

SUPPLEMENTARY INFORMATION

Synthesis and Characterization of Titania-Coated Hollow Mesoporous Hydroxyapatite Composites for Photocatalytic Degradation of Methyl red Dye in water

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Table S1. Structure and characteristics of the used dyes

| Dyes | Chemical structure | λ_{\max} (nm) | Molecular weight ($\text{g}\cdot\text{mol}^{-1}$) |
|------|--------------------|-----------------------|---|
| MR | | 437 | 269.298 |

The plots of $(A\hbar\nu)^{1/2}$ versus energy ($\hbar\nu$) were drawn in order to calculate the Band gap energies of the samples. The plots of $(A\hbar\nu)^{1/2}$ versus energy ($\hbar\nu$) produces a straight line near the absorption threshold from which the band gap energy is calculated. This is shown in Fig. S1, where A represents the measured absorbance. Extrapolation of the linear part of the curves in Fig. S1 yields the band gap energies of the corresponding synthesized samples, which are presented in Table S1.

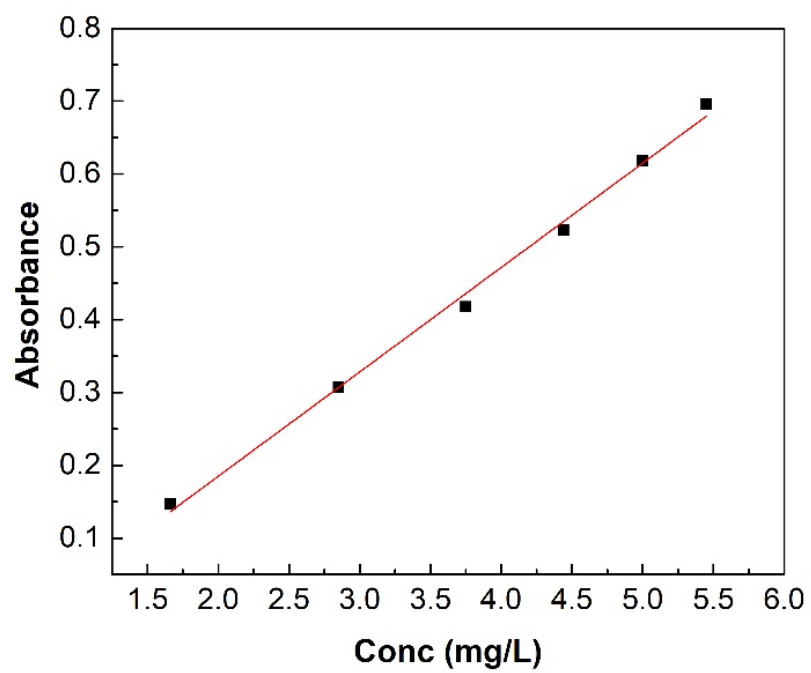


Fig. S1. Beer-Lambert law validation for MR at $\lambda = 437$ nm.

