Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Efficient Visible-Light Photocatalytic Activity by Band Alignment in Mesoporous Ternary Polyoxometalate/Ag_2S/CdS Semiconductors

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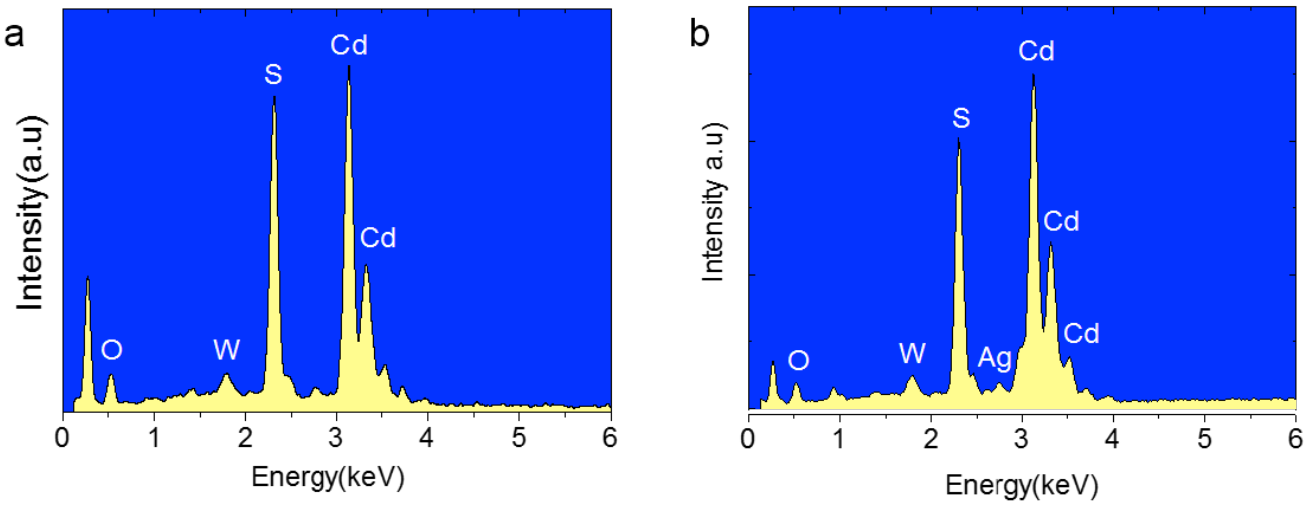

Fig. S1 Typical EDS spectra of template-free mesoporous (a) STA/CdS and (b) STA/A_2S/CdS hybrid materials. The EDS spectra show average atomic ratios of Cd/S/W ~48.7:49.8:1.5 for STA/CdS that correspond to a ~4.9 wt % $H_4SiW_{12}O_{40}$ (STA) loading and Cd/S/W/Ag ~47.6:47.9:1.5:3.0 for STA/A_2S/CdS that correspond to a ~4.7 wt % $H_4SiW_{12}O_{40}$ and ~4.9 wt % Ag_2S loading.

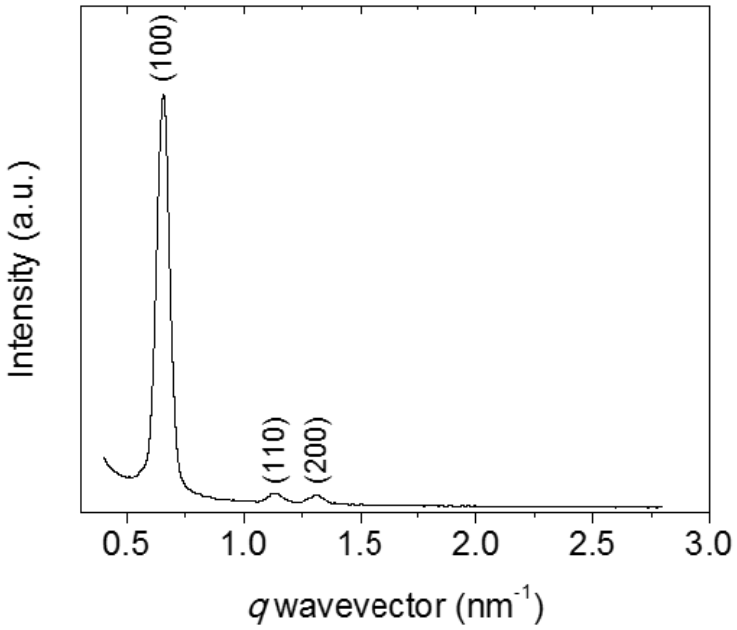

Fig. S2 SAXS pattern of mesoporous SBA-15. The indexing of the Bragg diffractions is consisted with a hexagonal *p6mm* unit cell with lattice parameter a_o=11.0 nm.

