Supplementary Information

Interfacial charge transfer–driven UV-activated photocatalytic degradation of metronidazole via δ-MnO_2/WO_3 heterojunction in aqueous media

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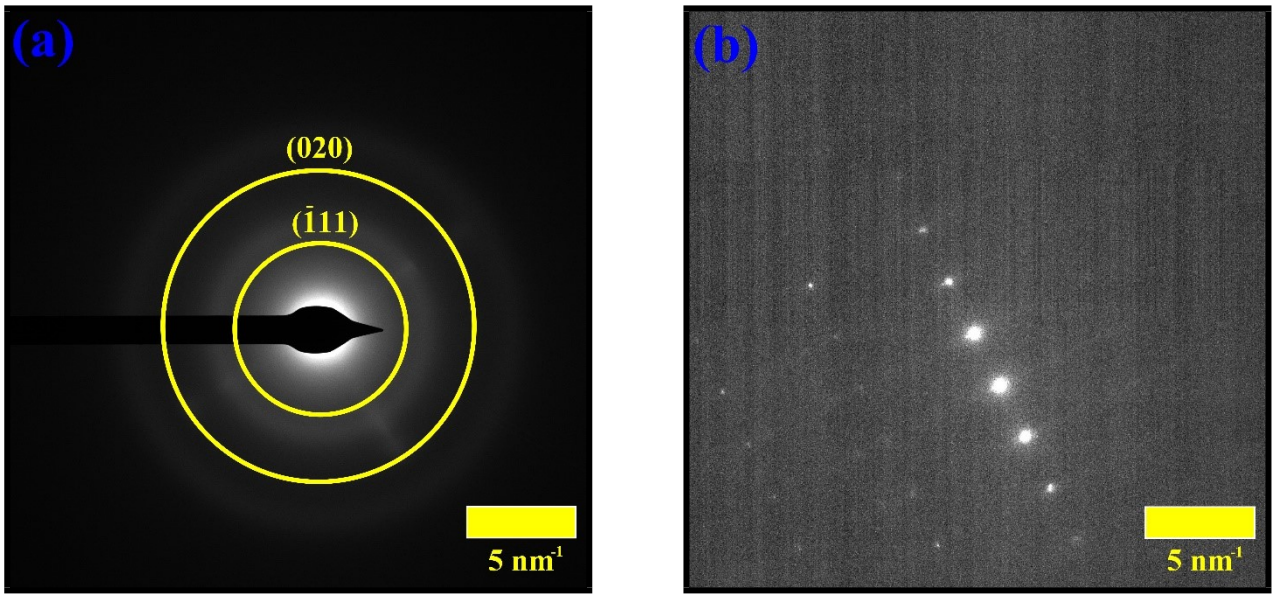

Figure S1: Selected area electron diffraction (SAED) patterns of (a) pristine δ-MnO_2 and (b) pure WO_3. The concentric diffraction rings observed for δ-MnO_2 correspond to the (11) and (020) crystallographic planes, indicating its polycrystalline nature. In contrast, the discrete diffraction spots in the SAED pattern of WO_3 suggest a higher degree of crystallinity with well-defined lattice ordering.

Calculations for E_{CBM} and E_{VBM}:

The electronegativity of the MnO_2 and WoO_3 NPs is calculated from the equation (3) is,

$\chi_{MnO_2} = \sqrt[3]{(3.232)_{Mn}^{1}(7.5395)_{O}^{2}} = 5.68$, so, the conduction band minimum value (E_{CBM}) and the maximum valence band value (E_{VBM}) of MnO_2 is calculated as 0.65 eV and 1.71 eV from equations (1) and (2). $\chi_{WO_3} = \sqrt[4]{(4.399)_{W}^{1}(7.5395)_{O}^{3}} = 6.58$ Conduction band minimum value (E_{CBM}) and the maximum valence band value (E_{VBM}) of WO_3 is calculated as 0.62 and 3.55.