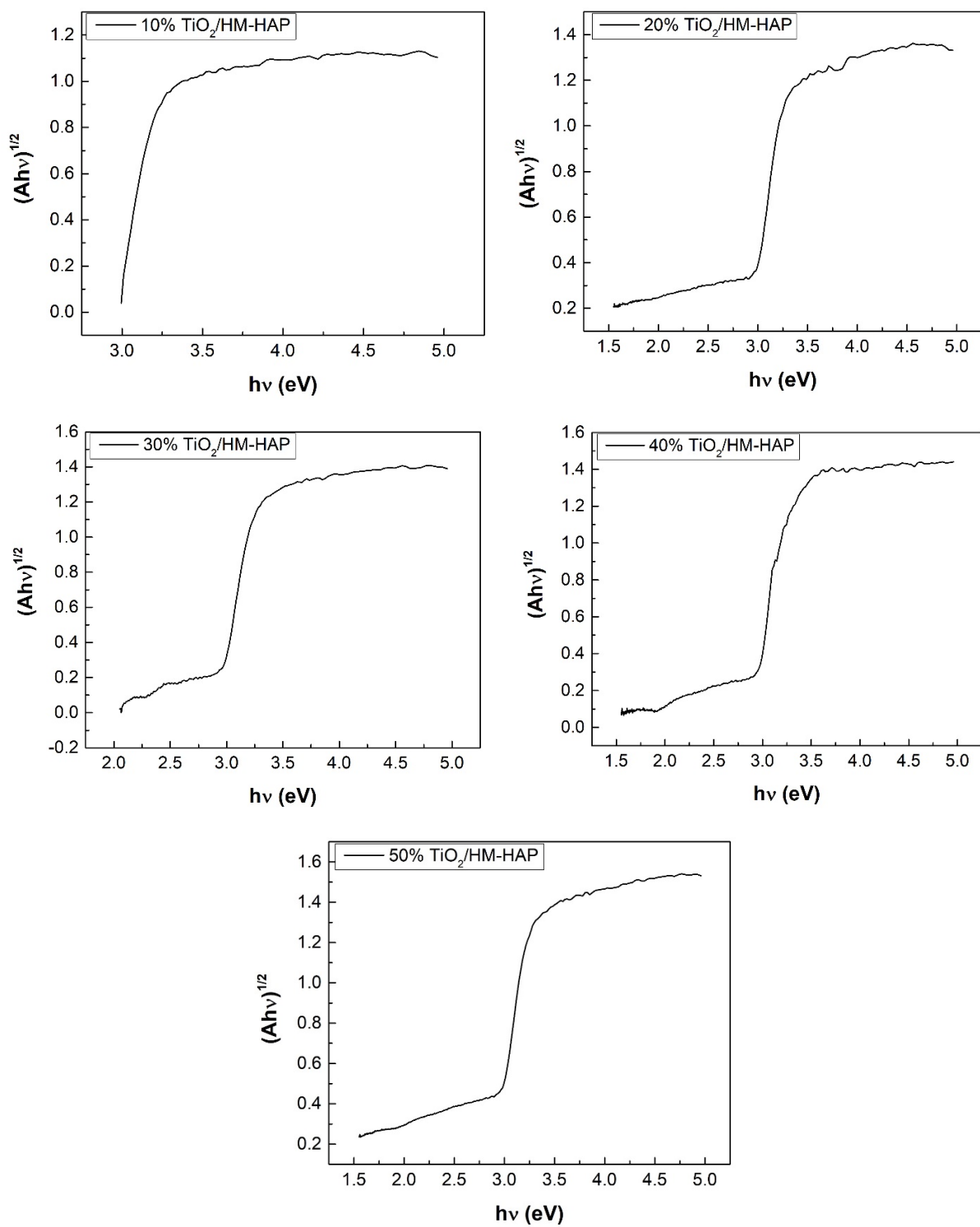


Fig. S2. Plot of $(Ah\nu)^{1/2}$ versus energy (eV).

Table S2. Calculated band gaps of pure TiO₂, HM-HAP and the synthesized TiO₂/HM-HAP samples.

| Sample | Band gap (eV) |
|-------------------------------|---------------|
| TiO ₂ | 3.01 |
| 10 % TiO ₂ /HM-HAP | 2.99 |
| 20 % TiO ₂ /HM-HAP | 2.87 |
| 30 % TiO ₂ /HM-HAP | 2.88 |
| 40 % TiO ₂ /HM-HAP | 2.91 |
| 50 % TiO ₂ /HM-HAP | 2.90 |
| HM-HAP | 3.97 |

Table S3. PZC values of the synthesized composites.