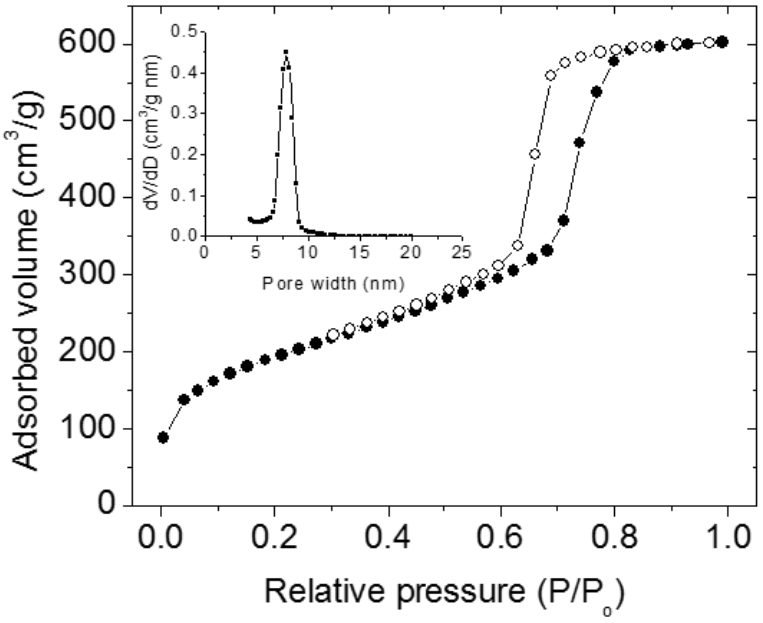

Fig. S3 Nitrogen adsorption and desorption isotherms at -196 ^{o}C of mesoporous SBA-15 silica. Analysis of the adsorption data with the BET method gives surface area of 674 m^2g^{-1} and total pore volume of 0.96 cm^3g^{-1}. (Inset) NLDFT pore size distribution calculated from the adsorption branch of isotherms. Given an estimation of the mesopore diameter (D_p) at 7.8 nm and the unit cell size (a_o) at 11.0 nm, the pore wall thickness (WT) is about 3.2 nm, according to the equation $WT=a_o-D_p$.

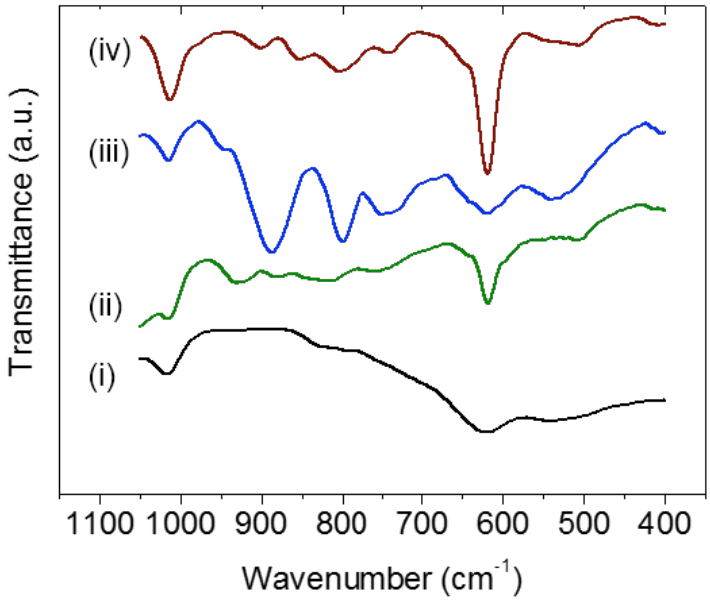

Fig. S4 Infrared spectra of mesoporous (i) *meso*-CdS, (ii) PTA/Ag_2/CdS, (iii) STA/Ag_2/CdS and (iv) PMA/Ag_2S/CdS materials.