Effect of pH (pure MnO_2):

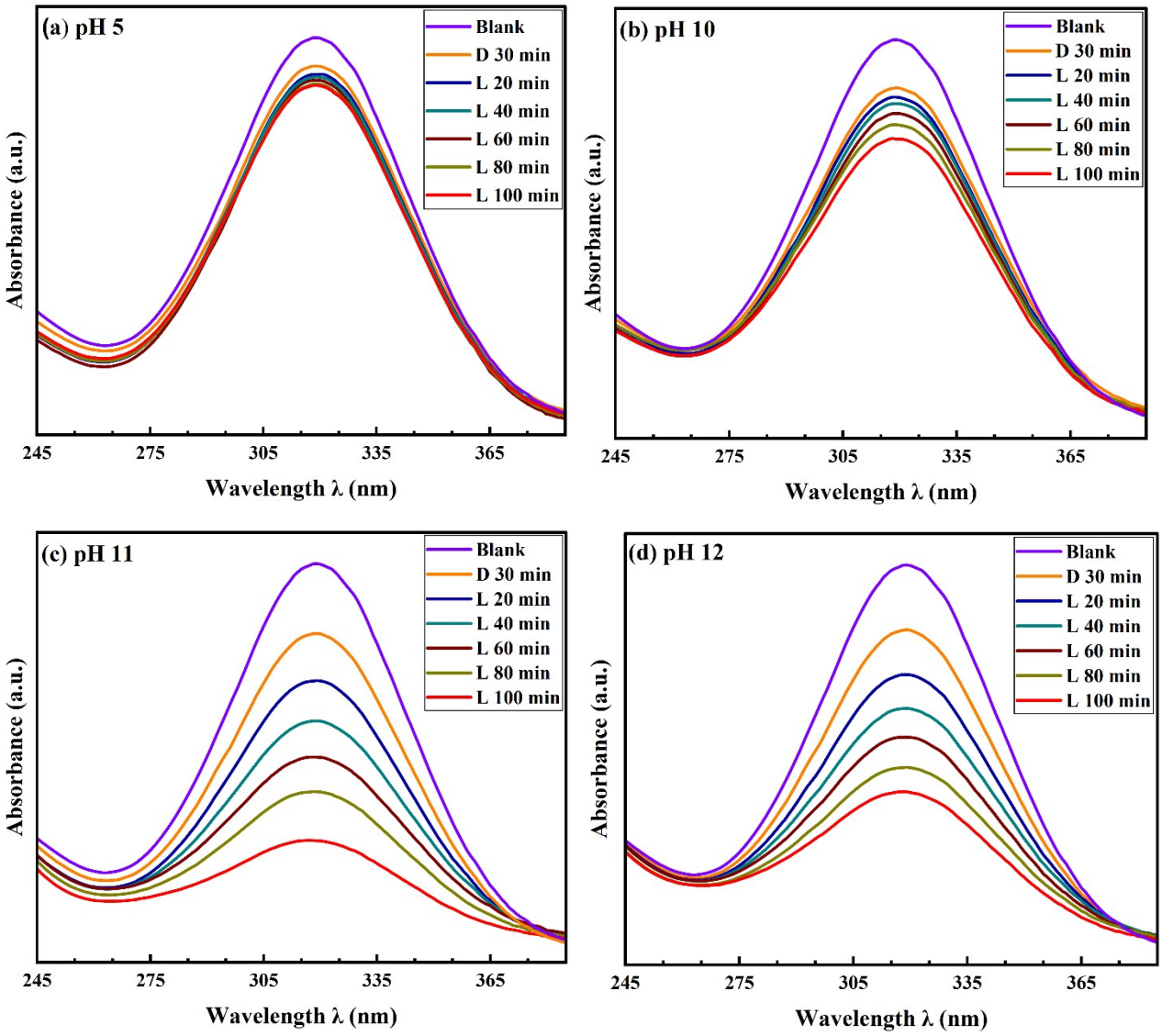

Figure S2: UV-Vis absorption spectra of MNZ degradation using MnO_2 as a catalyst at different pH values under UV irradiation: (a) pH 5, (b) pH 10, (c) pH 11, and (d) pH 12. The MnO_2 dosage was fixed at 0.5 g/L, and the initial MNZ concentration was 10 ppm.