| Sample | pH _{pzc} |
|------------------------------|-------------------|
| 10% TiO ₂ /HM-HAP | 7.95 |
| 20% TiO ₂ /HM-HAP | 7.58 |
| 30% TiO ₂ /HM-HAP | 7.67 |
| 40% TiO ₂ /HM-HAP | 7.40 |
| 50% TiO ₂ /HM-HAP | 7.74 |

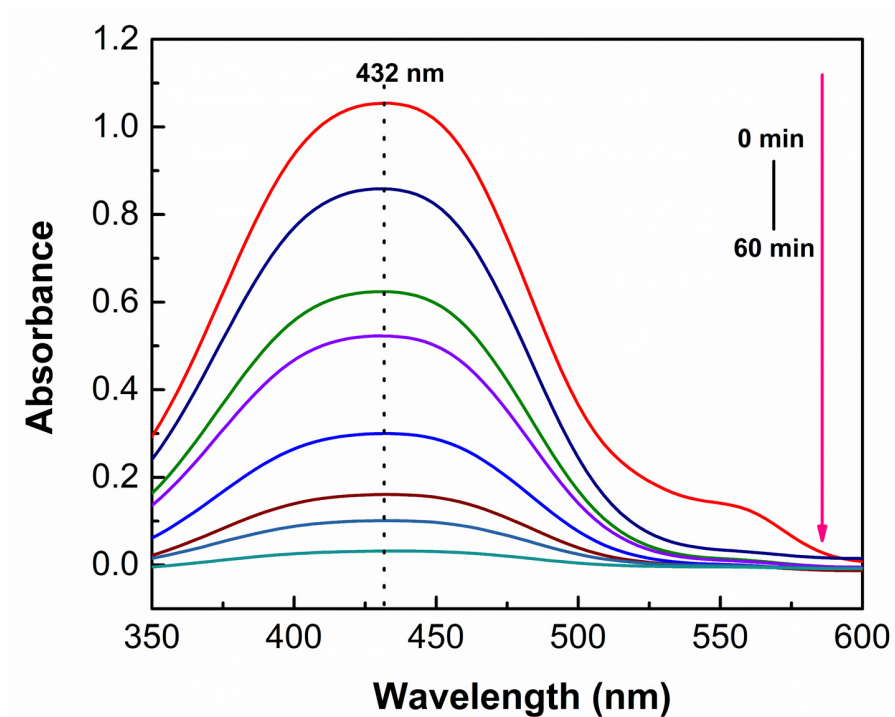


Fig. S3. UV-spectra of MR at different time intervals.

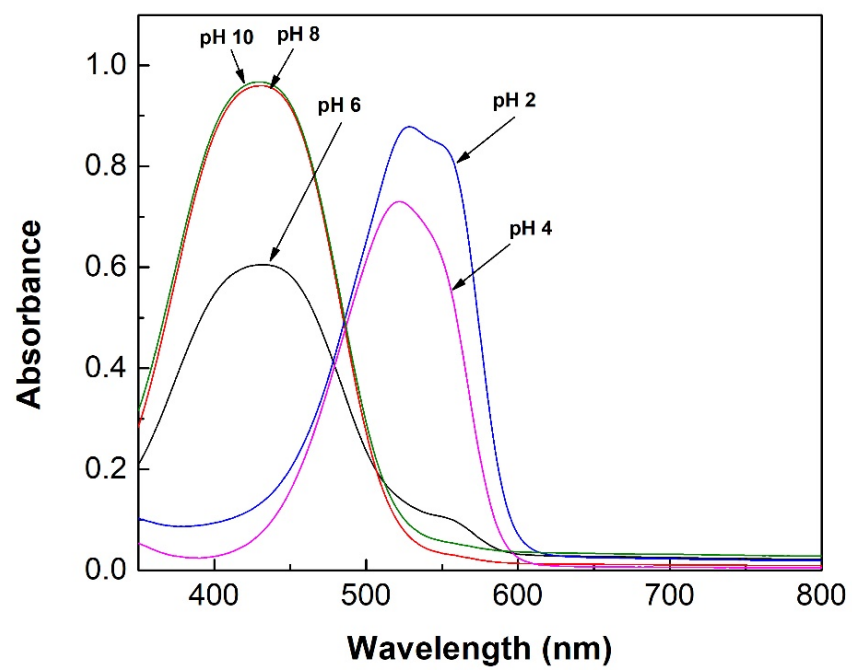


Fig. S4. UV-vis spectra of MR dye at different pH (2, 4, 6, 8, 2, 10).