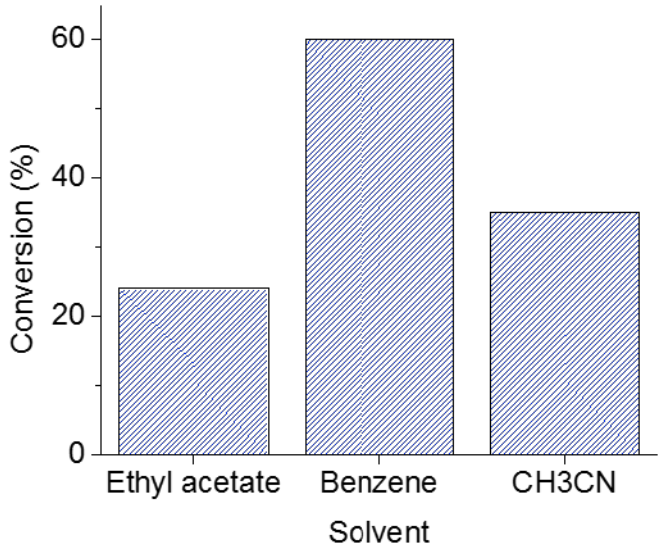

Fig. S5 Control experiments using different solvents for the photooxidation of 1-phenylethanol over PTA/Ag_2S/CdS photocatalyst. *Reaction conditions*: 0.1 mmol 1-phenylethanol, 15 mg catalyst, 1 mL/min O_2, 1.5 mL solvent, 20 ^oC, visible-light irradiation (λ>420 nm), 1 h.

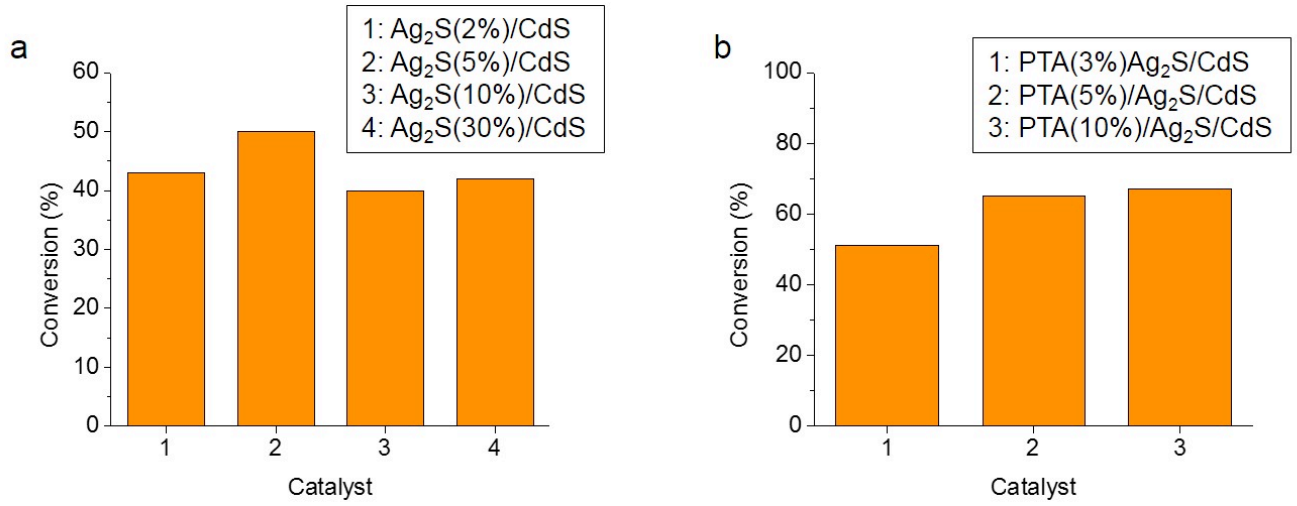

Fig. S6 Control experiments for the photooxidation of 1-phenylethanol to acetophenone using different mesoporous hybrid Ag_2S/CdS and PTA/Ag_2S/CdS photocatalysts. *Reaction conditions*: 0.1 mmol 1-phenylethanol, 15 mg catalyst, 1 mL/min O_2, 1.5 mL solvent, 20 ^oC, visible-light irradiation (λ>420 nm), 1 h.

