Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Information:

A tribo-positive Fe@MoS_2 piezocatalyst for durably degradation of tetracycline: Degradation mechanism and toxicity assessment

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Contents：

1. Detailed theoretical calculations:

1.1 DFT calculation method

To study structural and properties variation of adsorption of Fe atom modified MoS_2, layered MoS_2 was chosen as the simplified model for DFT studies [1-2]. First principles calculations in the framework of density functional theory, including structural and electronic properties, were carried out based on the Cambridge Sequential Total Energy Package known as CASTEP. The exchange-correlation functional under the generalized gradient approximation (GGA) with norm-conserving pseudopotentials and the Perdew Burke-Ernzerhof functional was adopted to describe the electron-electron interaction. An plane wave basis set cut-off energy of 340 eV was used and a k-point sampling set of 3 x 3 x 2 was tested to be converged. A force tolerance of 0.01 eV $Å^{-1}$, energy tolerance of 5.0×10^{-6} eV per atom and maximum displace-ment of 5.0×10^{-4} Å were considered. The vacuum space along the z direction was set to be 10 Å, which is sufficient to avoid interactions between two neighboring images. The adsorption energy E_{ads} of Fe on MoS_2 was defined as:

$$E_{ads} = E_{MoS_2} + E_A - E_{TOL}$$

where E_{TOL} denotes the adsorption of Fe atom on the MoS_2 substrates, E_{MoS_2} denotes the bare MoS_2 substrates, and E_A denotes the energy of Fe atom.

[1] Y.B Wu, Z.Y Huang, H.T Liu, C.Y He, L. Xue, X. Qi, J.X. Zhong. Transition metal atoms absorbed on MoS_2/h-BN heterostructure: stable geometries, band structures and magnetic properties. Phys. Chem. Chem. Phys., 2018, 20, 17387-17392.

[2] S. Tongay, J. Zhou, C. Ataca, K. Lo, T.S. Matthews, J. Li, J.C. Grossman, J. Wu,

Thermally Driven Crossover from Indirect toward Direct Bandgap in 2D Semiconductors: MoSe2 versus MoS_2. Nano Lett., 2012, 12, 5576-5580.

1.2 Toxicity assessment method

QSAR was used to assess the ecotoxicological potentials of TC and its intermediates with the aid of the ECOSAR program. QSAR uses the structural information of targeted compounds and provides LC50 values for fish (96 h) and daphnid (48 h), EC50 values for green algae (96 or 144 h), and the values of chronic toxicity.

2. Support figures

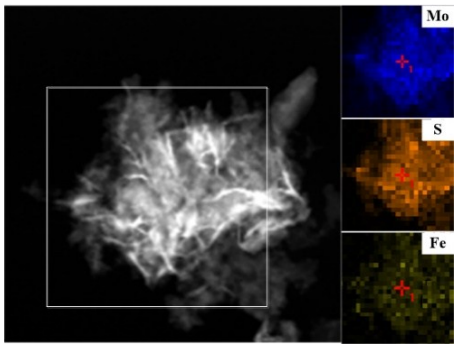

Fig. S1 TEM images and corresponding EDX elemental mapping of Fe, Mo, and S of as-prepared Fe@MoS_2.

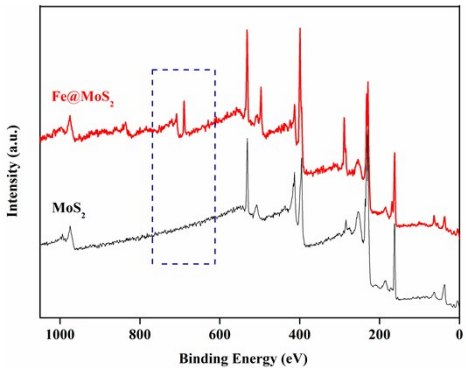

Fig. S2 The XPS spectra of the as-prepared MoS_2 and Fe@MoS_2.

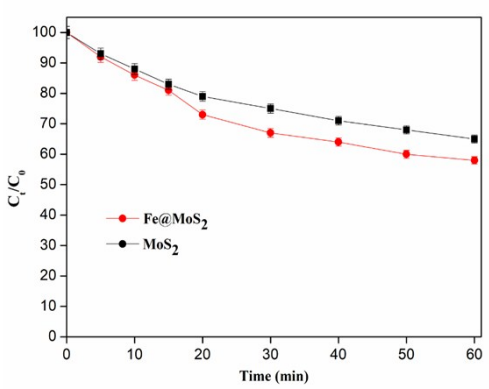

Fig. S3 The adsorption capacity of MoS_2 and Fe@MoS_2 on tetracycline.

