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Supplementary Information for

Efficiently harvesting ultrasonic vibration energy of two-dimensional graphitic carbon nitride for piezocatalytic degradation of dichlorophenols

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Experimental Procedures

1. Detection of hydroxyl and superoxide radicals

Terephthalic acid (TA), as a probe molecule for detecting piezocatalytically generated •OH radicals. TA forms the highly fluorescent 2-hydroxyterephthalic acid (TAOH) with a specific fluorescence emission maximum at wavelength of 425 nm when reacting with •OH radicals. In detail, 50 mg g-C_3N_4 were suspended in 25 mL aqueous solution containing 2 mM NaOH and 0.5 mM TA. The mixture was firstly stirred in dark for 60 min before the ultrasonic vibration treatment similar to the piezocatalytic process. By surveying the fluorescence intensity on Horiba FluoroMax-4 spectrophotometer with the excitation wavelength of 315 nm, the change of the •OH radical intensity with time can be obtained. The formation of $\bullet O_2^-$ was tested by degradation of nitroblue tetrazolium (NBT, 4.9×10^{-5} M), and the concentration of NBT was detected through an UV-vis spectrophotometer based on the absorbance at 259 nm. The process of NBT transformation was also similar to the piezocatalytic degradation, but with NBT replacing the 2,4-DCP.

2. Determination of the main active species

Disodium ethylenediaminetetraacetate (EDTA-2Na, 6 mM), benzoquinone (BQ, 0.5 mM) and tert-butylalcohol (TBA, 6 mM) were selected as scavengers for h^+, $\bullet O_2^-$ and •OH, respectively. The reaction conditions were the same as the piezocatalytic reaction except that additional radical scavengers were added into the reaction suspension.

3. Electrochemical Measurements

The current density of the sample was operated on an electrochemical workstation by using a typical three-electrode system (CHI 660E). The as-prepared g-C_3N_4, a Pt wire and Ag/AgCl electrode were used as working electrode, counter electrode and reference electrode, respectively. For the preparation of working electrode, 25 mg of g-C_3N_4 was dispersed into mixed solution of 1 mL of polyvinylidene fluoride (PVDF) and 20 μL of Nafion solution to produce slurry. The slurry was coated onto a 1.0×1.0 cm^2 conductive nickel foam substrates with subsequent drying. 0.5 M Na_2SO_4 was employed as the electrolyte. The current density-time curves of the sample were measured by using an ultrasonic cleaner (40 kHz, 120 W) to provide ultrasonic vibration.

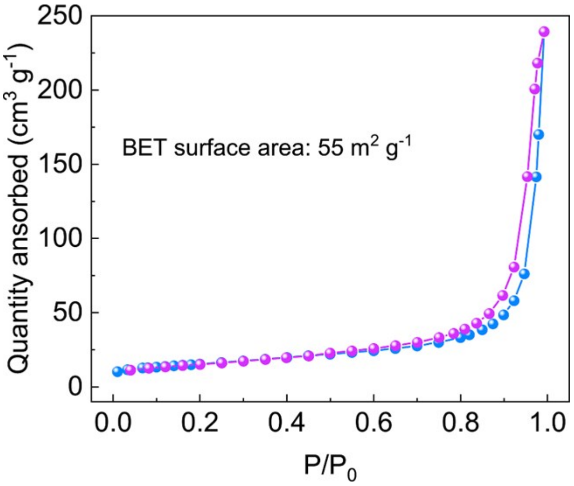

Fig. S1 The N_2 adsorption-desorption isotherm and BET surface area of the as-prepared 2D g-C_3N_4.

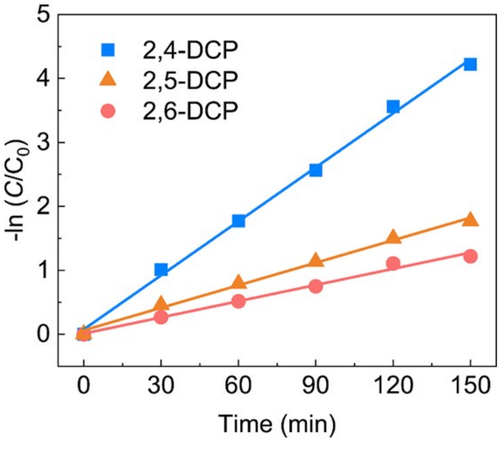

Fig. S2 Plots of -ln(C/C_0) vs the ultrasonic vibration time for the degradation of DCP on the 2D g-C_3N_4.

