Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Experimental

Materials

TiOSO$_4$, HF, AgNO$_3$ and MnSO$_4$·H$_2$O were purchased from Sinopharm Chemical Reagent Co., Ltd. ALL the reagents were used without further purification.

Synthesis

TiO$_2$ (20 %). 0.02 g Ti powder, 0.2 ml HF, 3.5 ml H$_2$O$_2$ and 54 ml H$_2$O were added into 100 ml dried Teflon autoclave, and then kept at 150 °C for 24 h. After cooling to the room temperature, the white powder was collected by centrifugation and washed with ethanol and deionized water to remove dissolvable ionic impurities. The samples were then dried at 80 °C in air overnight.

TiO$_2$ (40 %) and TiO$_2$ (60 %). 64 and 70 mg of titanium oxysulfate (TiOSO$_4$) powder was dissolved in 40 ml aqueous solution of HF with concentrations of 110 and 175 mM, respectively, to prepare the TiOSO$_4$ aqueous solution precursor for anatase TiO$_2$ (40 %) and TiO$_2$ (60 %) crystals. Then the solution were transferred to a Teflon-lined autoclave and heated at 180 °C for 12 h. After that, the products were washed by ethanol and deionized water for several times, then the white powders was collected by filtration. Finally, it was dried at 80 °C to obtain dry powder.

Ag-TiO$_2$. 0.1 g as-prepared TiO$_2$ was added in an aqueous solutions containing 8 mg AgNO$_3$, then the suspension was irradiated by a Xe lamp under continuous stirring for 10 min, then the suspension was filtered, washed with deionized water and ethanol more than three time, after that, it was dried at 30 °C for24 h.

TiO$_2$-MnO$_x$. 0.1 g TiO$_2$ was added in an aqueous solutions containing 5 mg MnSO$_4$, then the suspension was irradiated by a Xe lamp under continuous stirring for 10 min, Subsequent processing was similar to that of Ag-TiO$_2$.

Ag-TiO$_2$-MnO$_x$. 0.1 g TiO$_2$ was added in an aqueous solutions containing 8 mg AgNO$_3$, then the suspension was irradiated by a Xe lamp under continuous stirring for 10 min, 5 mg MnSO$_4$was then input to the suspension for another 10 min under light irradiation. The subsequent process was similar to that of Ag-TiO$_2$.

Material Characterization

X-Ray diffraction patterns (XRD) of the samples were performed by a smartlab 9 KW X-ray diffractometer using Cu Kα radiation at room temperature and the scan rate of 6° min-1 in the 2θ range from 10° to 80°. SEM images were recorded on a Zeiss SIGMA FESEM using 20 KV as its accelerating voltage. UV-vis diffuse reflectance spectra (DRS) were recorded using a Shimadzu UV-3600 spectrometer by using BaSO$_4$ as a reference. The oxidation states of of the samples were analyzed by X-ray photoelectron spectroscopy (XPS) which was operated on a ESCALAB 250Xi spectrometer (Thermo Electron Corp.) with an Al-Kα X-ray source, the step size of XPS date is 0.1 eV, and all the spectra were calibrated to the C 1s peak at 284.6 eV. The photoluminescence (PL) spectra were collected using a Jasco FP-6500 with λ_{exc}=290 nm.

Photocatalytic CO$_2$ reduction

The photocatalytic CO$_2$ reduction was carried out in a home-made closed gas system. In the photocatalytic CO$_2$ reduction reaction system, 0.1 g of photocatalyst was uniformly dispersed onto the watch-glass with an area of ~28 cm^2, then 1.55 g NaHCO$_3$ was put onto the bottom of reaction cell (Pyrex glass) with a total volume of 500 mL. Prior to the light irradiation, the above system was thoroughly vacuum-treated to completely remove air. After that, 5 mL of H_2SO_4 aqueous solution (1M) which was introduced into the reactor by syringe（CO_2 and H_2O vapor were in-situ generated by the reaction of $NaHCO_3$ and H_2SO_4 aqueous solution, which was then kept for 30 min to establish an adsorption–desorption balance. After that, the reactor was irradiated from the top by 300 W Xe-lamp (PerfectLight Co., Ltd. China), and the photoreaction temperature was kept at 20◦C. During their radiation, about 5 mL of gas was taken from the reaction cell for subsequent qualitative analysis by using SP 7820 gas chromatography (GC) equipped with flame ionization detector (GC-FID,GDX-502 columns) and thermal conductivity detector (GC-TCD,TDX-01 columns). The quantify-cation of the production yield was based on a calibration curve. The outlet gases were determined to be CH_4, CO and CO_2.