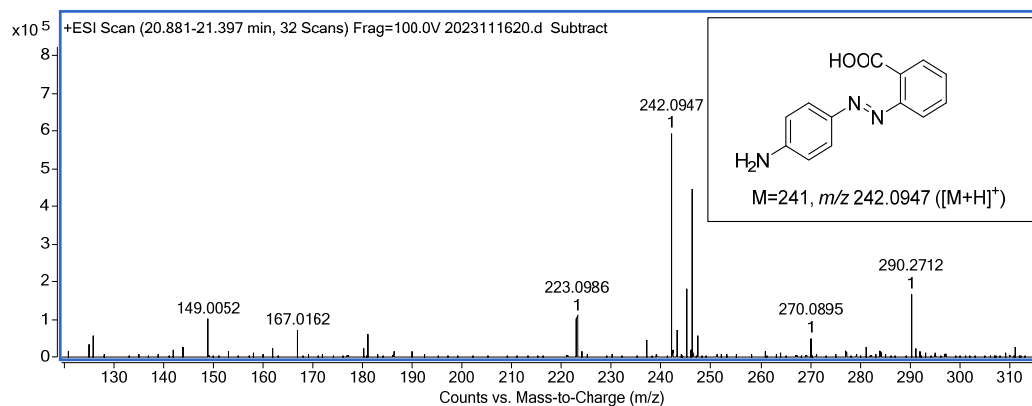
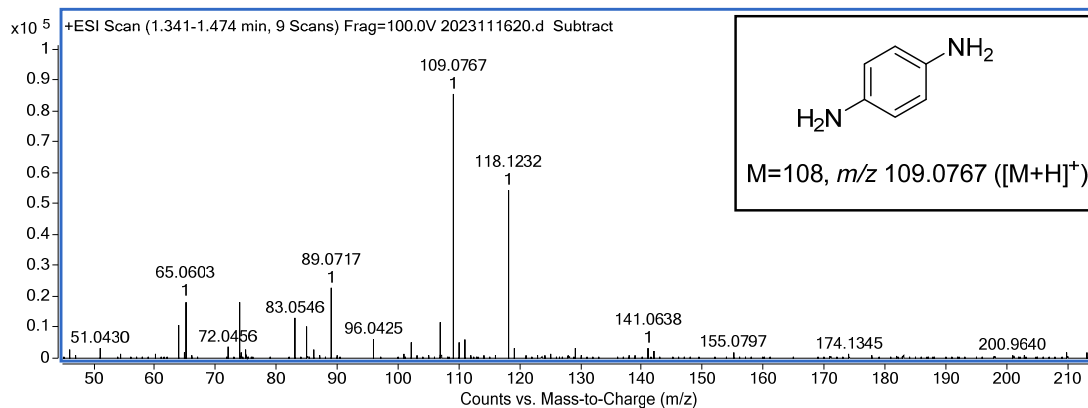