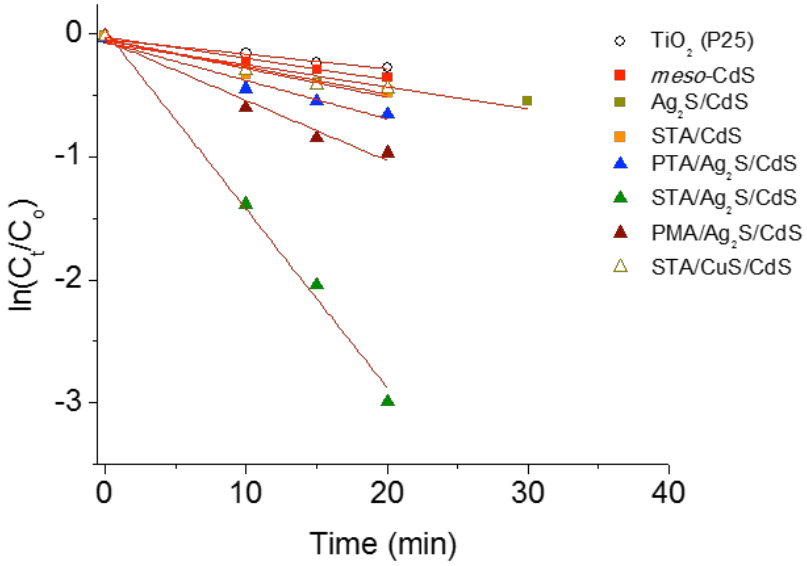

Fig. S7 Kinetic profiles (C_o, C_t are the initial and final (after time t) molar concentrations of 1-phenylethanol, respectively) of photooxidation of 1-phenylethanol using various mesoporous CdS-based catalyst. The corresponding data of TiO_2 Degussa (P25) nanoparticles are also given for comparison. The corresponding red lines are fit to the data.

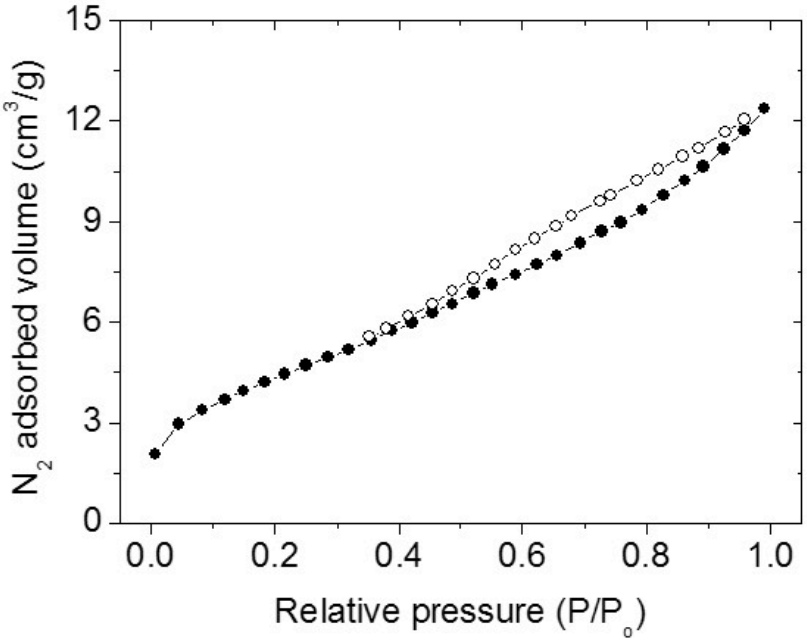

Fig. S8 Nitrogen adsorption and desorption isotherms at -196 ^{o}C of *b*-STA/Ag_2S/CdS composite material. Analysis of the adsorption data with the BET method gives surface area of 14 m^2g^{-1} and total pore volume of 0.02 cm^3g^{-1}.