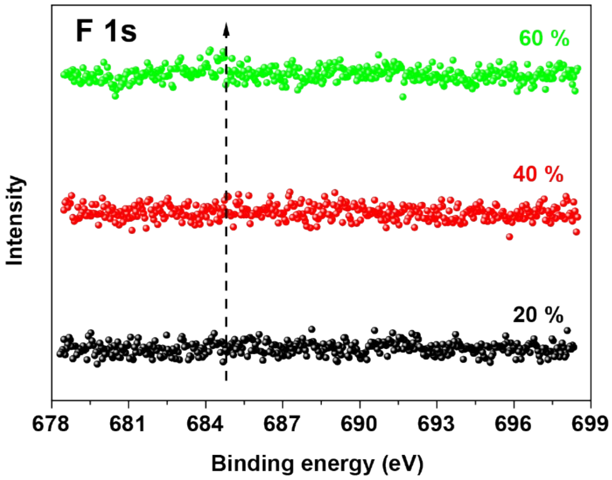

Fig. S1 XPS spectra of pure TiO_2 which was detected after calcination at 500 ^oC for 3h.

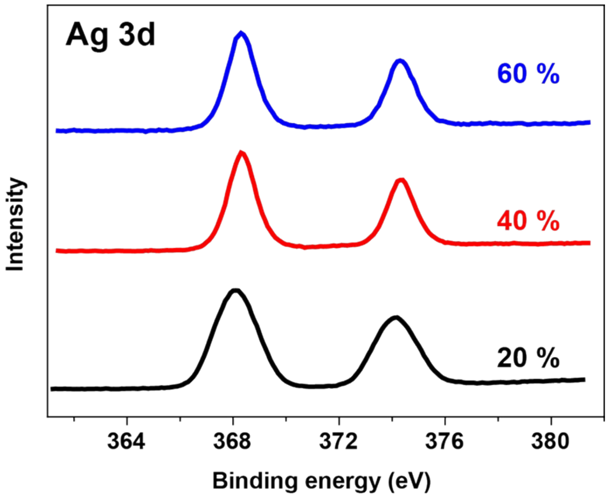

Fig.S2 Ag 3d XPS of three Ag-TiO_2-MnO_x samples

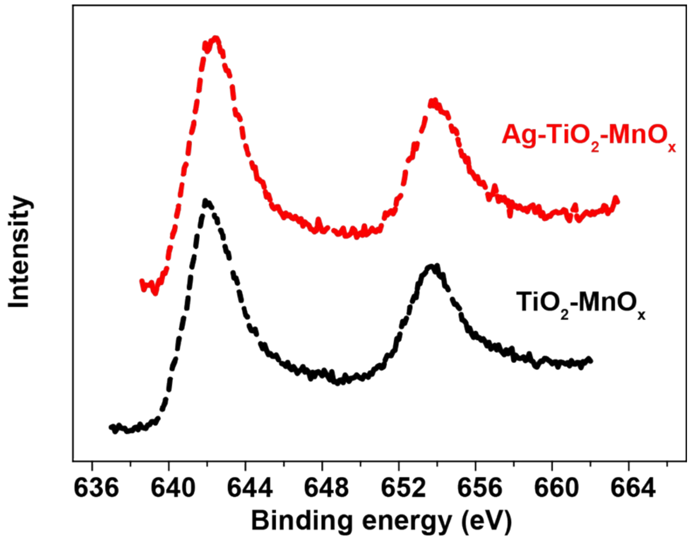

Fig.S3 Mn 2p XPS of TiO_2-MnO_x (40%) and Ag-TiO_2-MnO_x (40%) samples.

