Electronic Supplementary Information

Enhancement of the H₂ evolution activity of La₅Ti₂Cu(S_{1-x}Se_x)₅O₇ photocatalysts by coloading Pt and NiS cocatalysts

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Figure S1. The H₂ evolution rate of LTCSO modified with 1 wt% NiS as a function of the amount of LTCSO. Reaction conditions: 0–0.4 g of LTCSO loaded with 1 wt% NiS, 150 mL of an aqueous 10 mM Na₂S and 10 mM Na₂SO₃ solution, visible light top irradiation with a 300 W Xe lamp through a cut-off filter ($\lambda > 420$ nm).



Figure S2. Time courses for H₂ evolution over LTCSO loaded with (a) 1.0, (b) 1.5, (c) 2.0 and (d) 2.5 wt% Pt-pd. Reaction conditions: 0.2 g LTCSO loaded with varying amounts of Pt-pd, 150 mL of an aqueous 10 mM Na₂S and 10 mM Na₂SO₃ solution, visible light top irradiation with a 300 W Xe lamp through a cut-off filter ($\lambda > 420$ nm).



Figure S3. Time courses for H₂ evolution over LTCSO loaded with (a) 1.0 wt% NiS, (b) 2.0 wt% Pt-pd, (c) 2.0 wt% Pt-pd and 1.0 wt% NiS. Reaction conditions: 0.2 g LTCSO loaded with various cocatalysts, 150 mL of an aqueous 10 mM Na₂S and 10 mM Na₂SO₃ solution, visible light top irradiation with a 300 W Xe lamp through a cut-off filter ($\lambda > 420$ nm).



Figure S4. Time courses for H₂ evolution over LTCSO loaded with (a) 2.0 wt% Pt-pd and (b) 1.0 wt% NiS followed by 2.0 wt% Pt-pd. Reaction conditions: 0.2 g LTCSO loaded with various cocatalysts, 150 mL of an aqueous 10 mM Na₂S and 10 mM Na₂SO₃ solution, visible light top irradiation with a 300 W Xe lamp through a cut-off filter ($\lambda > 420$ nm).



Figure S5.Time courses for H₂ evolution over LTCS_{0.8}Se_{0.2}O loaded with (a) 1.0 (b) 1.5, (c) 2.0, and (d) 2.5 wt% Pt-pd.Reaction conditions: 0.2 g LTCS_{0.8}Se_{0.2}Oloaded with varying amounts of Pt-pd, 150 mL of an aqueous 10 mM Na₂S and 10 mM Na₂SO₃ solution, visible light top irradiation with a 300 W Xe lamp through a cut-off filter ($\lambda > 420$ nm).



Figure S6. Time courses forH₂ evolution over LTCSO coloaded with 0.3 wt% Pt-imp and 1.0 wt% NiS in aqueous solutions containing (a) 10, and (b) 70mM each of Na₂S and Na₂SO₃. Reaction conditions: 0.2 g LTCS_{1-x}Se_xO loaded with various cocatalysts, 150 mL of an aqueous Na₂S and Na₂SO₃ solution, top irradiation with a 300 W Xe lamp through a cut-off filter ($\lambda > 420$ nm).



Figure S7. Long-term H₂ evolution reaction data using (a) LTCSO coloaded with 0.3 wt% Ptimp and 1.0wt% NiS, and (b) LTCS_{0.8}Se_{0.2}O modified with 2.0 wt% Pt-pd and 0.5 wt% NiS. Reaction conditions: 0.2 g LTCS_{1-x}Se_xO loaded with cocatalysts, 150 mL of an aqueous 70 mM Na₂S and70 mM Na₂SO₃ solution, visible light top irradiation with a 300 W Xe lamp through a cut-off filter ($\lambda > 420$ nm). The arrows indicate the points at which the apparatus was evacuated.



Figure S8. Time courses for H₂ evolution over (a) LTCSO loaded with 0.3 wt% Pt-imp and 1.0 wt% NiS, and (b,c) LTCS_{0.8}Se_{0.2}O loaded with (b) 0.5 wt% NiS and (c) 2.0 wt% Pt-pd and 0.5 wt% NiS under red light irradiation ($\lambda = 680 \pm 30$ nm). Reaction conditions: 0.2 g LTCS_{1-x}Se_xO loaded with various cocatalysts, 150 mL of an aqueous 10 mM Na₂S and 10 mM Na₂SO₃ solution, top irradiation with a 300 W Xe lamp through a band-pass filter ($\lambda = 680 \pm 30$ nm).



Figure S9. HR-TEM images of LTCSO and LTCS_{0.8}Se_{0.2}O coloaded with Pt and NiS after a photocatalytic reaction under visible light irradiation ($\lambda > 420$ nm). The white ellipses indicate partly crystalline Pt nanoparticles. The scale bars represent 5 nm.



Figure S10. EDS line analyses of (A) LTCSO, and (B) LTCS_{0.8}Se_{0.2}O coloaded with Pt and NiS after a photocatalytic reaction under visible light irradiation ($\lambda > 420$ nm). The scale bars in the images are 50 nm.