

ELECTRONIC SUPPLEMENTARY INFORMATION

Surface Oxygen Vacancy Assisted Electron Transfer and
Shuttling for Enhanced Photocatalytic Activity of Z-scheme
CeO₂-AgI Nanocomposite

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1. Experimental section

1.1 Preparation of photocatalysts

Silver iodide (AgI) nanoparticles were synthesized by hydrothermal process and in a typical synthesis, potassium iodide (KI) (Daejung Chemicals, South Korea) (0.48 g) dissolved in 30 mL DI water and silver nitrate (AgNO_3) (Daejung Chemicals, South Korea) (0.49 g) dissolved in 30 mL DI water containing 0.5 g polyvinylpyrrolidone (PVP) (Daejung Chemicals, South Korea) and both of the solutions were sonicated for 30 minutes. Immediately after sonication, KI solution was added drop wise into PVP containing AgNO_3 solution under constant magnetic stirring. After 1 h magnetic stirring, the mixture was transferred into 100 mL Teflon-lined autoclave and subsequently heated at 140 °C for 12 h and afterward cooled to the room temperature. The resulting AgI product was centrifuged, washed with DI water and ethanol for several times and dried at 80 °C for 8 h and finally grind into powder form for further experiment.

CeO_2 -AgI composites were prepared by precipitation method. In a typical process, CeO_2 (Daejung Chemicals, South Korea) (0.05 g) was added into DI water (30 mL) and simultaneously AgI (0.45 g) was also added into DI water (30 mL) in a separate beaker and both of the samples were sonicated for 30 minutes. After sonication, CeO_2 suspension was mixed with the AgI solution very slowly under vigorous magnetic stirring for 1 h at room temperature. Then the precipitate was collected by centrifugation, washed with DI water and dried for 8 h at 80 °C. This composite was fabricated at 10 wt. % CeO_2 -AgI and denoted as CA-1. Under the same experimental condition 20, 30, 40 wt. % of CeO_2 -AgI composites were prepared and denoted as CA-2, CA-3 and CA-4, respectively.

2. Characterization

The surface morphologies and elemental analysis were evaluated using a HITACHI S-4800 field emission scanning electron microscope (FESEM) equipped with an energy-dispersive spectrometer (EDS, Inca 400, Oxford Instruments). The crystal structure of these samples was characterized by X-ray diffraction spectroscopy (XRD) through a Bruker D8 Advanced X-ray diffractometer with Cu K α radiation as the X-ray source. Fourier-transform infrared spectroscopy (FTIR) was recorded between 4000 and 500 wavenumber (cm⁻¹) at a spectral resolution of 4 cm⁻¹ (Nicolet 380 FTIR spectrometer). X-ray photoelectron spectroscopy (XPS) measurements were carried out to evaluate the chemical status and element composition of the samples with a monochromated Al K α X-ray source ($h\nu = 1486.6$ eV) at an energy of 15 kV/150 W. The diffuse-reflectance spectrum (DRS) was recorded with a UV-Vis spectrometer (UV-1800 SHIMADZU, Japan). The Photoluminescence (PL) spectra of the photocatalysts were collected at room temperature using a Hitachi F-7000 fluorescence spectrometer.

3. Photocatalytic experiments

Photocatalytic activities of different photocatalyst (CeO₂, AgI or CeO₂-AgI nanocomposite) were explored by the degradation of RhB (Daejung Chemicals, South Korea) (10 mg/L) in aqueous solution under solar simulator (Model 10500 Low Cost Solar Simulator with a Model 10513 90° Uniform Illumination Accessory) equipped with an AM 1.5G filter and 150W Xe lamp as the light source. (ABET technologies). 100 mg of photocatalyst was dispersed in 100 mL RhB dye solution in a 150 mL conical flask. Before irradiation, the photocatalyst suspension was magnetically stirred for 30 min in the dark at room temperature to attain adsorption-desorption equilibrium and 2.0 mL of suspension was taken out to measure to adsorption efficiency. (To confirm adsorption-

desorption equilibrium time, 100 mg of 20 wt. % CeO₂-AgI nanocomposite was dispersed in 100 mL RhB (10 mg/L) aqueous solution, which was magnetically stirred in the dark up to 170 min at room temperature. Every specific time interval, 2.0 mL of suspension was taken out, centrifuged and measured the concentration of RhB in the supernatant liquid at 553.8 nm (maximum wavelength) using a UV-Vis spectrophotometer (UV-1650PC, Shimadzu, Japan). After adsorption-desorption equilibrium, the simulator was turned on and during irradiation, 2.0 mL suspension was withdrawn at regular 10 min time intervals and centrifuged to remove the photocatalyst and then the dye concentration was analyzed at 553.8 nm of characteristic maximum absorption wavelength of RhB with a UV-Vis spectrophotometer at room temperature. To further investigate the visible light photocatalytic activity, a colorless phenol, was also chosen as a model pollutant. To measure the photocatalytic degradation of phenol, similar to the dye degradation experiment, 100 mg of photocatalyst was dispersed in 100 mL aqueous solution of phenol (Daejung Chemicals, South Korea) (10 mg/L) in a 150 mL conical flask, then magnetically stirred for 30 min in the dark at room temperature to achieve adsorption-desorption equilibrium and withdrawn 2.0 mL of suspension (compare to RhB dye, phenol showed less adsorption efficiency). After that during irradiation time, 2.0 mL suspension was withdrawn at regular 10 min time intervals and centrifuged to remove the photocatalyst and then the phenol concentration was analyzed at its maximum absorption wavelength of 269.9 nm with a UV-Vis spectrophotometer (UV-1650PC, Shimadzu, Japan) at room temperature. The visible light photocatalytic activity of the AgI and CeO₂-AgI nanostructures were tested through the degradation of phenol. For the recycling experiment, previously used CeO₂-AgI nanocomposite photocatalyst was centrifuged out from solution, dried at 80 °C for 8 h and then reused again for the degradation of the same concentration of the RhB dye.

