Supporting Information

Photocatalytic conversion of polylactic acid waste to ethyl acetate in alkaline solution under mild conditions

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Supplementary Methods

Preparation of CdS NRs

The CdS NRs were synthesized via a classical hydrothermal method. Initially, cadmium nitrate and thiourea were dissolved in 50 mL of ethylenediamine at a 1:3 molar ratio. The solution was stirred at room temperature for 30 min to ensure thorough mixing. Following this, the solution was transferred to a Teflon liner housed within a stainless-steel autoclave. The autoclave was heated to 160 ℃ and maintained at this temperature for 48 h in an oven. Upon completion of the reaction, the autoclave was allowed to cool naturally to room temperature. The resulting yellow precipitate was washed repeatedly with deionized water and ethanol to remove impurities. Finally, the precipitate was centrifuged and dried at 60 ℃ to obtain the desired CdS NRs.

Synthesis of CdS-TiO_2-Ag NRs, CdS-Ag NRs, and CdS-TiO_2 NRs

The CdS-TiO_2-Ag NRs were fabricated via the $NaBH_4$ reduction method. Initially, 100 mg of CdS NRs were dispersed in 100 mL of deionized water and combined with 10 mL of $AgNO_3$ solution (20 μM) and 10 mL of TiO_2 NPs (20 μM). The resultant mixture was stirred for 30 min to ensure thorough mixing. Subsequently, a freshly prepared 0.01 M $NaBH_4$ solution (20 mL) was slowly added dropwise to the reaction mixture while continuously stirring in an ice-water bath for an additional 30 min. Upon completion of the reaction, the product was collected and thoroughly washed with ethanol and deionized water to remove any unreacted species or impurities. The final product was then dried at 60 °C for subsequent characterization and application. Besides, the same method was employed to synthesize CdS-Ag and CdS-TiO_2 NRs, using $AgNO_3$ solution or TiO_2 NPs as the respective precursors for Ag NPs or TiO_2 decoration.

Electrochemical measurements

All the electro/photochemical measurements were conducted on the CHI 760E workstation, using a standard three-electrode system and performed in 0.1 M PBS solution. The light source was a 300-watt xenon lamp. The working electrode was a 15 mm × 10 mm FTO glass coated with a photocatalyst. A slurry was prepared, which contained 3 mg of photocatalyst and 1 ml of ethanol, and was coated onto the FTO glass by dip coating method. The reference electrode was a platinum wire, and the reference electrode was Ag/AgCl.

Photocatalytic experiments

The photocatalytic reaction was performed at a constant room temperature of 25 °C within a stainless-steel autoclave equipped with a quartz glass window. Specifically, 10 mg of the photocatalyst was dispersed in 10 mL of an ammonia solution containing 100 mg of polylactic acid (PLA). Subsequently, the reaction mixture was purged and pressurized with N_2 gas to a stable pressure of 1.0 bar. The reaction was initiated by irradiating the mixture with a Xe lamp ($\lambda > 420$ nm) at an intensity of 150 mW/cm^2. Upon completion of the photocatalytic process, the reaction solution was evaporated at 40 °C for 2 h to remove ammonia. The remaining solution was then subjected to double-filtration using a 0.22-μm PES membrane to separate the products. For quantitative analysis, Nuclear Magnetic Resonance (NMR) spectroscopy was employed. The analysis samples were prepared by mixing 600 μL of the filtrate with 100 μL of D_2O, and 2.0 μL of DMSO was added as an internal standard for accurate quantification.