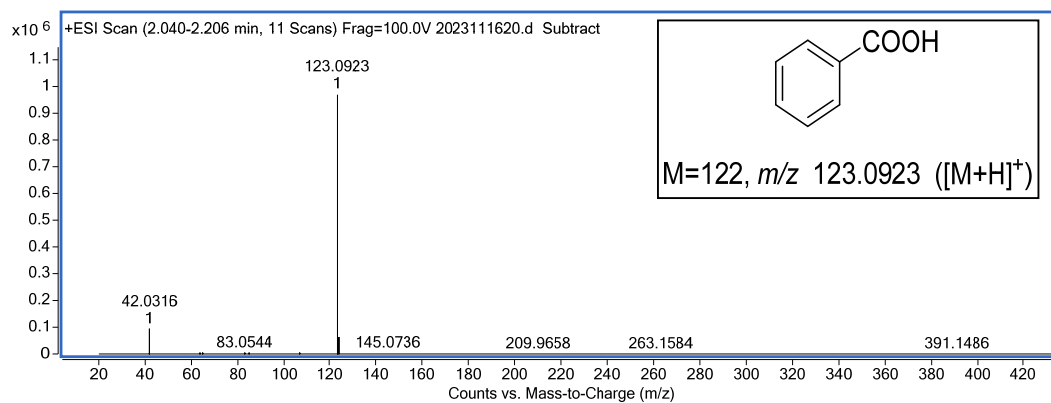
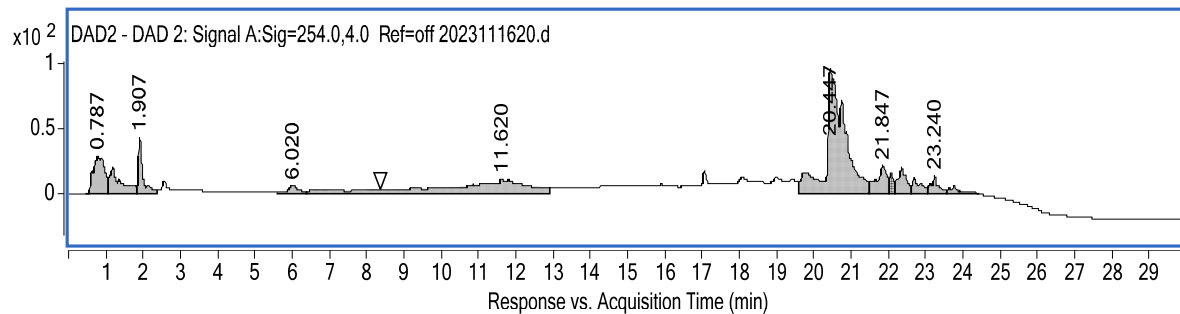