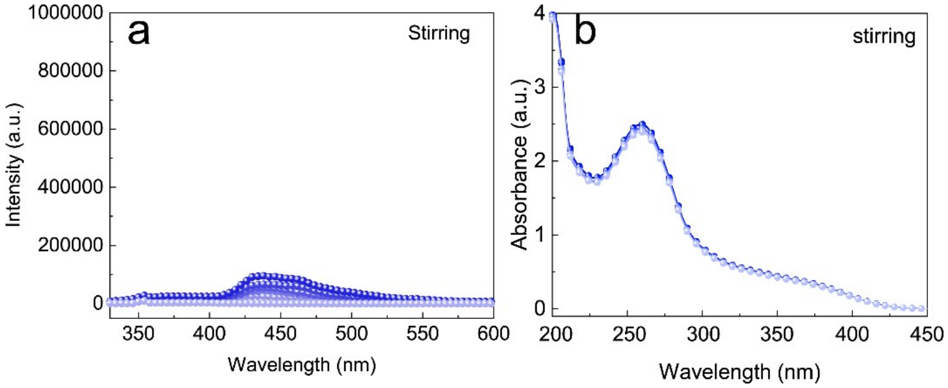

Fig. S3 (a) PL spectral evolution of TA solution with the 2D g-C_3N_4 under magnetic stirring for 150 min, (b) absorption spectral evolution of NBT solution with the 2D g-C_3N_4 under magnetic stirring for 150 min.

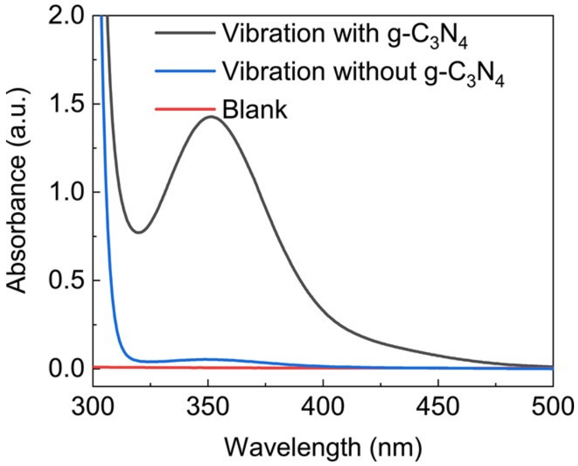

Fig. S4 UV-vis spectra of solution in iodimetry method for detecting the generation of H_2O_2 in the g-C_3N_4 piezocatalytic process.

According to the equation: $H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$, the generation of H_2O_2 was detected using an iodimetry method *via* a UV-vis spectrophotometer. As shown in Fig. S4, negligible H_2O_2 is produced during ultrasonic vibration in the absence of catalyst (blue line), which means the cavitation effect leads to H_2O decompose to form H_2O_2 is extremely low. In the presence of both the catalyst and ultrasonic vibration (black line), the concentration of the characteristic absorption peak at 350 nm increases significantly, which proves the generation of hydrogen peroxide.

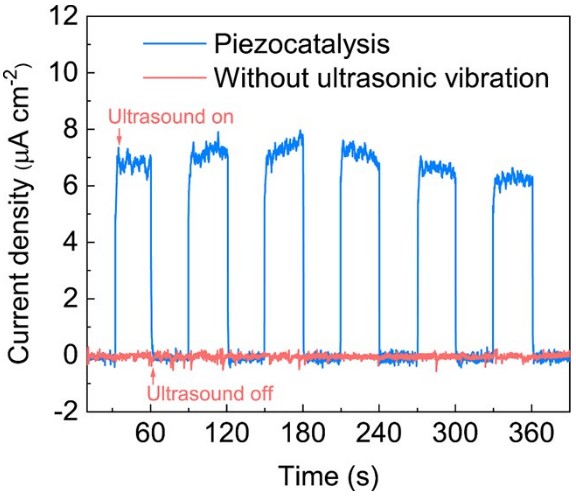

Fig. S5 Transient current response of the 2D g-C_3N_4 under different experiment condition.