Supporting Figures

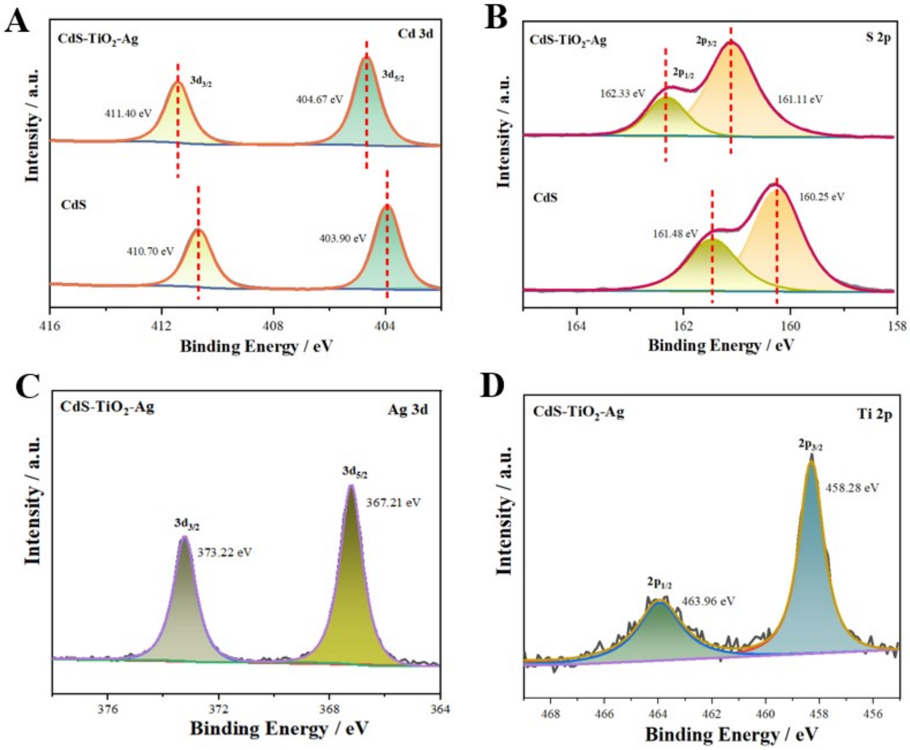

Fig. S1. The high-resolution Cd 3d (A), S 2p (B), Ag 3d (C) and Ti 2p (D) XPS spectra of various samples.

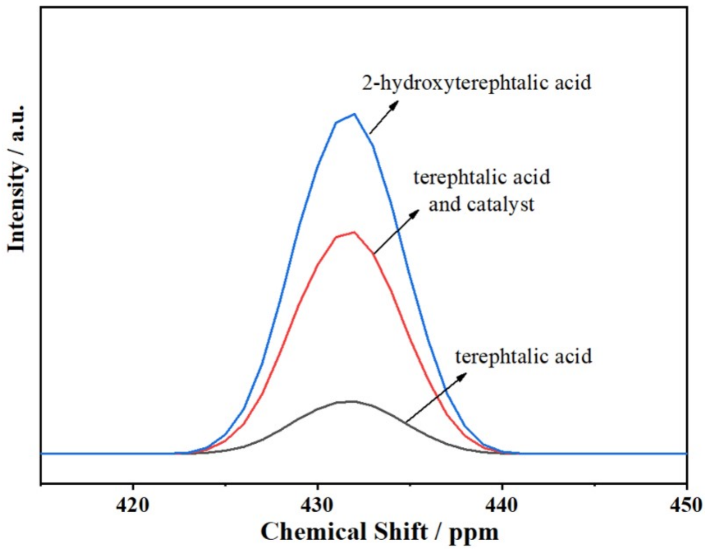

Fig. S2. Fluorescence emission spectra (λ_{ex} = 315 nm) of the reaction system employing terephthalic acid (TA) as a hydroxyl radical (•OH) probe. The characteristic emission peak at 430 nm indicates the formation of 2-hydroxyterephthalic acid (TAOH). Conditions: 5 mg CdS-TiO_2-Ag catalyst, 50 mg TA, 2 mL of 1 M aqueous KOH, AM 1.5 G irradiation (100 mW cm^{-2}), 25 °C, and 20 min. The spectrum of pure TAOH in 1 M KOH is included as a standard reference.

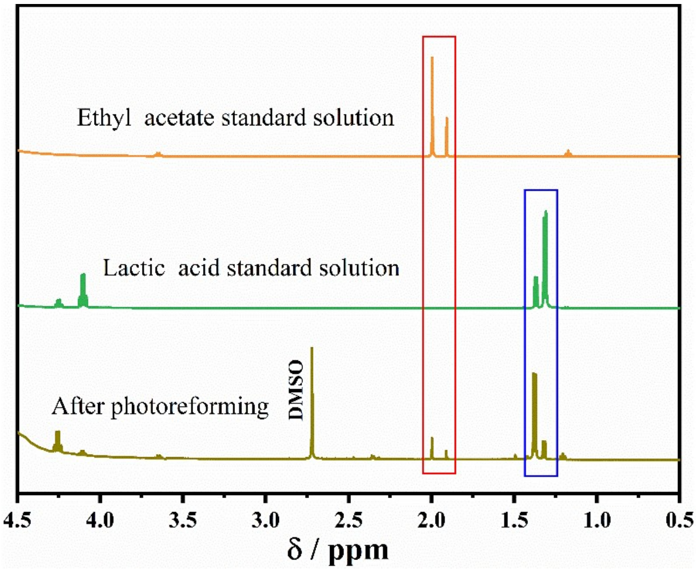

Fig. S3. Measured ^1H NMR spectra of commercial ethyl acetate standard solution, lactic acid standard solution, and the products of PLA after photoreforming for 20 h using CdS-TiO_2-Ag in N_2 atmosphere.