Particle Variation (Pure MnO_2):

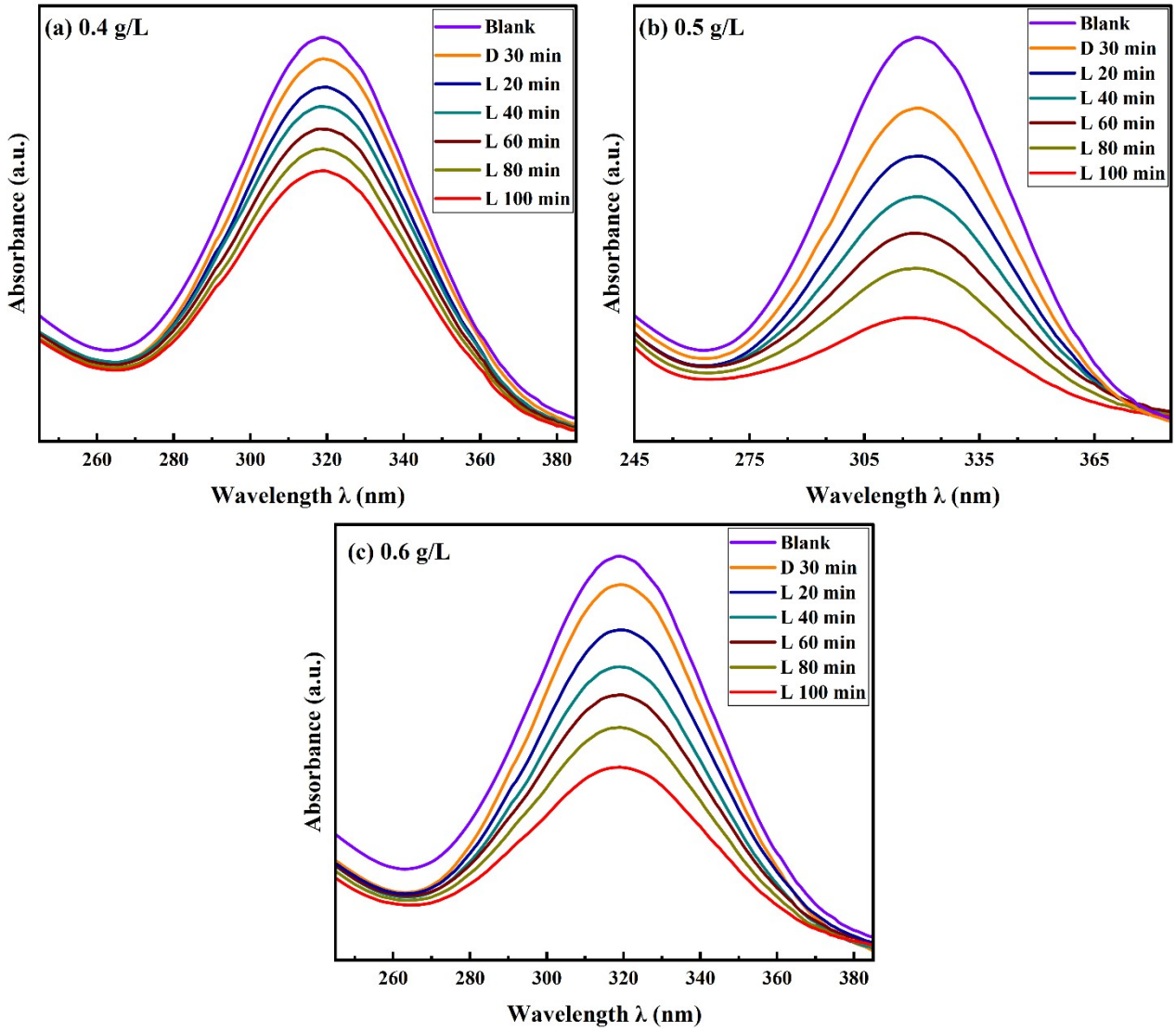

Figure S3: UV-Vis absorption spectra illustrating the photocatalytic degradation of MNZ over MnO_2 at different catalyst dosages: 0.4, 0.5, and 0.6 g/L, under UV irradiation. The initial MNZ concentration was fixed at 10 ppm, and the solution pH was maintained at 11.