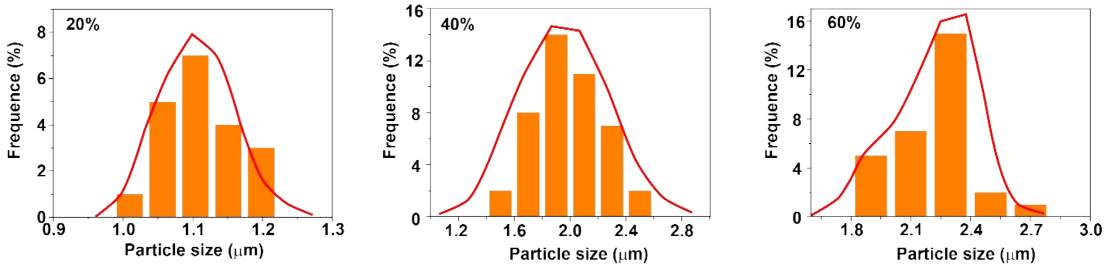

Fig.S4 Size distribution of TiO_2 in our experiment.

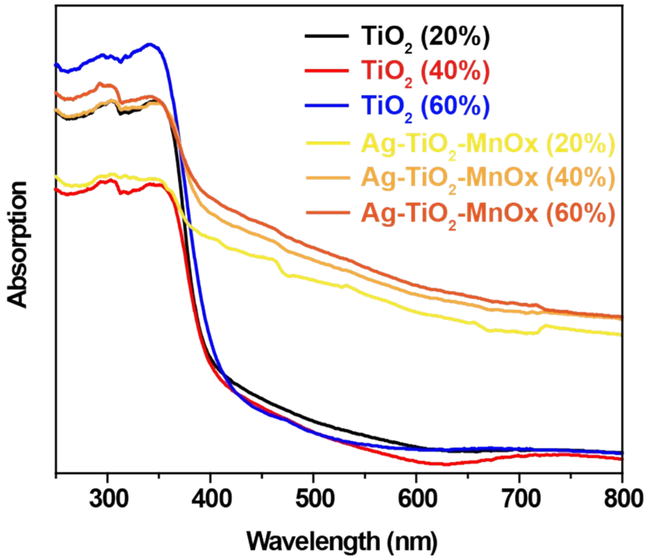

Fig.S5 DRS spectrum of pure TiO_2 and dual loaded TiO_2.

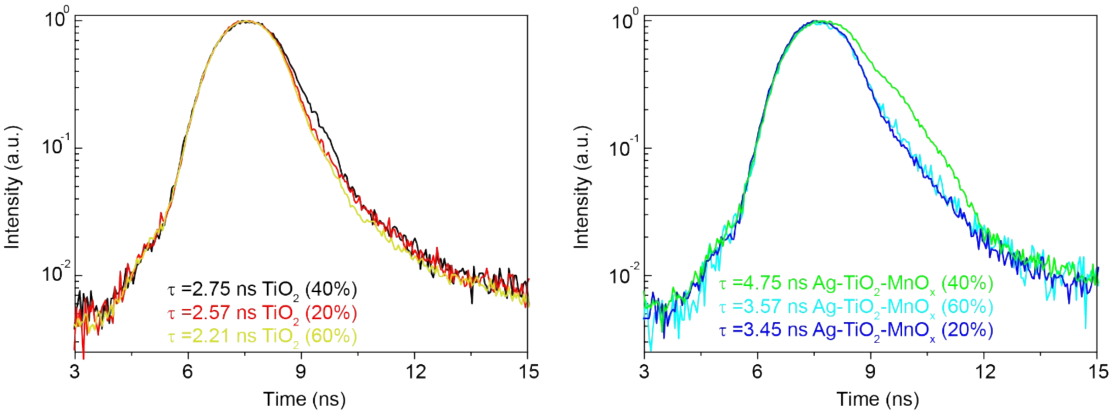

Fig.S6 Time-resolved PL spectra of the above samples.