2. Supporting Figures

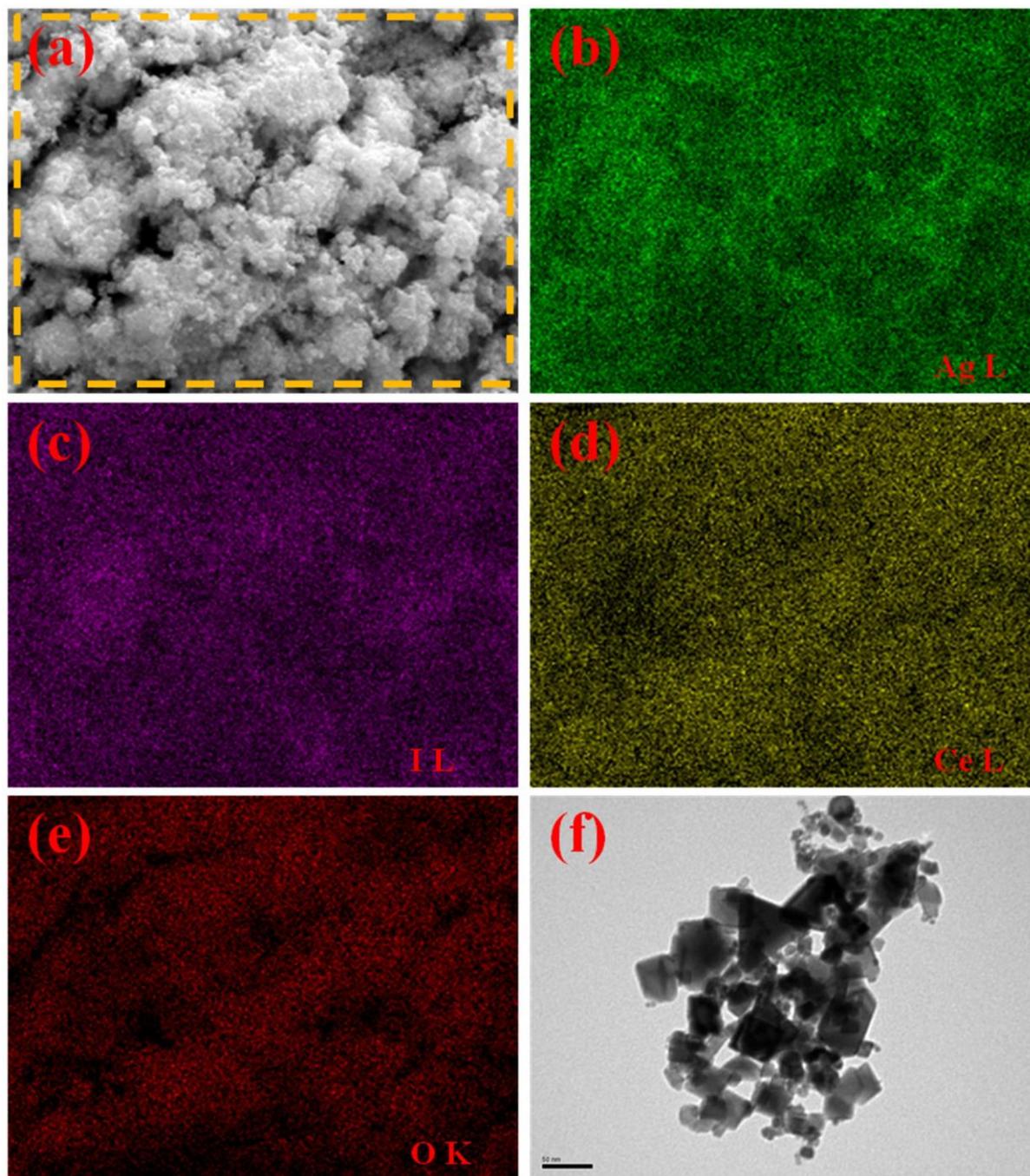


Figure S1. FESEM image of CeO₂-AgI composite (a) and corresponding EDS element mapping of Ag, I, Ce, O (b) – (e); TEM image of CeO₂ (f), respectively.