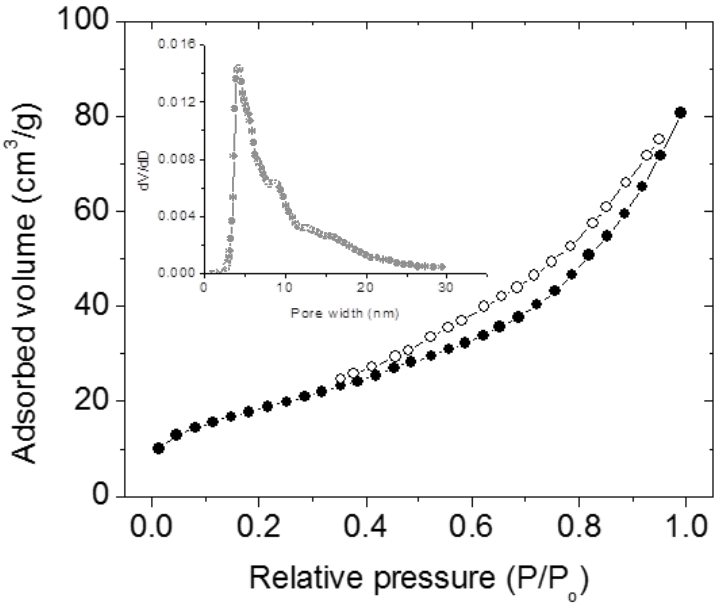

Fig. S9 Nitrogen adsorption and desorption isotherms at -196 ^{o}C of mesoporous STA/CuS/CdS ternary semiconductor. Analysis of the adsorption data with the BET method gives surface area of 68 m^2g^{-1} and total pore volume of 0.11 cm^3g^{-1}. (Inset) NLDFT pore size distribution calculated from the adsorption branch of isotherms, indicating pore diameter of ~4.3 nm.

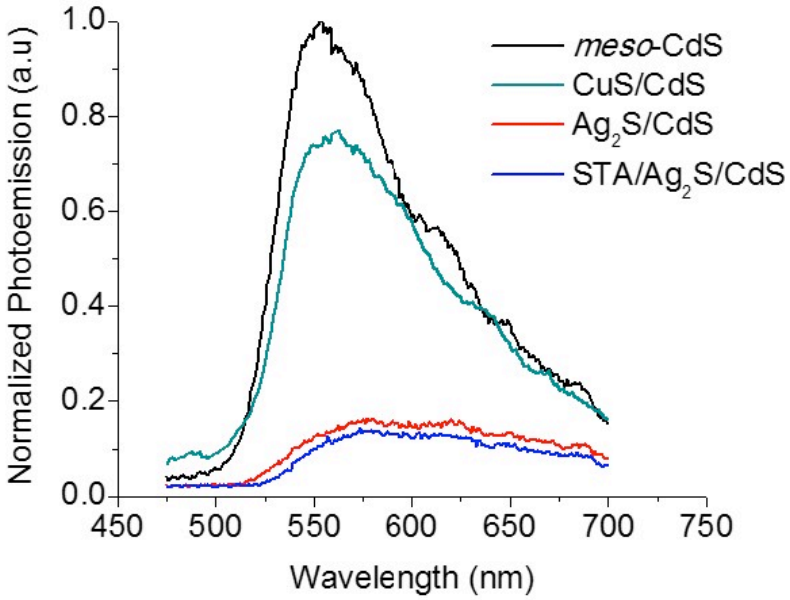

Fig. S10 Normalized photoluminescence (PL) spectra for mesoporous CdS (*meso*-CdS), CuS/CdS, Ag_2S/CdS and STA/Ag_2S/CdS semiconductors (excitation: 380 nm).