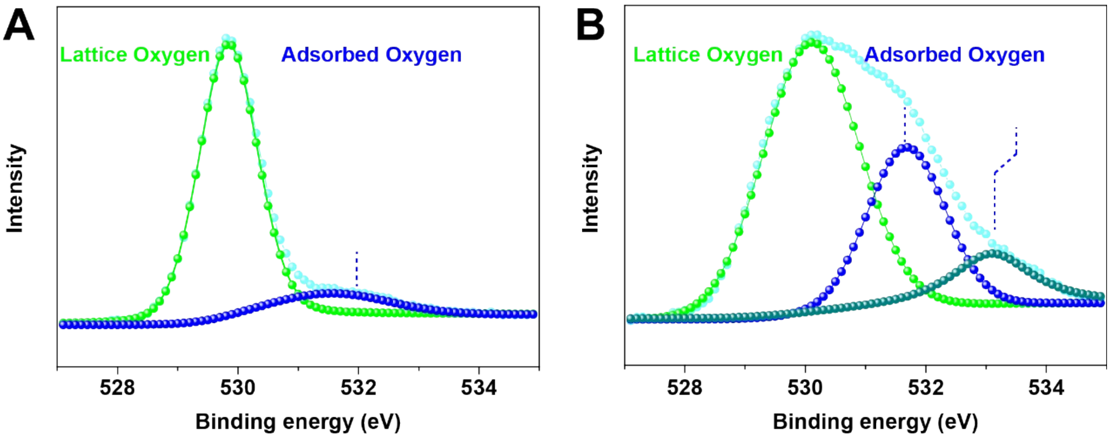

Fig.S7 Fitted O1s XPS signal of (A) TiO_2 (20 %) and (B) Ag-TiO_2-MnO_x (20 %).