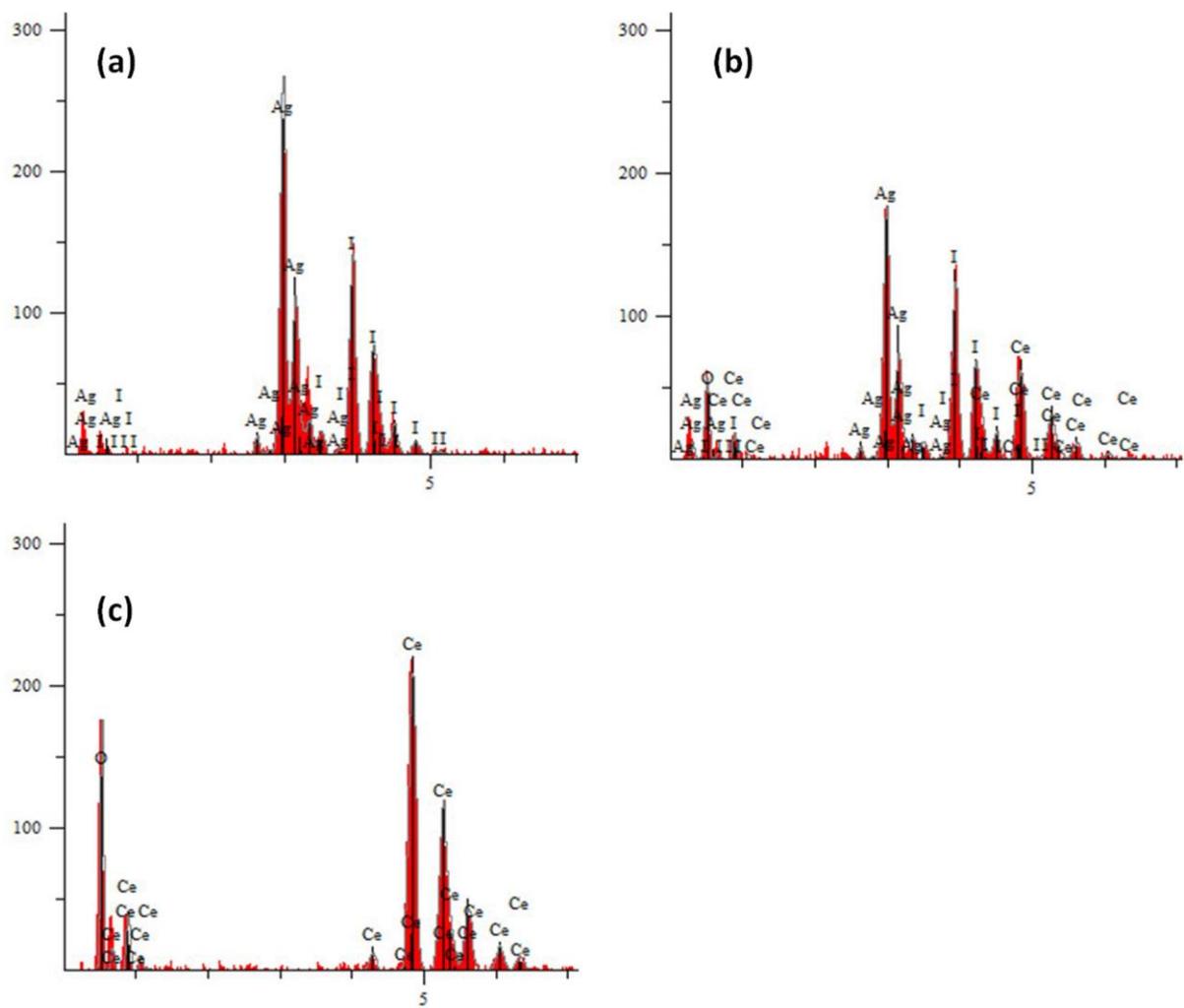


Figure S2. EDS spectra of (a) AgI, (b) CeO₂-AgI nanocomposite and (c) CeO₂ nanostructures.