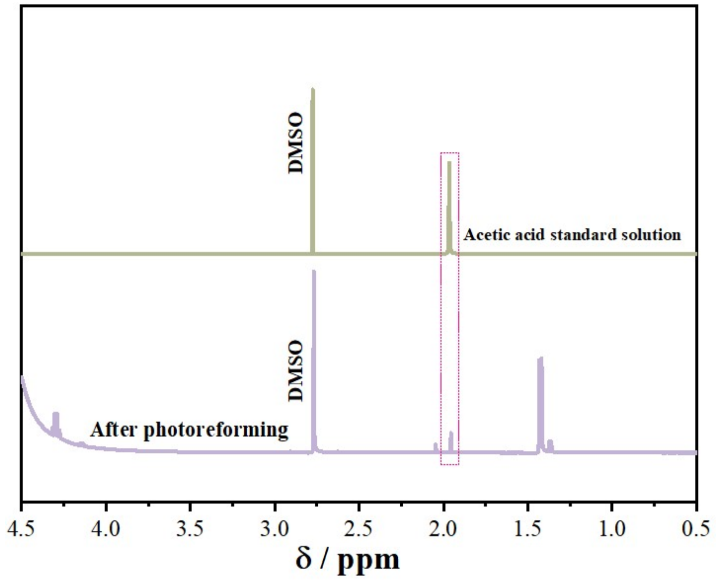

Fig. S4. Measured ^{1}H NMR spectra of commercial Acetic acid standard solution, and the products of PLA after photoreforming for 5 h using CdS-TiO$_2$-Ag in O$_2$ atmosphere.

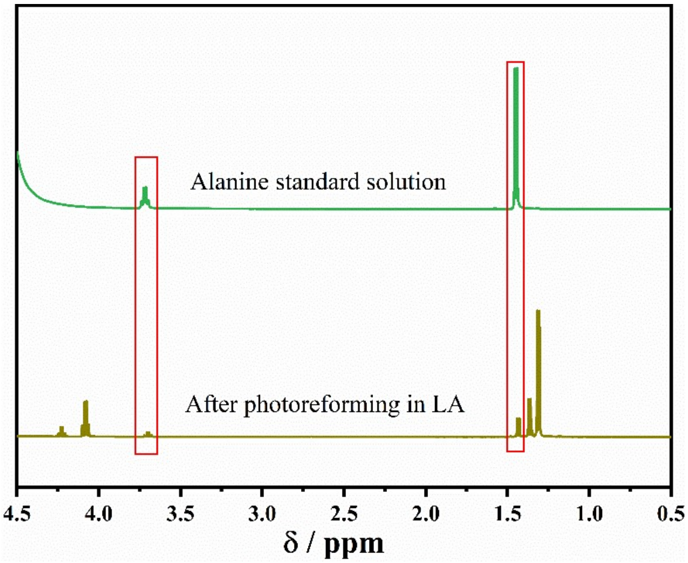

Fig. S5. ^{1}H NMR spectra using lactic acid (LA) as the substrate production.

