Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION

Oxygen Deficient ZnO_{1-x} Nanosheets with High Visible Light Photocatalytic Activity

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Fig. S1 Photographs of ZnO_{1-x} sample obtained at gram level by one-pot synthesis using a 1000 mL Teflon-lined stainless steel autoclave.

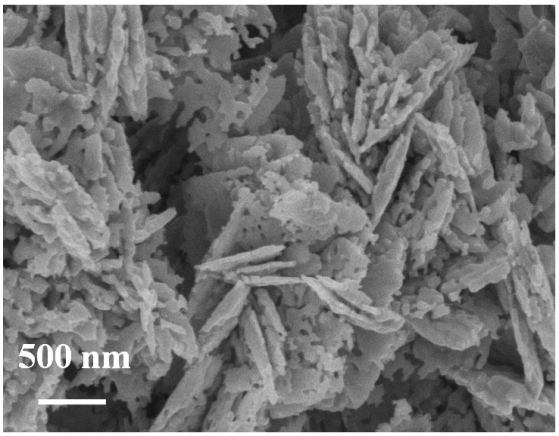

Fig. S2 SEM image of ZnO after calcination at 500 °C in air.

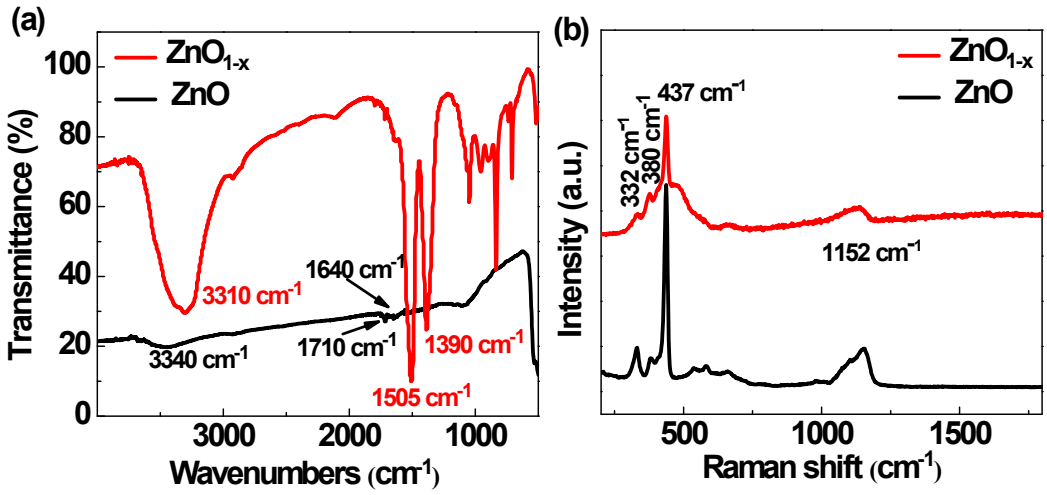

Fig. S3 The FT-IR (a) and Raman (b) spectra of ZnO_{1-x} and ZnO samples.

The IR spectra of ZnO_{1-x} and ZnO samples were compared in Fig. S3a. Absorption band near 3300 cm^{-1} represents stretching and bending modes of hydroxyl group (O-H), those near 2920 cm^{-1} are stretching and bending modes of C-H bonds. The peaks at 1390-1710 cm^{-1} are the C=O stretching mode, the peak around 1050 cm^{-1} is attributed to the stretching mode of C-O bond. The Raman spectra of ZnO_{1-x} and ZnO samples are displayed in Fig. S3b. ZnO falls in the space group C4 6v and has hexagonal wurtzite structure with two formula units per primitive cell. Brillouin zone of phonon has irreducible forms like $1A_1 + 2B_1 + 1E_1 + 2E_2$. A_1 is transverse optical (TO) and E_1 is longitudinal optical (LO) modes, these are polar modes for Raman and IR. B_1 and E_2 are non-polar modes, B_1 is active for IR and E_2 for Raman. Three common prominent vibration peaks of ZnO_{1-x} and ZnO samples can be observed at about 330, 380, 437 cm^{-1}, the peak at 437 cm^{-1} is

attributed to the nonpolar E_2 optical phonon mode while the 330 cm^{-1} peak is ascribes to the second order Raman process as well as the $2E_2$ mode, the last at about 380 cm^{-1} peak belongs to polar A_1 mode. The peak at 578 cm^{-1} positioned between A1 (LO) and E1 (LO) optical phonon mode of ZnO sample indicates the perfect structure with no oxygen deficiency. In contrast, our as-prepared ZnO_{1-x} sample has no peak around 580 cm^{-1}, confirming the existence of a large amount of oxygen vacancies.[S1,S2]