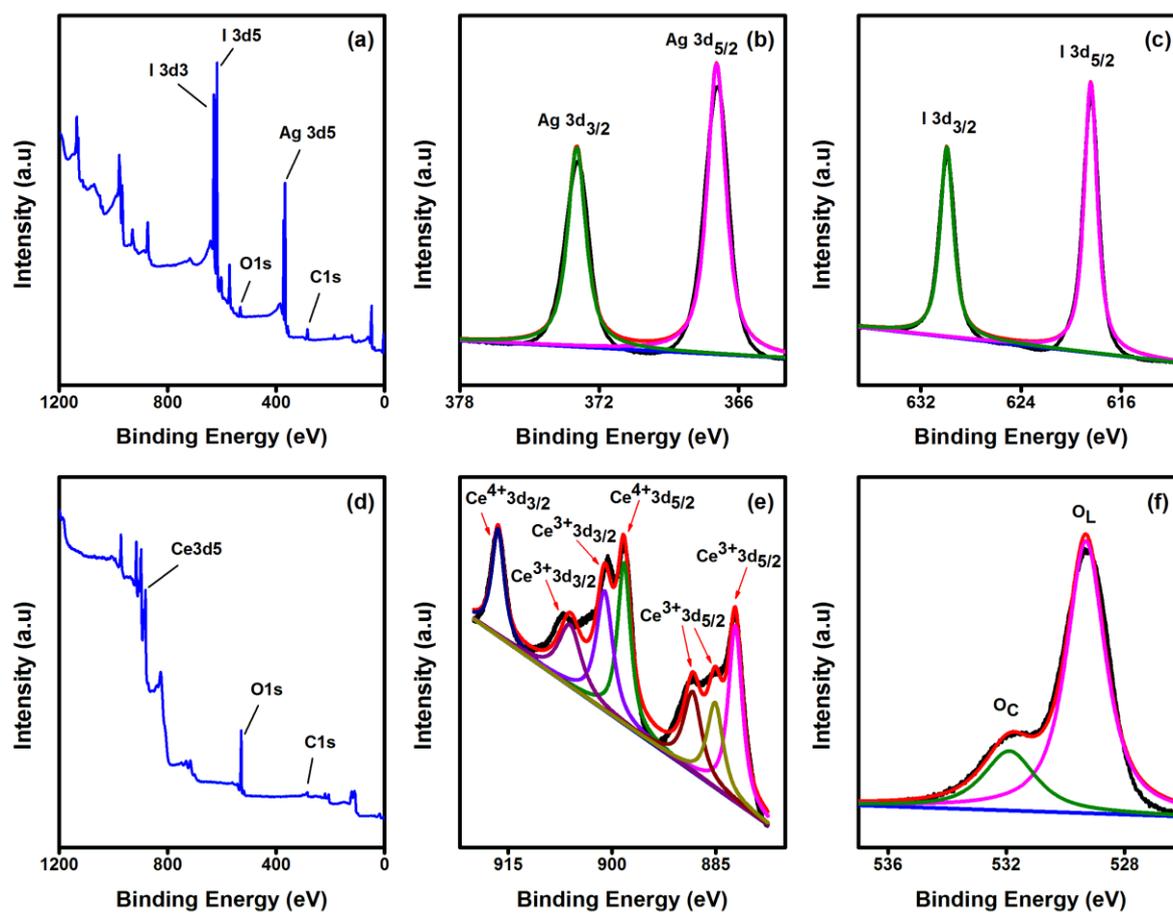


Figure S3. Survey XPS spectrum of AgI (a) and CeO₂ (d); narrow spectrum of Ag3d (b), I3d (c), Ce3d (e) and O1s (f).

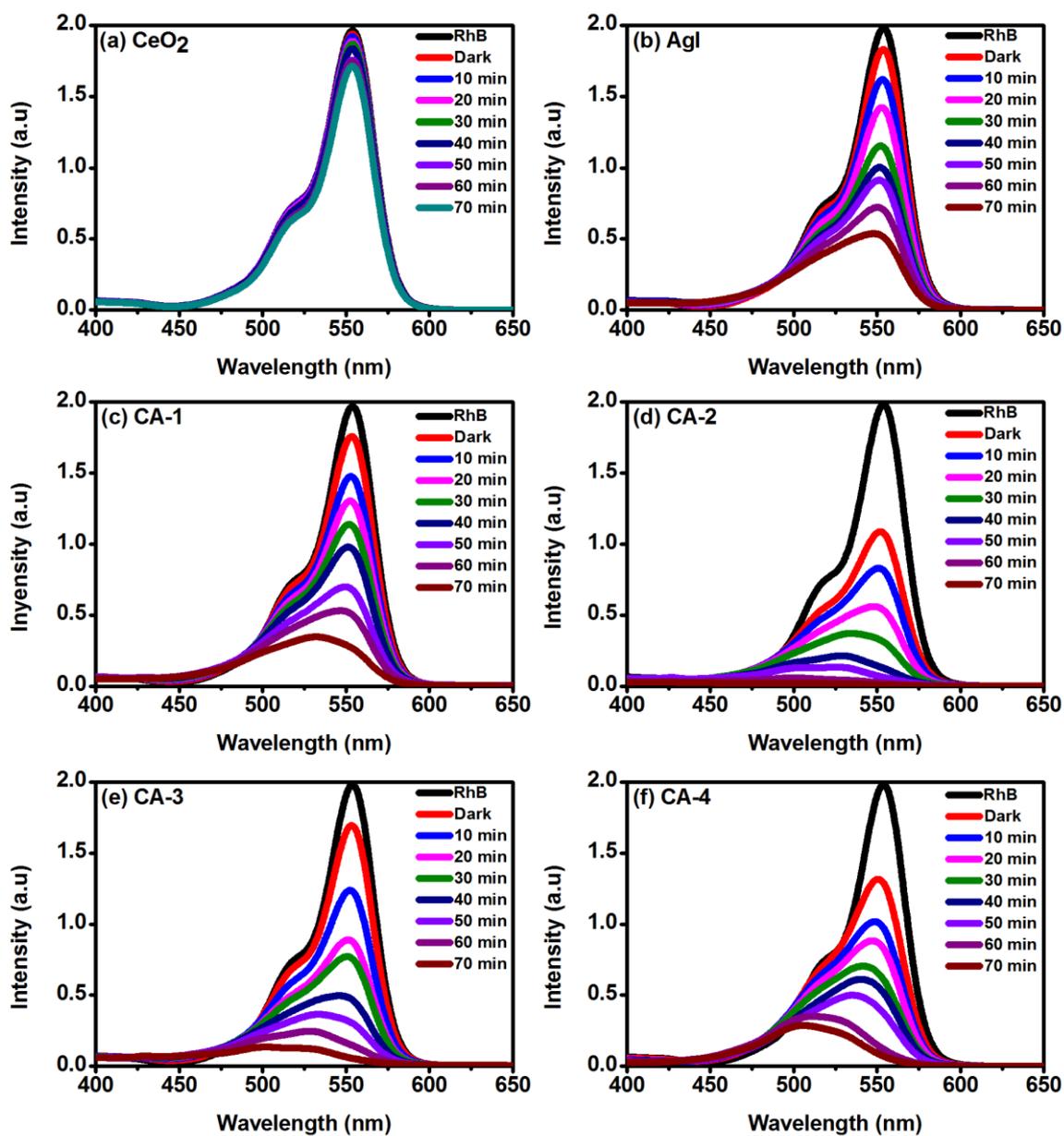


Figure S4. UV-Vis absorption spectra of RhB aqueous solution containing (a) CeO₂, (b) AgI, and CeO₂-AgI (10 (c), 20 (d), 30 (e), 40 (f) wt. %).