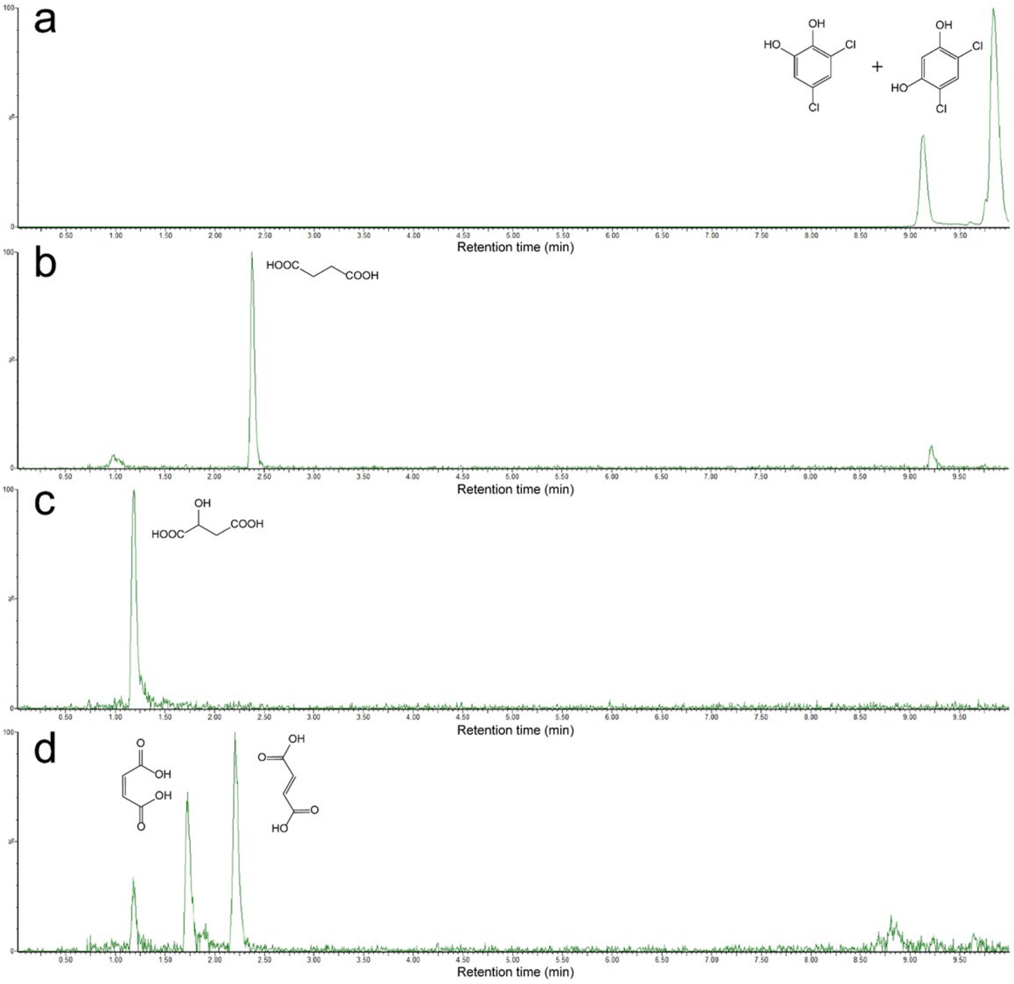

Fig. S6 Extract ion chromatography (EIC) analysis of the reaction intermediates for 2,4-DCP degradation over the 2D g-C_3N_4 for 1.5 h. The identified reaction intermediates: (a) 3,5-dichlorobenzene-1,2-diol and 4,6-dichlorobenzene-1,3-diol; (b) succinic acid; (c) 2-hydroxysuccinic acid; (d) fumaric acid and maleic acid.

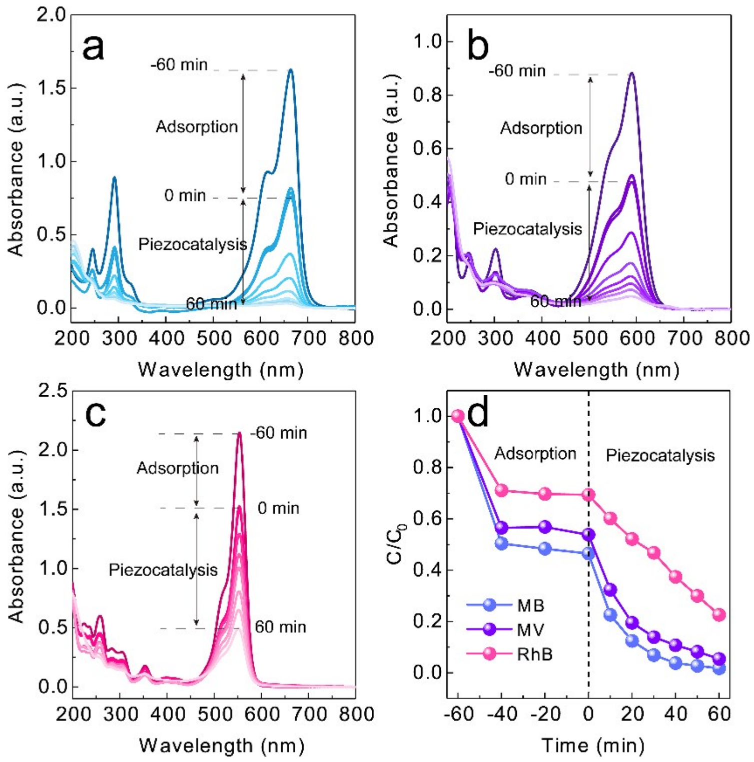

Fig. S7 Absorbance spectra of different dyes with the different degradation time using the 2D g-C_3N_4 under the piezocatalytic process: (a) RhB (b) MB and (c) MV; (d) Catalytic efficiencies of different dyes.