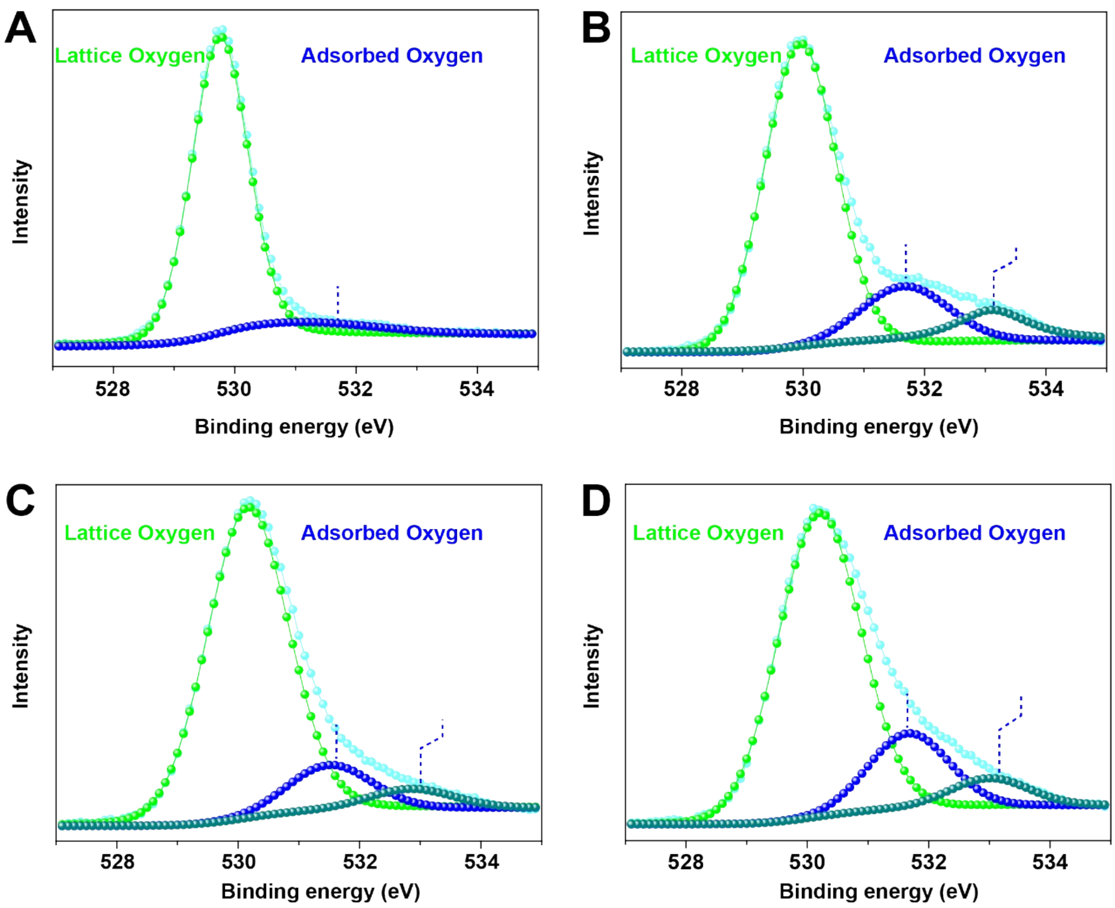

Fig.S8 Fitted O1s XPS signal of (A) TiO_2 (40 %), (B) Ag-TiO_2 (40 %), (C) TiO_2-MnO_x (40 %) and (D) Ag-TiO_2-MnO_x (20 %).

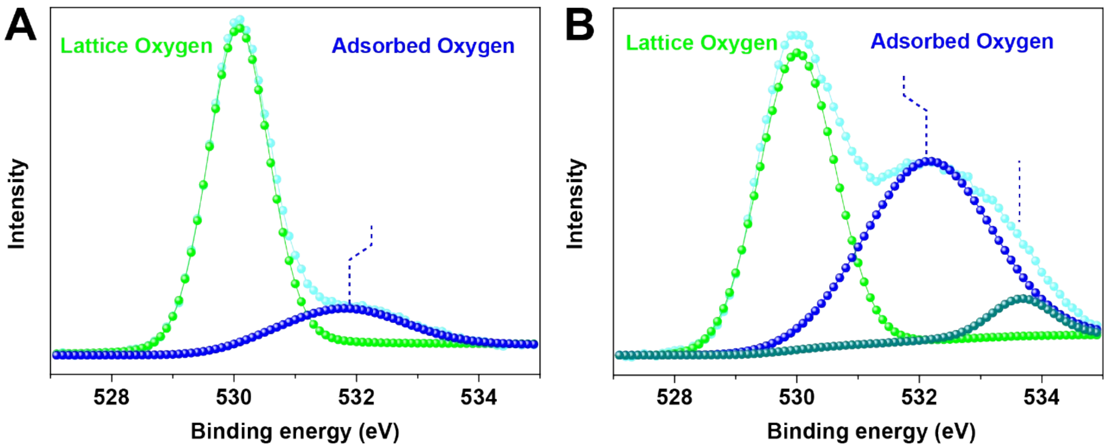

Fig.S9 Fitted O1s XPS signal of (A) TiO_2 (60 %) and (B) Ag-TiO_2-MnO_x (60 %).