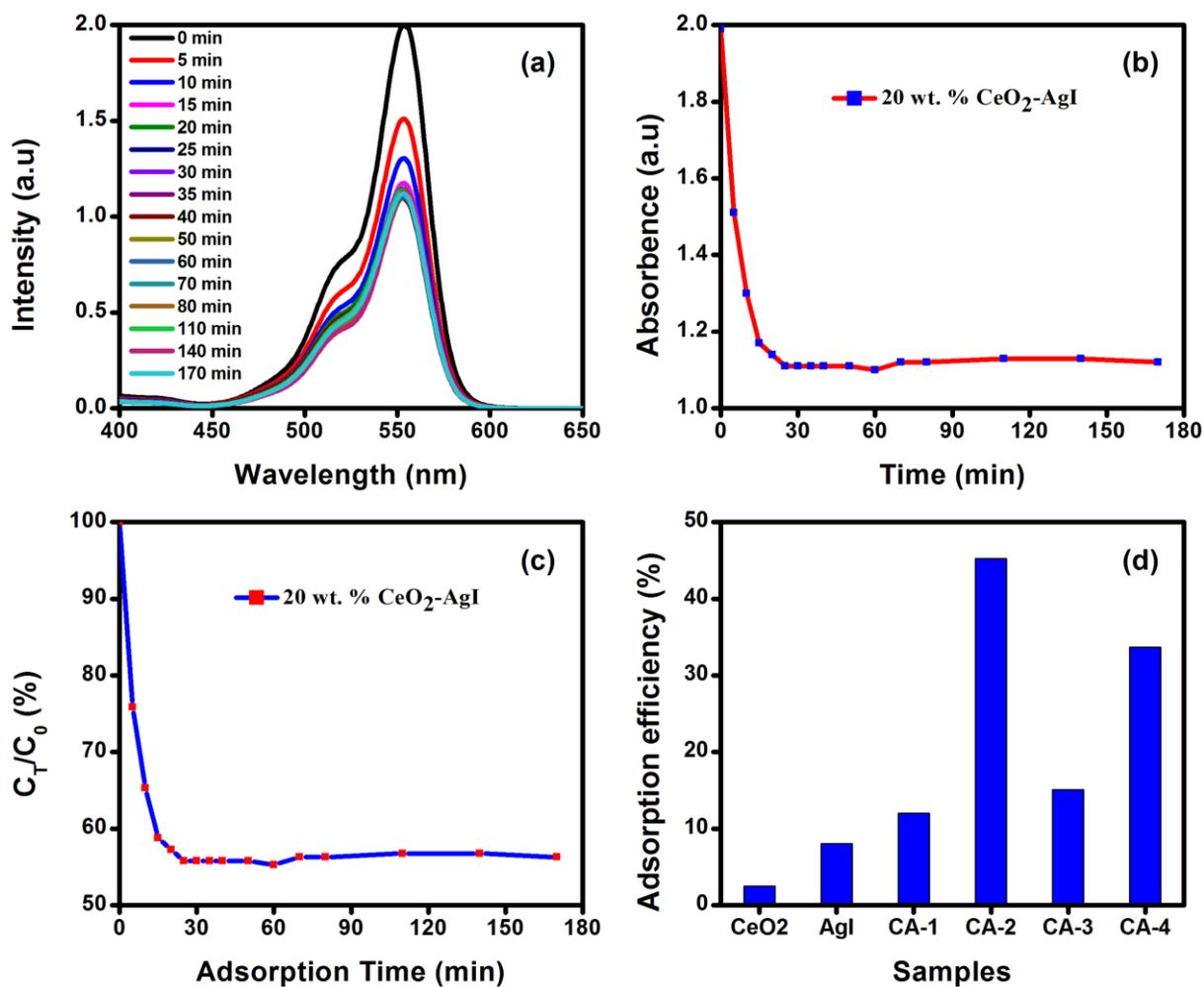


Figure S5. (a) Absorption spectra of the RhB aqueous solution in the presence of 20 wt.% CeO₂-AgI adsorbent; (b) Effect of contact time on RhB adsorption by 20 wt.% CeO₂-AgI; (c) The curve of adsorption-desorption equilibrium of 20 wt.% CeO₂-AgI photocatalyst by RhB dye and (d) Adsorption efficiency of different nanostructures in 30 min. dark condition with 100 mg of nanocomposite and 10 mg/L of RhB room temperature in room temperature aqueous solution.

