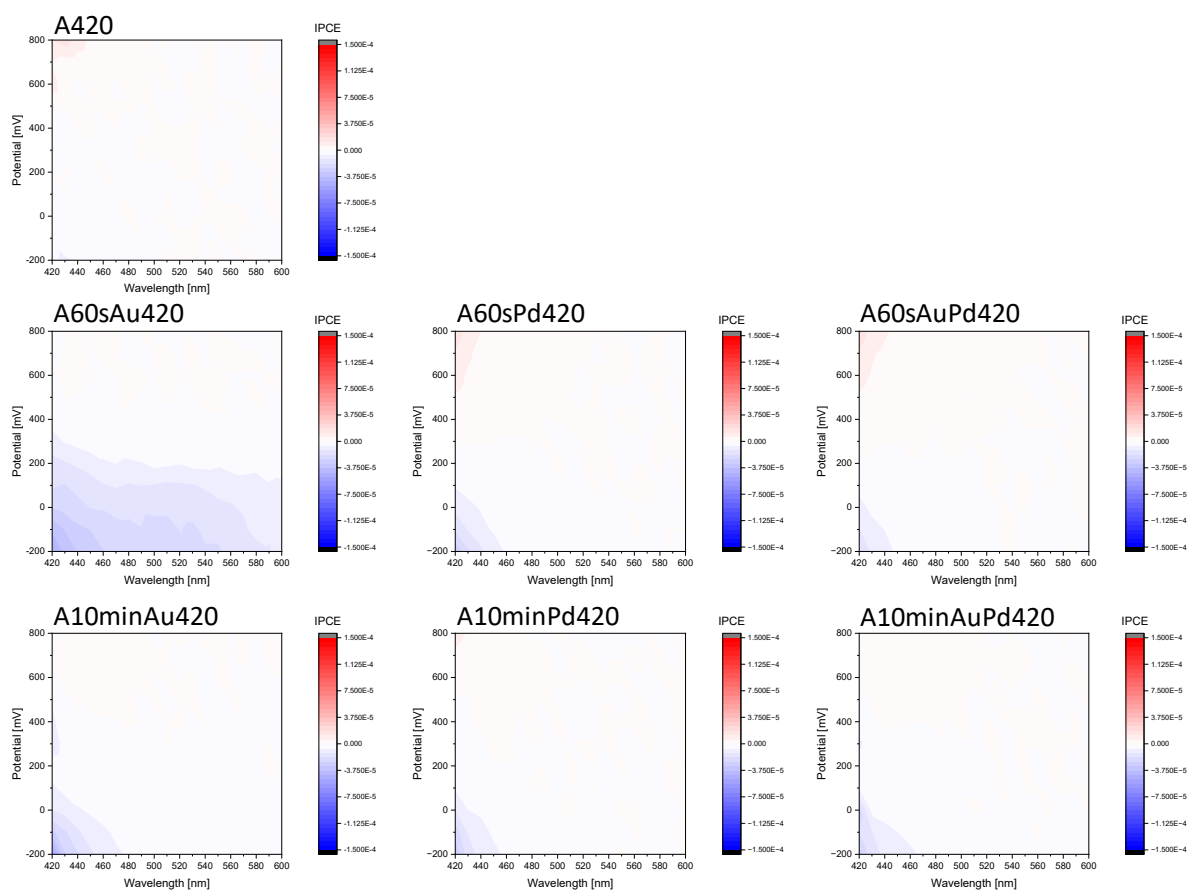


Fig. S3. IPCE maps in the range of visible light (420-600 nm).

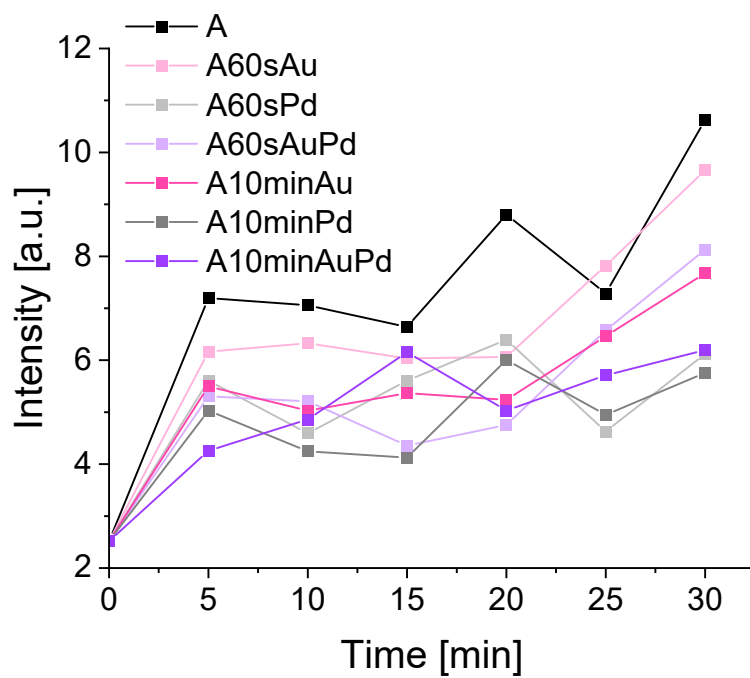


Fig. S4. Photocatalytic tests with terephthalic acid upon visible light irradiation ($\lambda > 420$ nm).