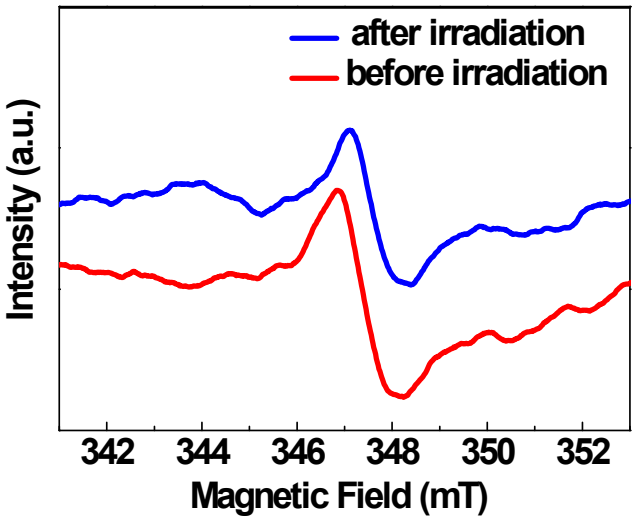

Fig. S4 EPR spectra of the sample measured before and after the photocatalytic reaction by visible light irradiation ($\lambda \geq 400$ nm).

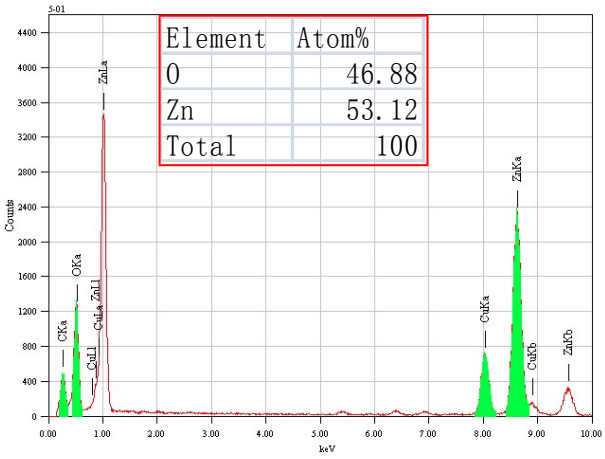

Fig. S5 EDS spectrum of ZnO_{1-x} nanosheets.

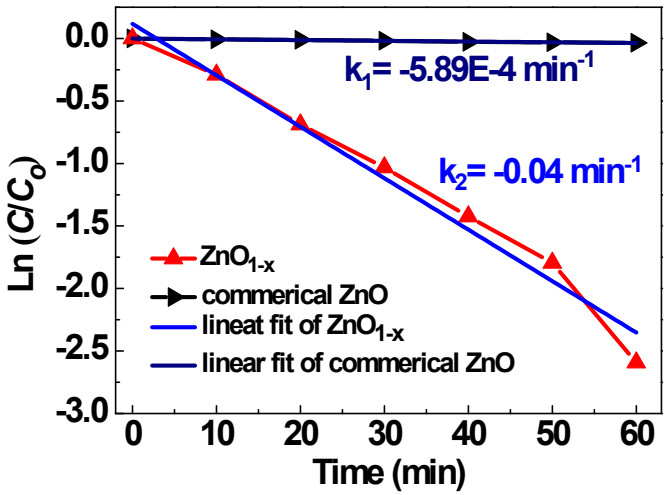

Fig. S6 The Plot of [Ln(C/C$_0$)] vs. time curves of photodegradation of MO with respect to irradiation time. The apparent rate constant k_{MO} of MO photodegradation for ZnO_{1-x} NSs (−0.04 min^{-1}) is more than 68 times higher than that for ZnO NSs (−5.89E-4 min^{-1}).

The decomposition of MO could be assigned to a pseudo-first-order kinetics reaction with a simplified Langmuir–Hinshelwood model:

$$Ln(C_0/C) = kt$$

This model is generally used for the photocatalytic degradation process, where k is the pseudo-first-order rate constant, and was determined from a linear fit to the data as shown in Fig. S6.

References

S1 C. A. Arguello, D. L. Rousseau and S. P. S. Porto, *Phys. Rev.*, 1969, **181** 1351.

S2 S. A. Ansari, M. M. Khan and M. O. Ansari, *J. Phys. Chem. C*, 2013, **117**, 27023.