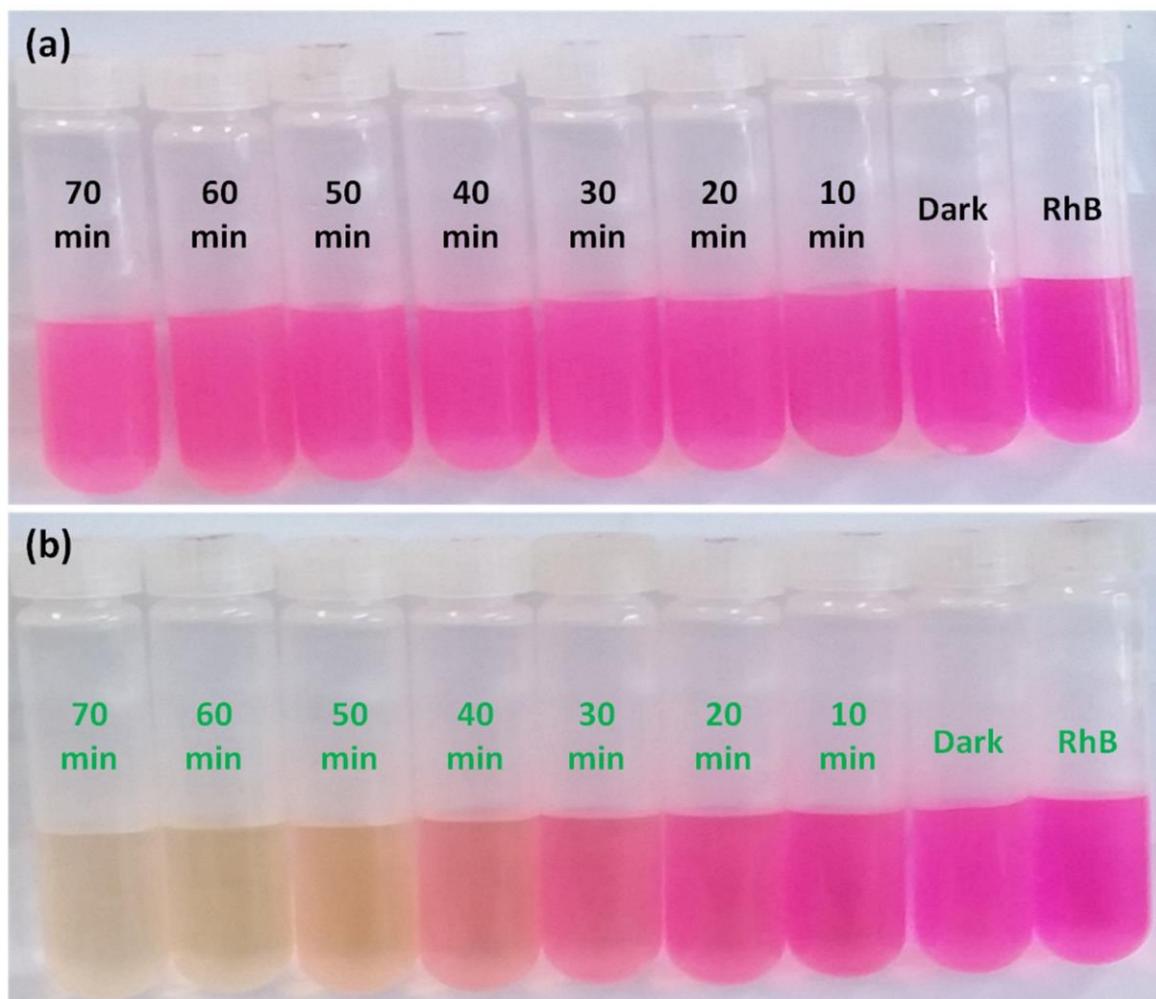


Figure S6. Digital image of the aliquots indicating the color change of the RhB dye solutions in the presence of (a) AgI and (b) CA-2 nanocomposite.

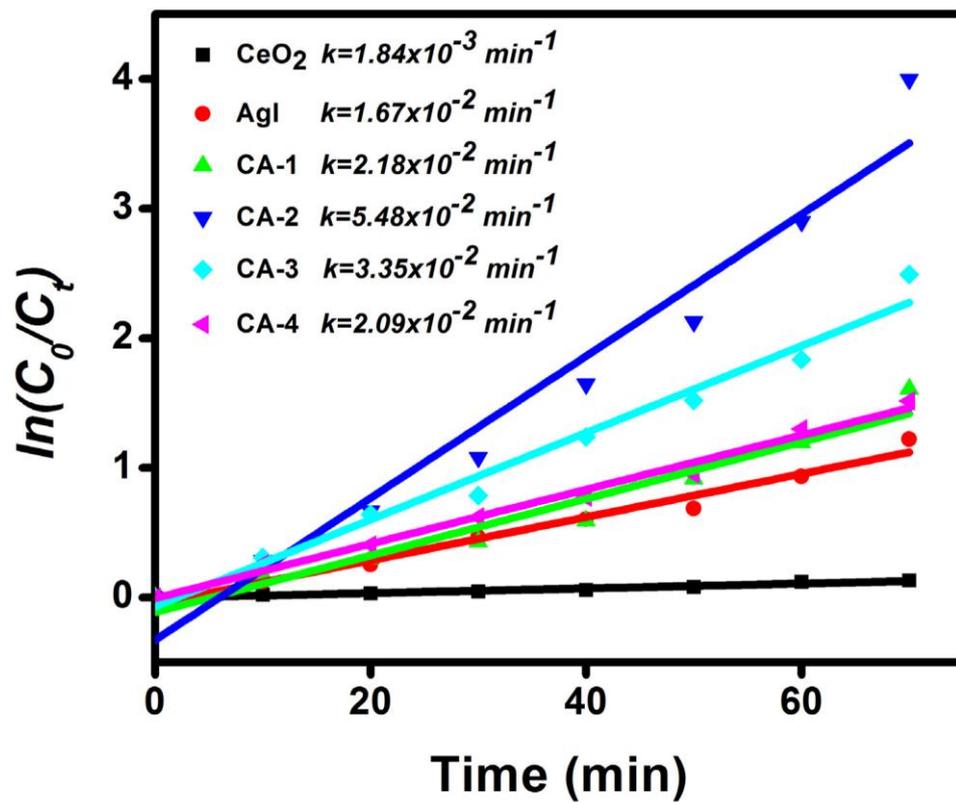


Figure S7. Plot of $\ln(C_0/C_t)$ as a function of irradiation time for kinetic fit using pseudo first-order kinetics for degradation of RhB dye by various photocatalyst.