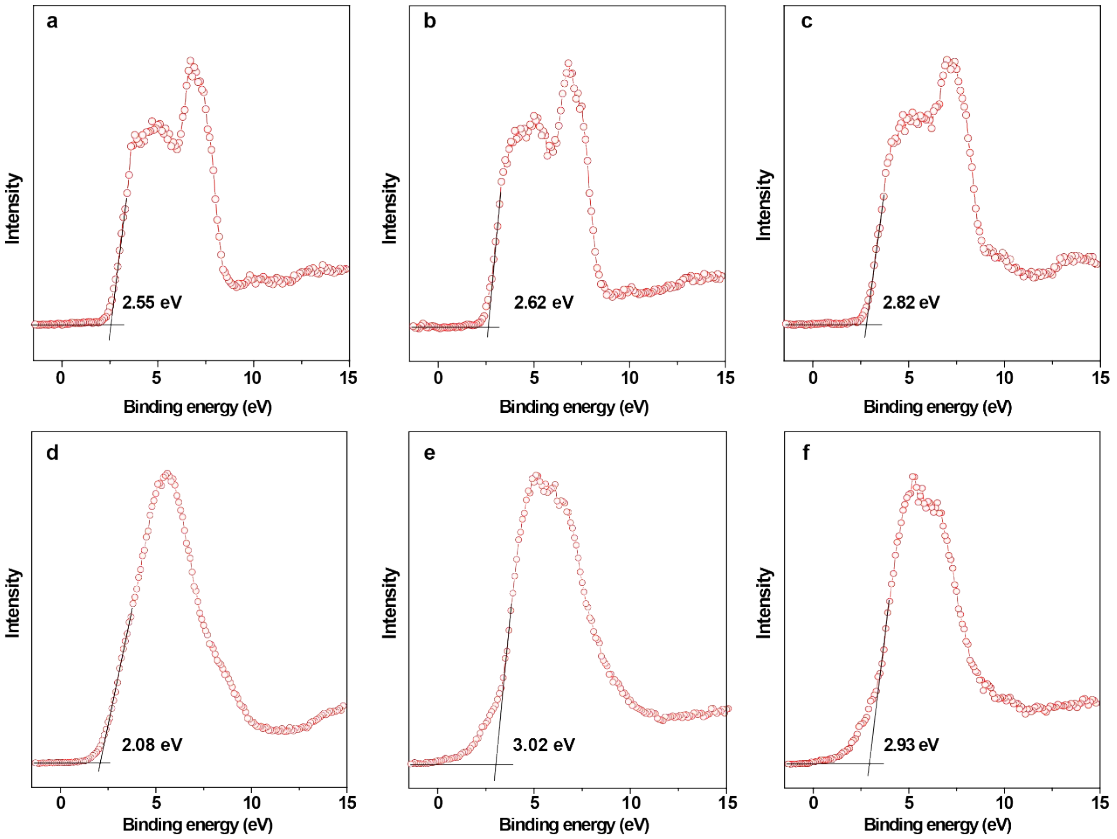

Fig.S10 XPS valance spectrum of samples; a: TiO_2 (20%), b: TiO_2 (40%), c: TiO_2 (60%), d: Ag-TiO_2-MnO_x (20%), e: Ag-TiO_2-MnO_x (40%), f: Ag-TiO_2-MnO_x (60%).

The valance band edge strongly depend on the electronic structure or coordination number of surface atoms. We detected the VB band of TiO_2 and dual loaded TiO_2 by XPS, the result was shown in Fig. S10. The VB band edge of TiO_2 (20%), TiO_2 (40%) and TiO_2 (60%) were 2.55 2.62 and 2.82 eV, respectively. The band edge of Ag-TiO_2-MnOx (20%) was located at 2.08 eV seems result from a physical mixing of MnOx (VB band of MnO_2: 1.58 eV) and TiO_2 (20%). The band edge of Ag-TiO_2-MnO_x (40 %) was located at 3.02 eV, an apparent positive shift (0.4 eV) was observed for Ag-TiO_2-MnO_x (40 %) while compared to TiO_2 (40%), which means a higher energy was needed to excite these valance electrons after the formation of Ti-O-Mn. This is consistent with the positive shift of Ti 2p and O 1s spectrum for Ag-TiO_2-MnO_x (40 %). A small positive shift (0.11 eV) was found in Ag-TiO_2-MnO_x (60%) after the formation of Ti-O-H bonds which suggested the change of coordination number for surface Ti atoms.

Table 2 ICP-OES results of as-prepared samples.

	Ag (wt %)	**Mn (wt %)**
Ag-TiO_2-MnO_x (20%)	4.7	3.9
Ag-TiO_2-MnO_x (40%)	4.6	3.3
Ag-TiO_2-MnO_x (60%)	5.0	4.1
Ag-TiO_2 (40%)	4.0	
TiO_2-MnO_x (40%)		3.5