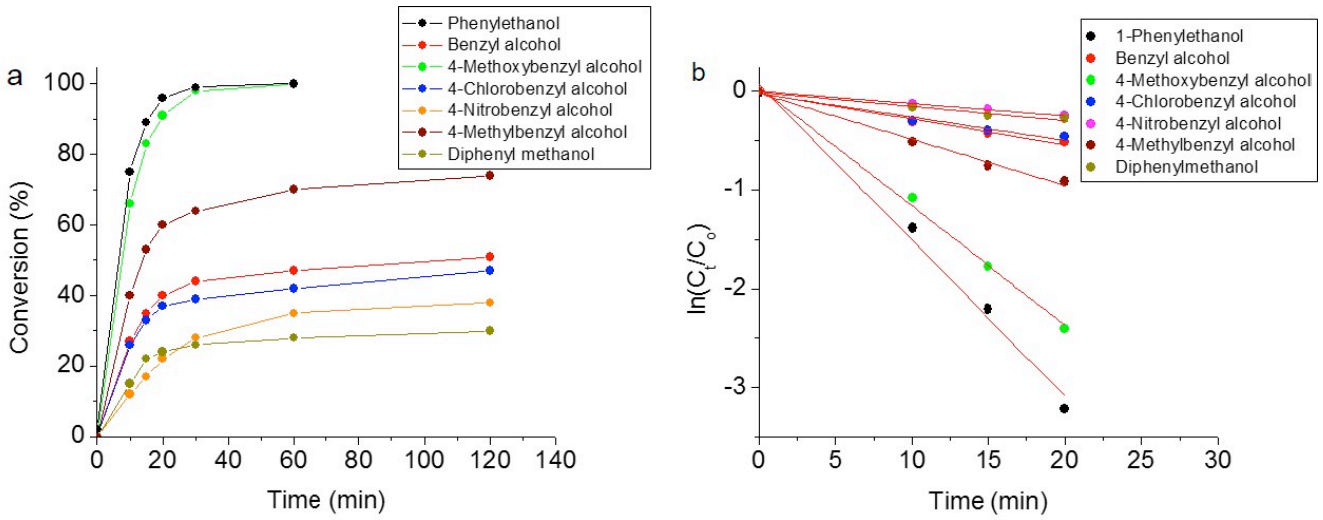

Fig. S11 (a) Time evolution and (b) kinetic profiles (C_o, C_t are the initial and final (after time t) molar concentrations of substrate, respectively) of the photooxidation of various *para*-substituted benzyl alcohols catalyzed by mesoporous STA/Ag_2S/CdS photocatalyst. In pane b: The corresponding red lines are fit to the data, indicating reaction rate constant (*k*) of 0.148 min^{-1} for phenylethanol, 0.026 min^{-1} for benzyl alcohol, 0.121 min^{-1} for 4-methoxybenzyl alcohol, 0.024 min^{-1} for 4-chlorobenzyl alcohol, 0.012 min^{-1} for 4-nitrobenzyl alcohol, 0.048 min^{-1} for 4-methylbenzyl alcohol and 0.014 min^{-1} for diphenylmethanol.