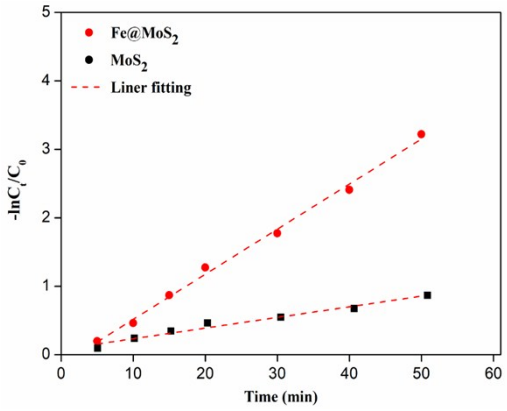

Fig. S4 Plots of $-\ln(C_t/C_0)$ versus the ball-milling vibration time, showing the fitting results using the pseudo-first-order reaction.

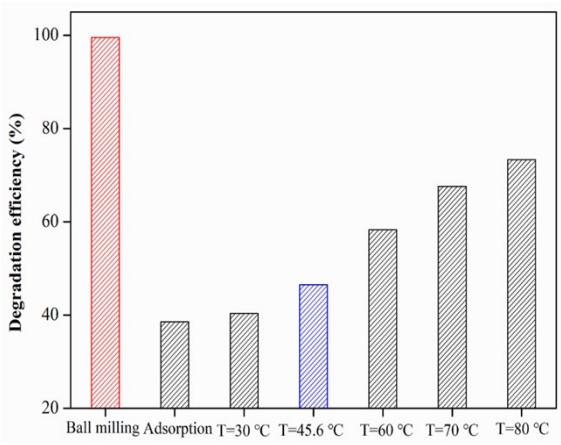

Fig. S5 The degradation of tetracycline by Fe@MoS_2 via thermocatalytic process.

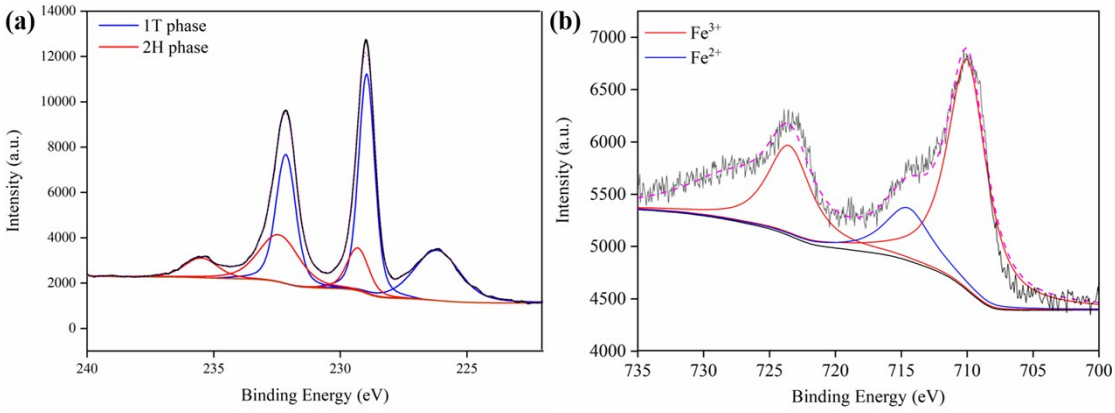

Fig. S6 XPS spectra of the "use" Fe@MoS_2 samples: (a) Mo 3d, (b) Fe 2p.

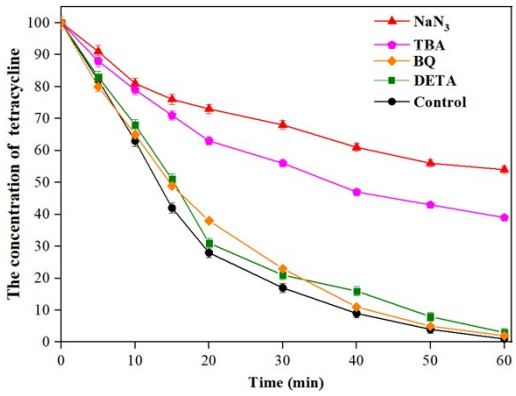

Fig. S7 The effect of different radical quenching agents on the degradation of tetracycline by Fe@MoS_2.