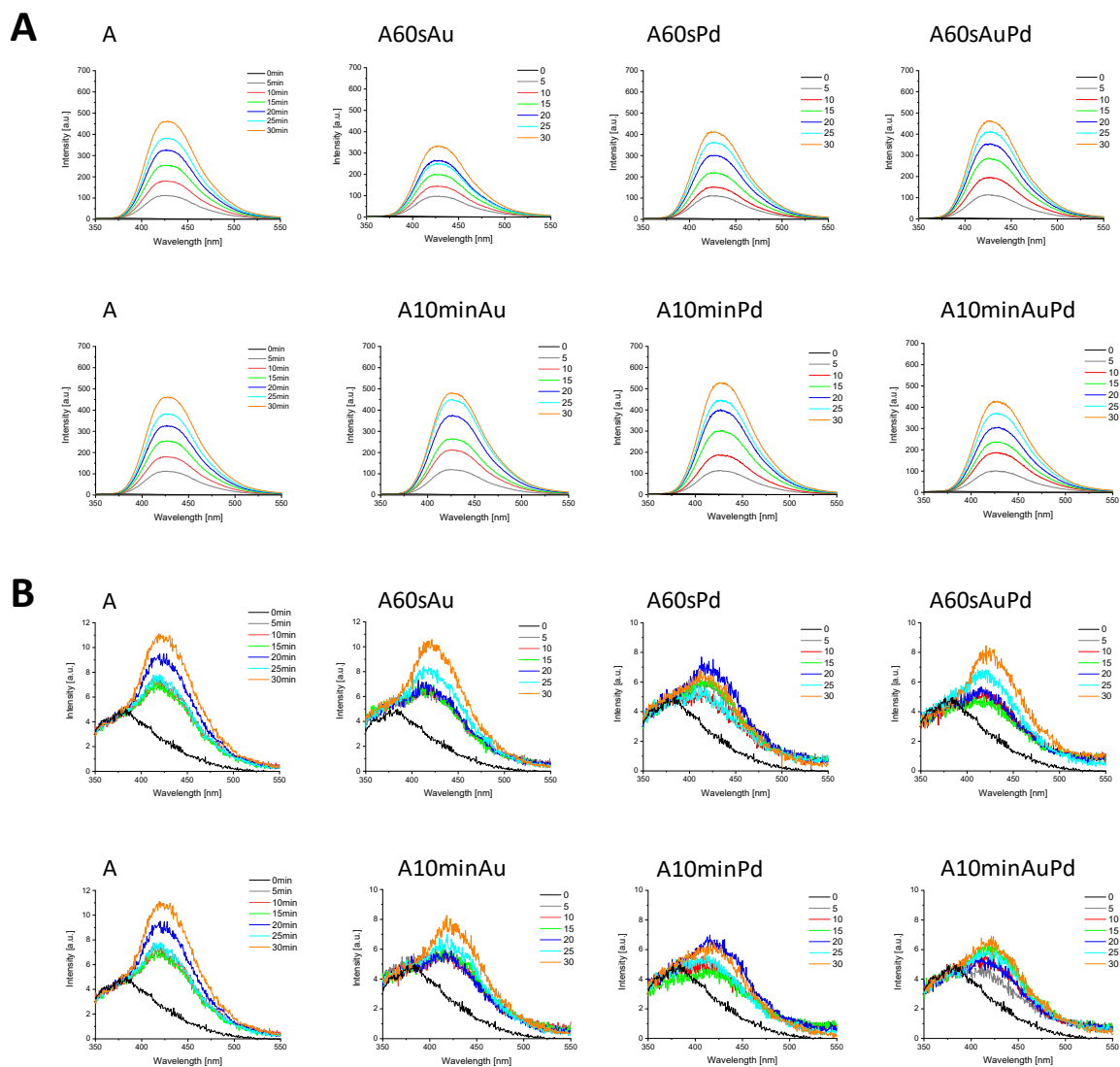


Fig. S5. Emission spectra of hydroxyterephthalic acid formed during irradiation with simulated solar light (A) and visible light ($\lambda > 420$ nm) (B) compared with reference in every line.