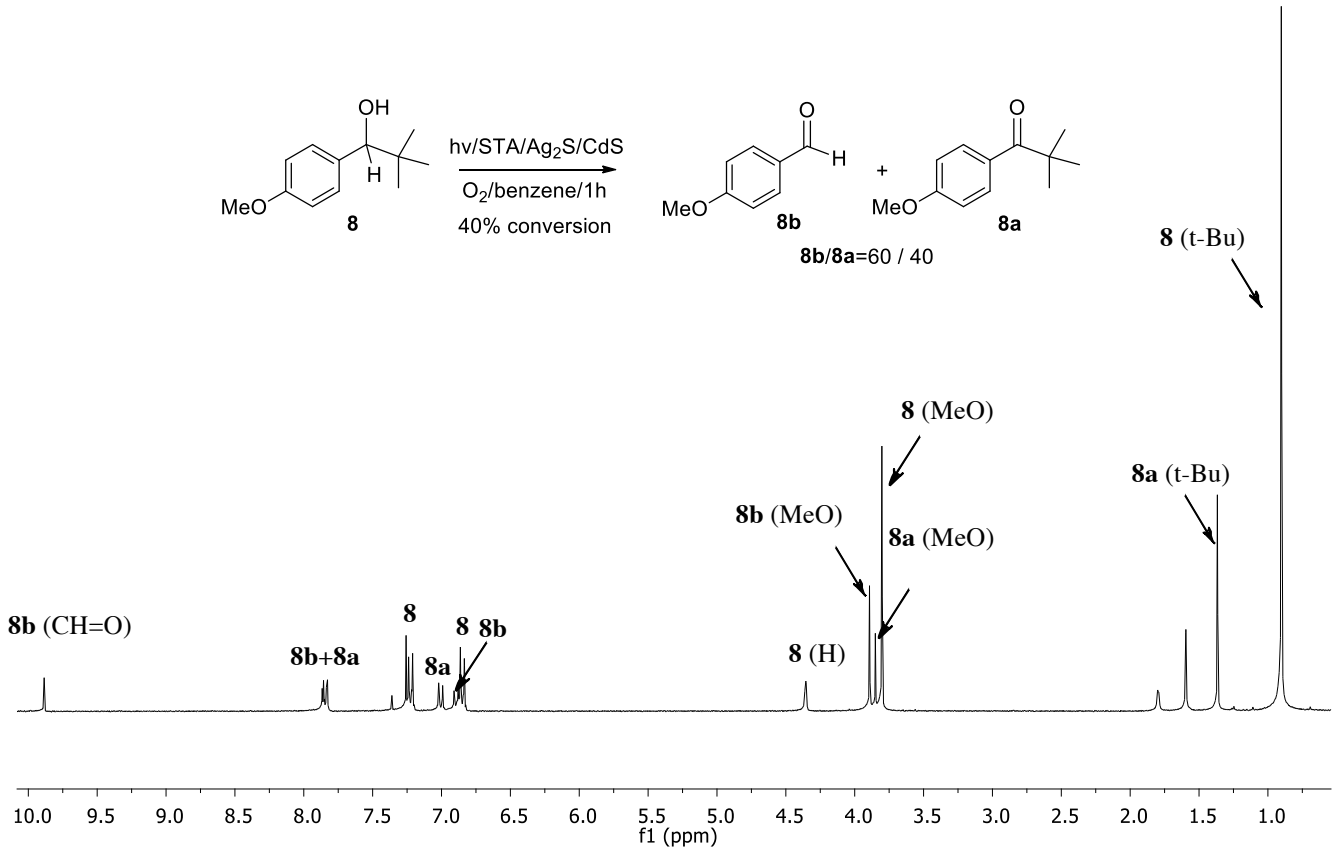

Fig. S12 ^{1}H NMR spectrum of the crude mixture of the oxidation of **8** in the presence of oxygen catalyzed by STA/Ag_2S/CdS after 1 h irradiation.

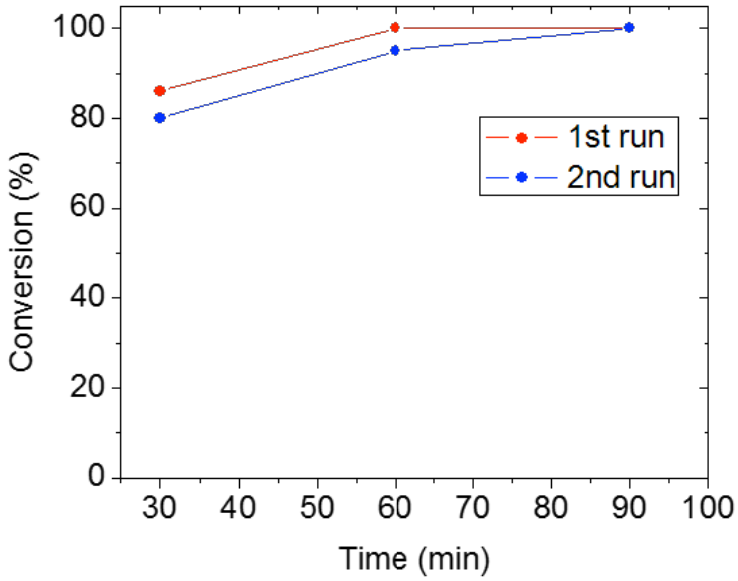

Fig. S13 Recycling study of the mesoporous STA/Ag_2S/CdS photocatalyst. *Reaction conditions*: 0.1 mmol 1-phenylethanol, 15 mg catalyst, 1 mL/min O_2, 1.5 mL benzene, 20 ^{o}C, visible-light irradiation (λ>420 nm).

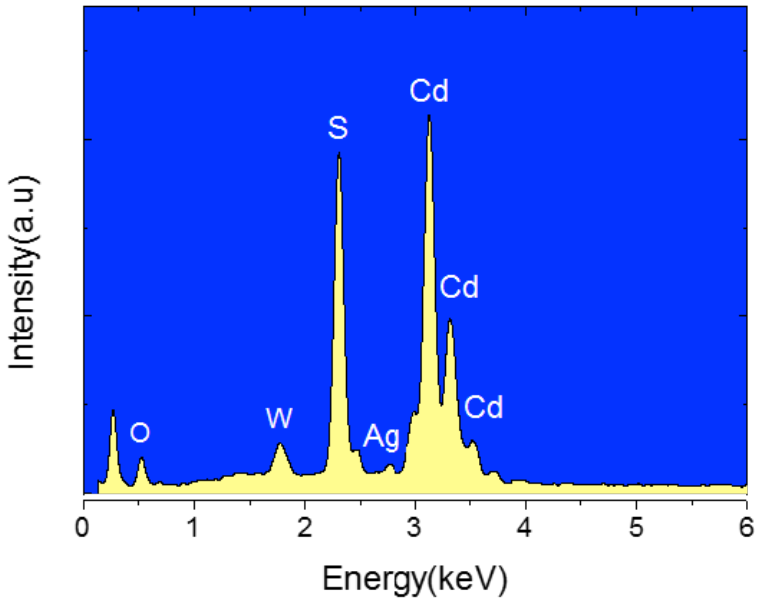

Fig. S14 Typical EDS spectrum of recycled STA/A_2S/CdS catalyst. The EDS spectrum shows average atomic ratios of Cd/S/W/Ag ~47.6:47.9:1.6:2.9 that correspond to a ~5 wt % $H_4SiW_{12}O_{40}$ and ~4.8 wt % Ag_2S loading.