Effect of pH (pure WO_3):

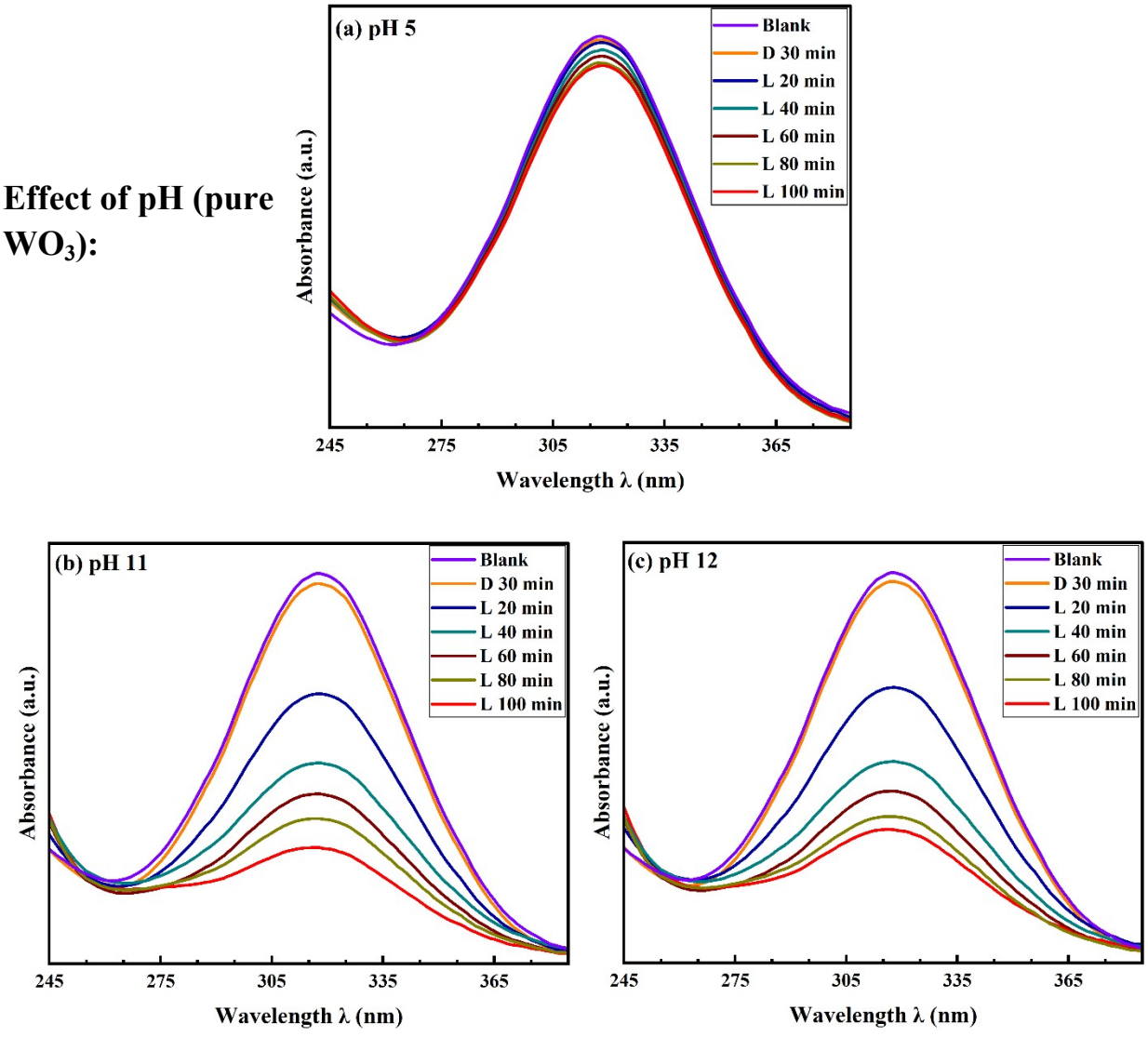

Figure S4: UV-Vis absorption spectra illustrating the photocatalytic degradation of MNZ over pure WO_3 at different pH values under UV irradiation: (a) pH 5, (b) pH 11, and (c) pH 12. The initial MNZ concentration was fixed at 10 ppm.