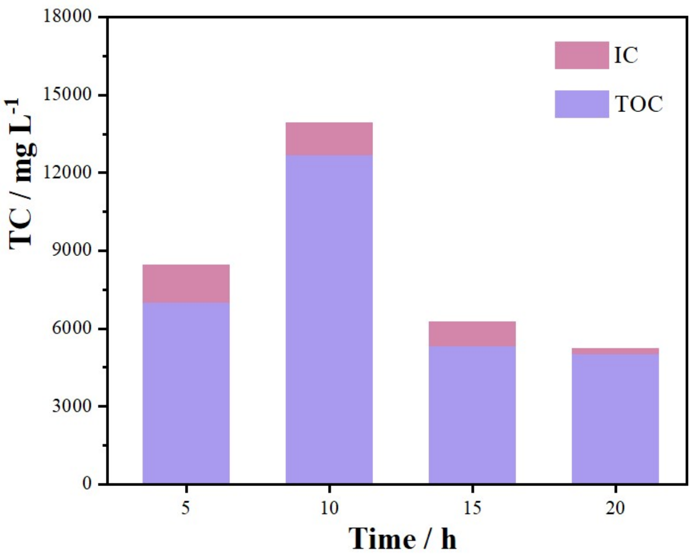

Fig. S6. Changes in total carbon (TC), inorganic carbon (IC), total organic carbon (TOC) concentrations, and the yield determined by quantifying the organic products using ^{1}H NMR spectroscopy as a function of reaction time.

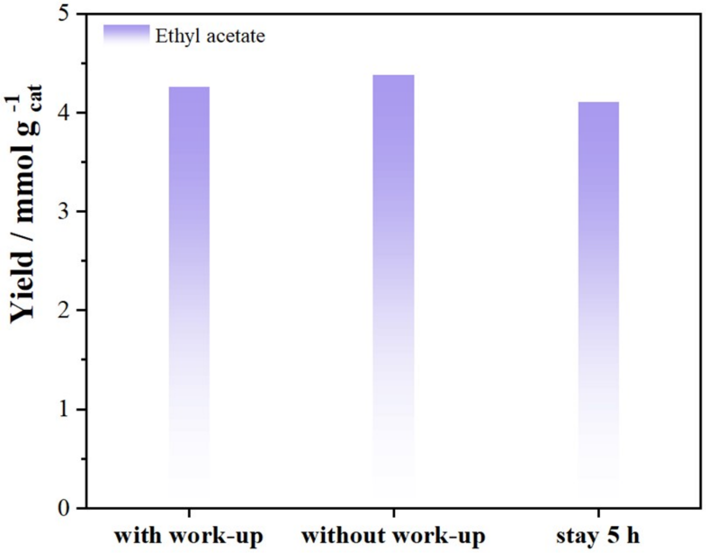

Fig. S7. Comparison of ethyl acetate yields for samples processed with work-up (after ammonia evaporation), without work-up (direct NMR analysis), and after a 5 h stability test in 1 M ammonia solution.

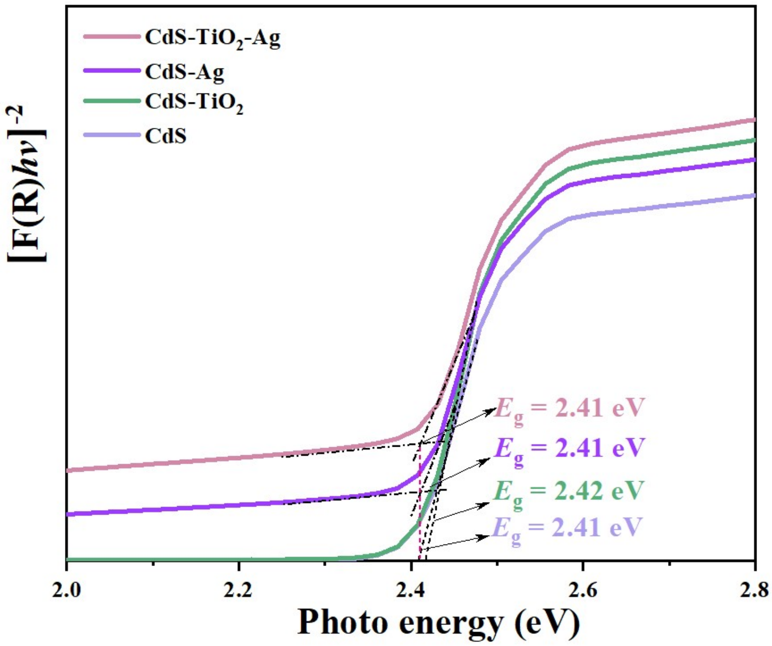

Fig. S8. Tauc plots of the various samples.