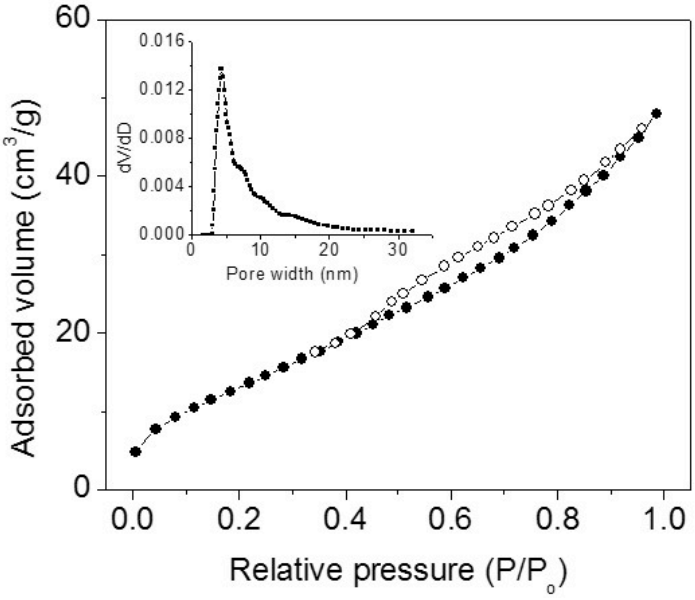

Fig. S15 Nitrogen adsorption and desorption isotherms at -196 ^oC of recycled STA/Ag_2S/CdS catalyst. Analysis of the adsorption data with the BET method gives surface area of 53 m^2g^{-1} and total pore volume of 0.09 cm^3g^{-1}. (Inset) NLDFT pore size distribution calculated from the adsorption branch of isotherms, indicating pore diameter of ~4.4 nm.

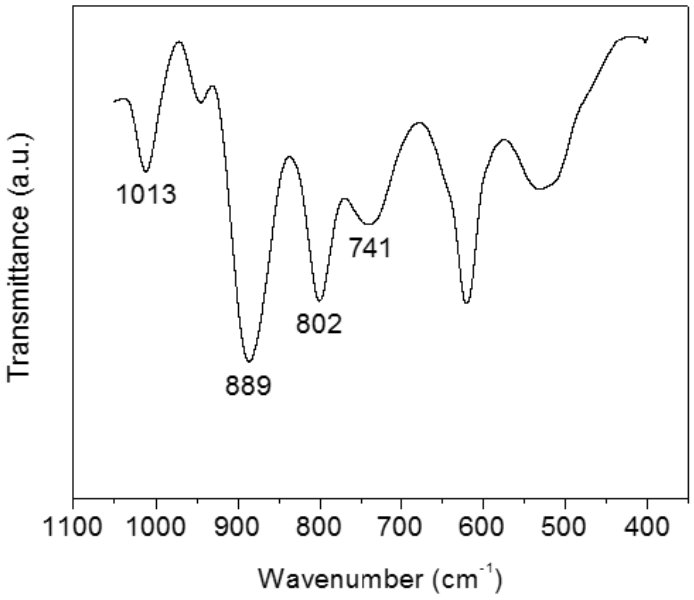

Fig. S16 Infrared spectrum of the recycled STA/Ag_2S/CdS catalyst. The strong absorption peaks at ~889, ~802 and 741 cm^{-1} are assigned to the stretching vibration bands of W=O_d terminal bonds and W-O_b-W and W-O_c-W bridging bonds between the corner-sharing and edge-sharing WO_6 octahedral of the $[SiW_{12}O_{40}]^{4-}$ cluster, respectively. The absorption at ~1013 cm^{-1} can be assigned as Si–O_a stretching vibrational bands of the SiO_4 central unit in $[SiW_{12}O_{40}]^{4-}$ Keggin cluster.