Composite:

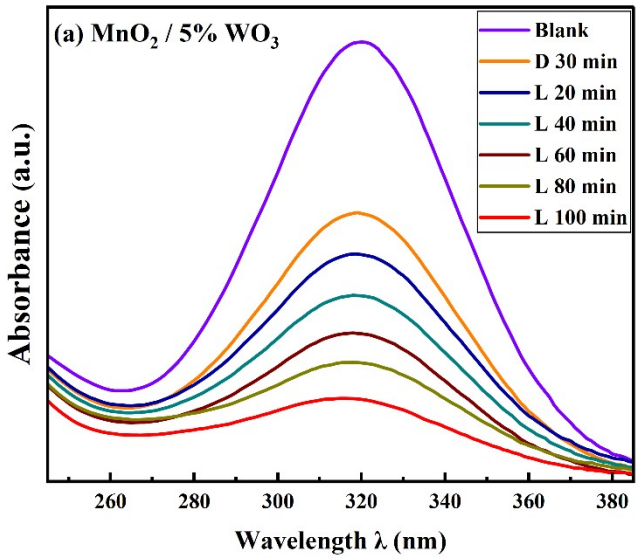

Figure S5: UV-Vis absorption spectra showing the photocatalytic degradation of MNZ over MnO_2-WO_3 composite photocatalysts of δ-MnO_2/5% WO_3, under UV irradiation. The initial MNZ concentration was fixed at 10 ppm.

Table S1: Pseudo First-order Fitting parameters.

pH	R^2 value	
	WO_3	MnO_2
5	0.9859	0.5812
10	--	0.83443
11	0.92183	0.97303
12	0.96205	0.95361

MnO_2 particle Variation (g/L)	R^2 value
0.4	0.97303
0.5	0.98487
0.6	0.97814

Species	R^2 value
MnO_2	0.97303
WO_3	0.93014
MnO_2/WO_3 (5%)	0.96977

Reusability of the photocatalyst:

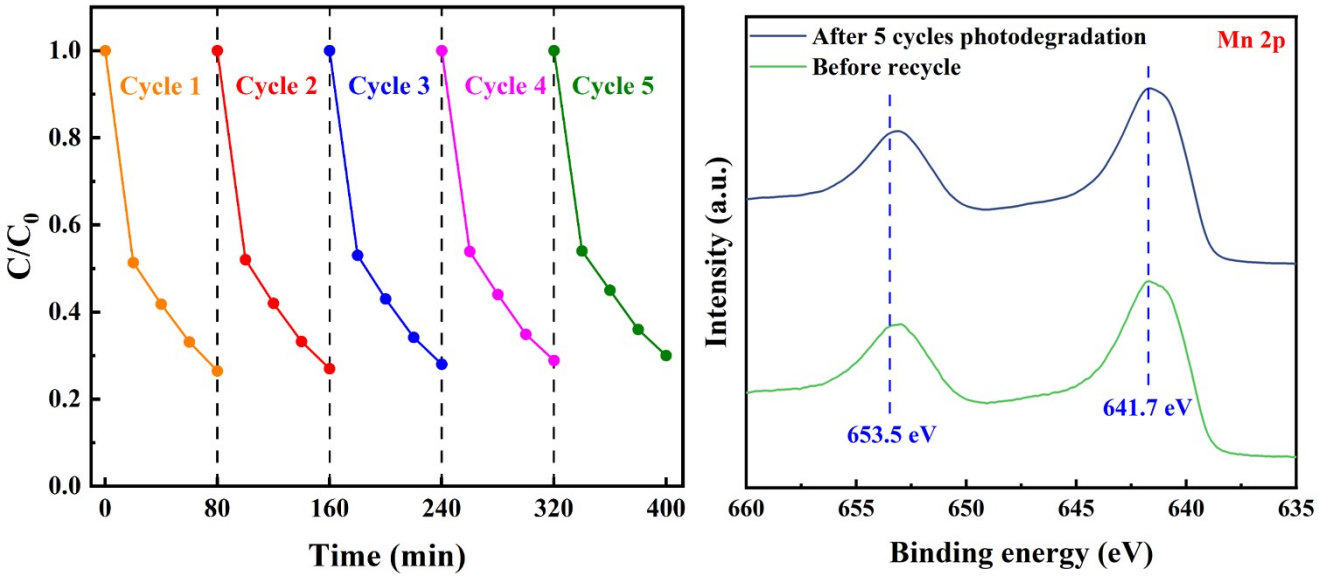

Figure S6: Recyclability and post-reaction stability analysis of the δ-MnO_2/WO_3 (5%) heterojunction. (a) Degradation efficiency over five successive photocatalytic cycles (80 min each). (b) Mn 2p XPS spectra before and after five cycles, showing negligible variation in binding energies, which confirms the structural and chemical robustness of the photocatalyst during repeated operation.