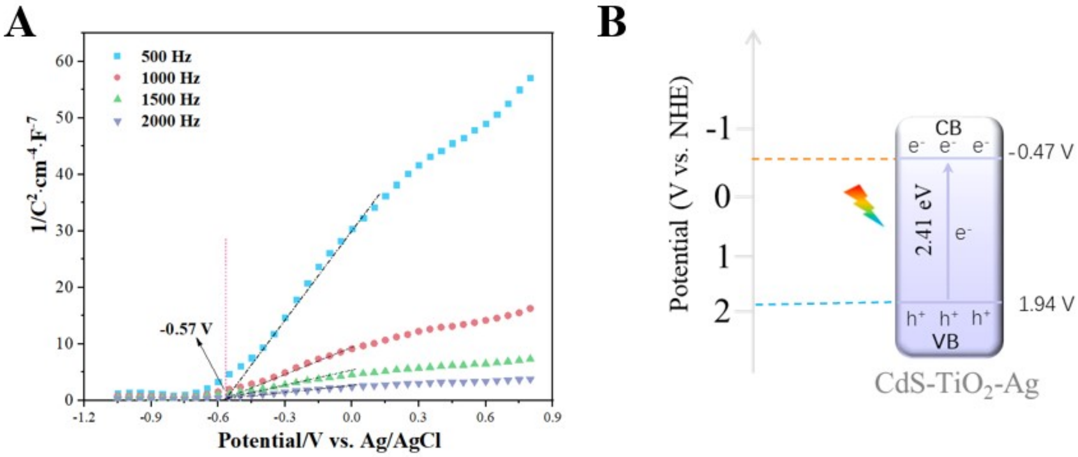

Fig. S9. Mott-Schottky plots (A) and schematic diagram of electronic band structure (B) of the CdS-TiO$_2$-Ag sample.

As shown in Fig. S9A, the Mott-Schottky plots were employed to determine the flat-band position. As a result, the flat-band potentials for CdS-TiO$_2$-Ag sample is ca. −0.37 V (vs. NHE, $E_{\mathrm{NHE}} = E_{\mathrm{Ag/AgCl}} + 0.197$), respectively.[S1] Next, the band gap energy (E_g) for CdS-TiO$_2$-Ag is calculated (2.41 eV), via Tauc plots (Fig. S8).[S2] Generally, for n-type semiconductors that exhibit a positive slope in Mott-Schottky curves, the conduction band (CB) potential is slightly higher than the flat-band potential, typically by about 0.1 V.[S3, S4] Therefore, the conduction band (CB) position for CdS-TiO$_2$-Ag (vs. NHE) is determined to be −0.47 V. Utilizing the relationship $E_g = E_{\mathrm{VB}} - E_{\mathrm{CB}}$, the valence band (VB) potential of CdS-TiO$_2$-Ag can be approximated as 1.94 V (vs. NHE). And the electronic bandgap structure of the CdS-TiO$_2$-Ag sample is depicted in Fig. S9B.

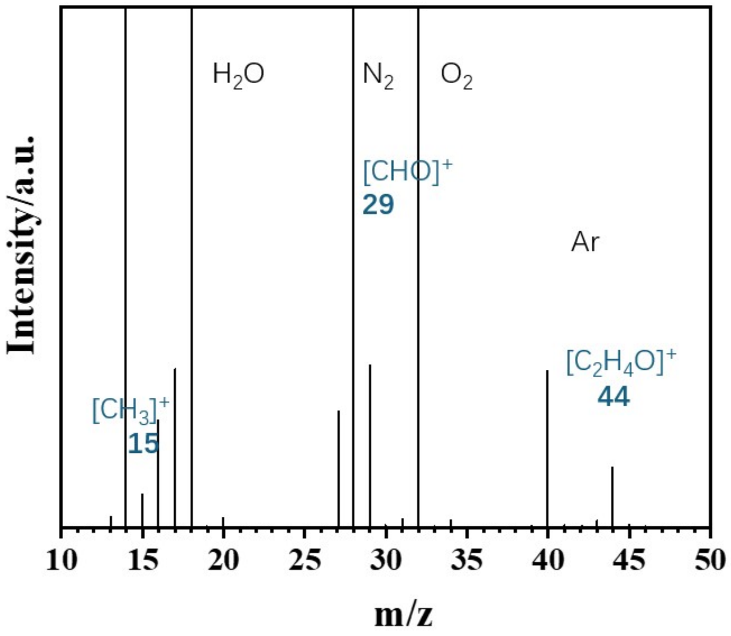

Fig. S10. GC-MS analysis of the photoreforming products from PLA over the CdS-TiO_2-Ag catalyst after 5 h of reaction.

References

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S4. S. Sun, W. Wang, D. Li, L. Zhang, D. Jiang, ACS Catal. 4 (2014) 3498−3503.