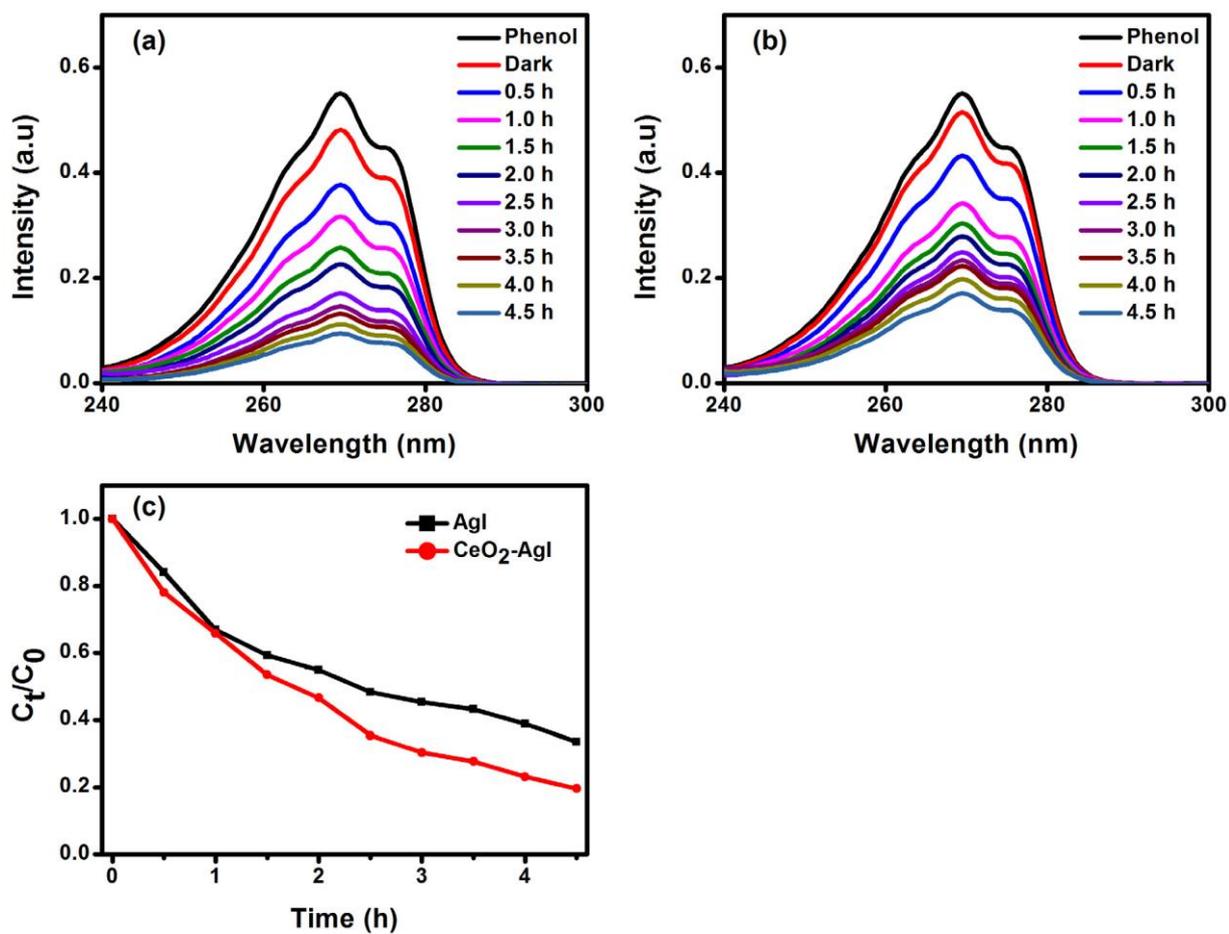


Figure S8. (a) UV-Vis absorption spectra of phenol solution in the presence of (a) 20 wt. % CeO₂-AgI photocatalyst and (b) AgI photocatalyst. (c) Comparison of the photocatalytic activities of AgI and CeO₂-AgI nanocomposites for the degradation of phenol.

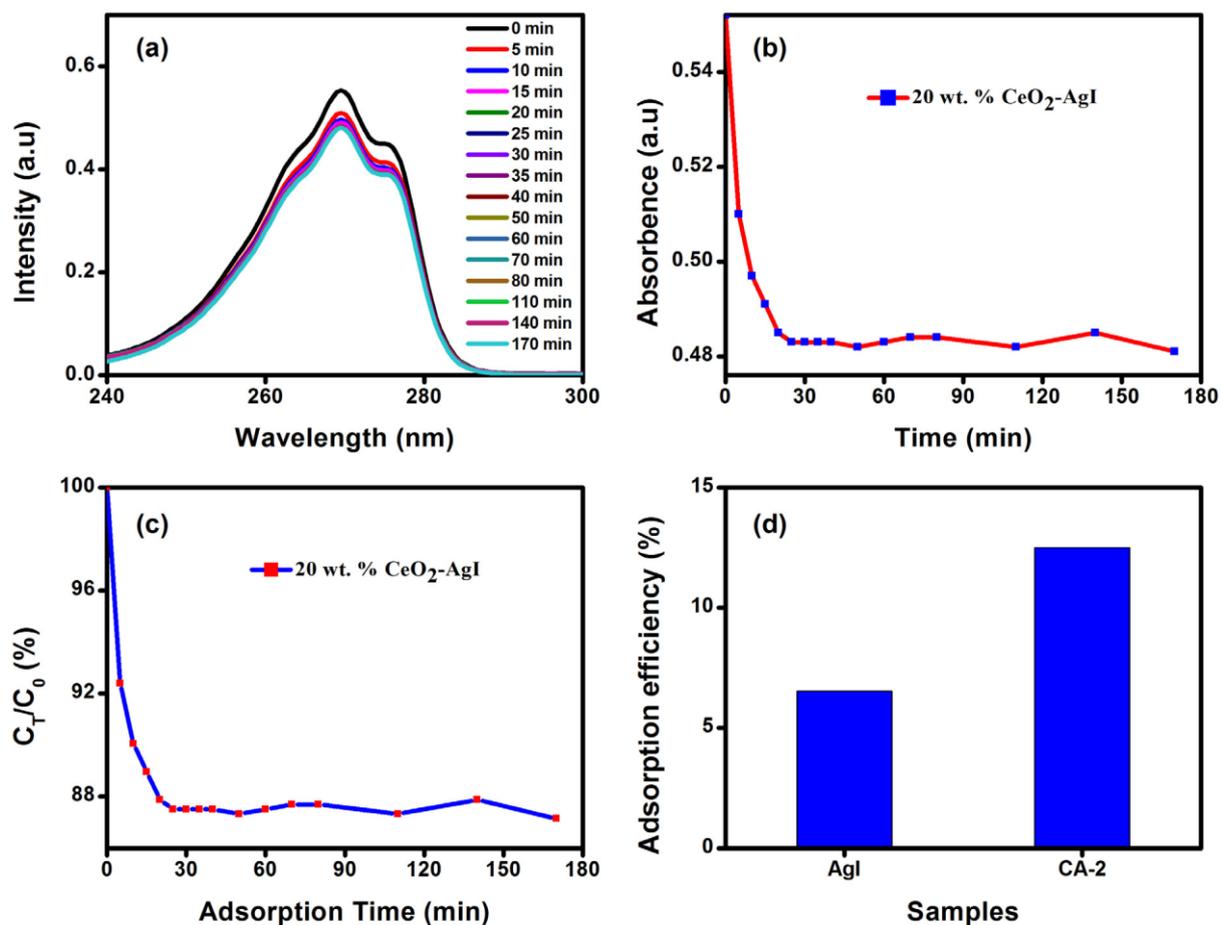


Figure S9. (a) Absorption spectra of the phenol aqueous solution in the presence of 20 wt.% CeO₂-AgI adsorbent; (b) Effect of contact time on Phenol adsorption by 20 wt.% CeO₂-AgI; (c) The curve of adsorption-desorption equilibrium of 20 wt.% CeO₂-AgI photocatalyst by phenol and (d) Adsorption efficiency of AgI and CA-2 nanostructures in 30 min dark condition with 100 mg of nanocomposite and 10 mg/L of Phenol in room temperature aqueous solution.

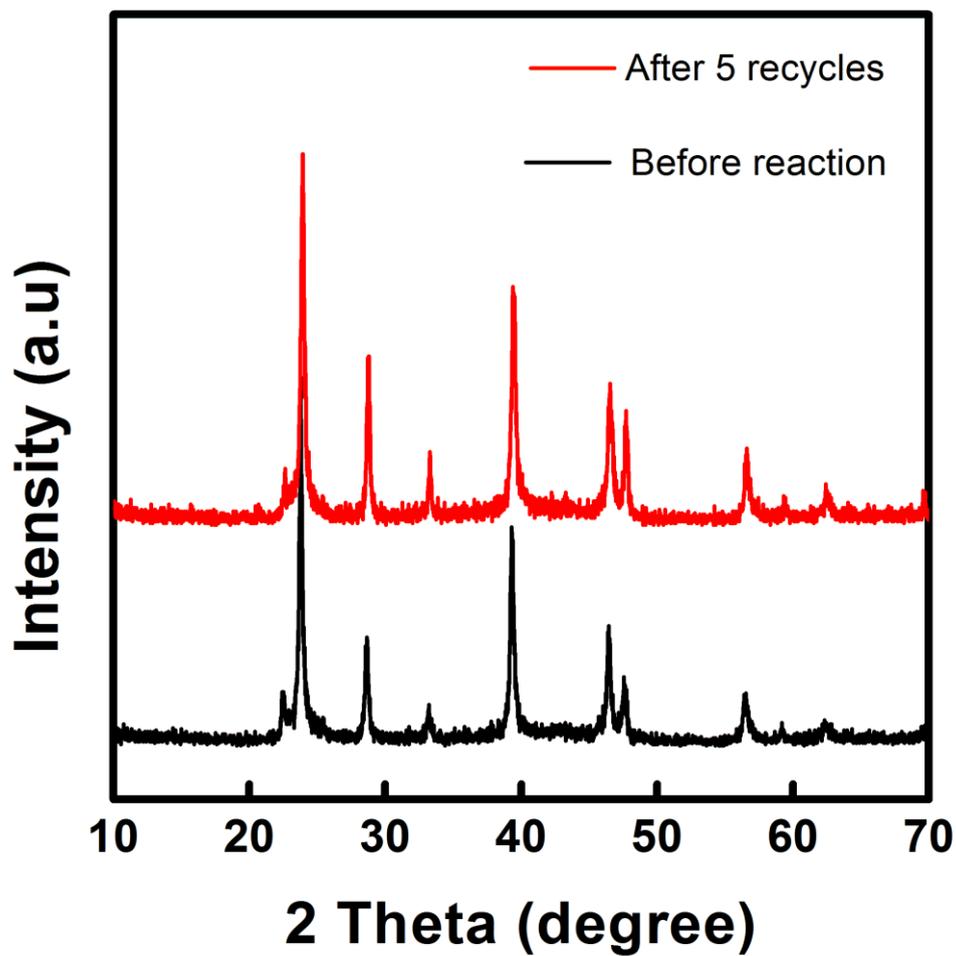


Figure S10. XRD patterns of the 20 wt. % CeO₂-AgI nanocomposite after 5 recycling runs.