Fig. S5. LC-MS spectra of MR dye solution

The LC-MS spectra of degraded products are provided in Fig. S5. In Fig. S6, oxidation (demethylation) of MR was mediated by reactive oxygen species ($\text{O}_2^{\cdot-}$, $\cdot\text{OH}$) that react with the dye to produce simpler products. The product was identified as 2-[(4-aminophenyl) diazenyl] benzoic acid ($M=241$, m/z 242.0947 ($[\text{M}+\text{H}]^+$). The biodegradation by reactive oxygen species resulted into formation of two further by-products identified as 1, 4-diaminobenzene ($M=108$, m/z 109.0767 ($[\text{M}+\text{H}]^+$) and benzoic acid ($M=122$, m/z 123.0923 ($[\text{M}+\text{H}]^+$). Hence, the LC-MS analysis of the methyl red by products suggested the conversion of methyl red into the low molecular weight derivatives.

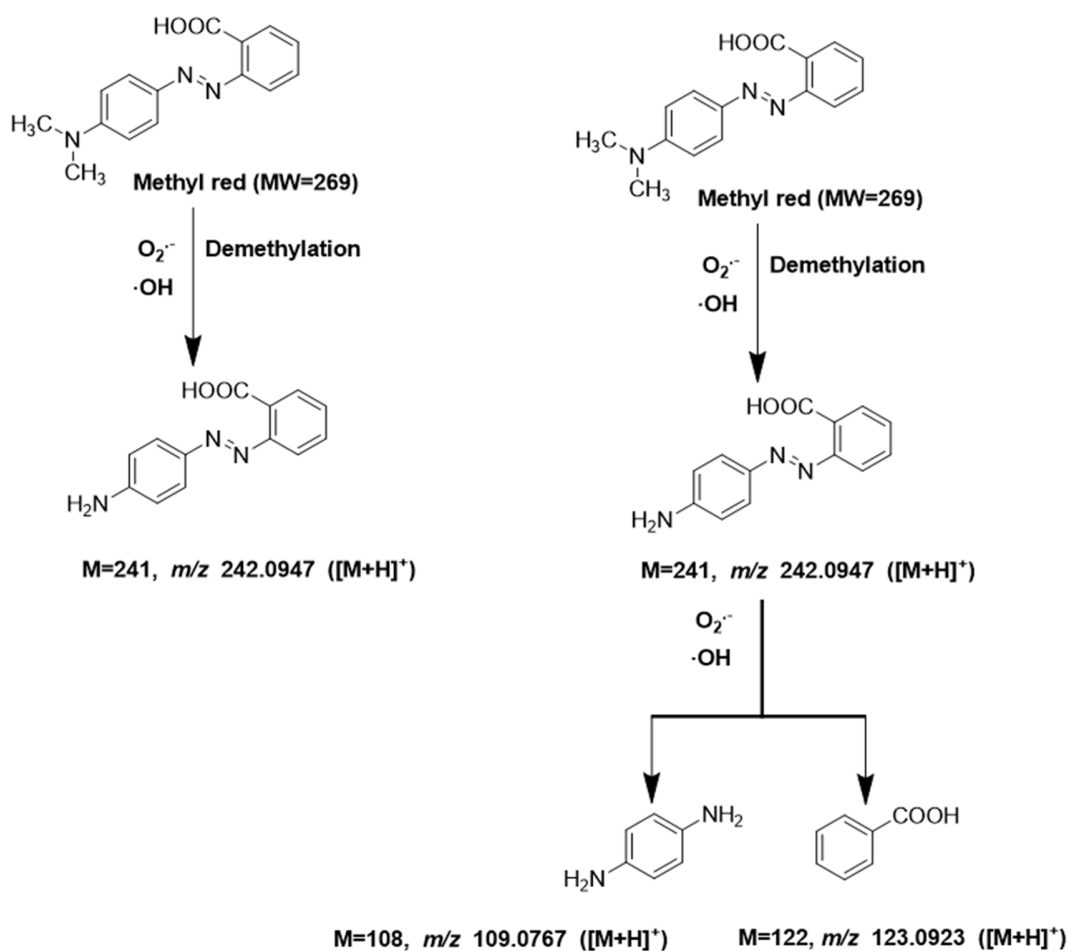


Fig. S6. Identified degraded by-products of MR dye by LC-MS.

Section 1: The degradation degree (DD) per unit of TiO₂ for each composite is calculated. The degradation degree per unit of TiO₂ (DD/TiO₂) can be calculated using the following equation:

$$DD \text{ per unit of } TiO_2 = \frac{\text{Percentage degradation of pollutant}}{\text{Percentage of } TiO_2 \text{ in composite}}$$

Applying this equation to our data, the DD per unit of TiO₂ for each composite is as follows:

$$10\% \text{ TiO}_2 / \text{HM-HAP} = 86\% / 10 = 8.6$$

$$20\% \text{ TiO}_2 / \text{HM-HAP} = 88\% / 20 = 4.4$$

$$30\% \text{ TiO}_2 / \text{HM-HAP} = 81\% / 30 = 2.7$$

$$40\% \text{ TiO}_2 / \text{HM-HAP} = 75\% / 40 = 1.875$$

$$50\% \text{ TiO}_2 / \text{HM-HAP} = 64\% / 50 = 1.28$$

From this analysis, it is evident that the 10% TiO₂/HM-HAP composite exhibits the highest efficiency per unit of TiO₂, followed by 20% TiO₂/HM-HAP. The data clearly show that 10% TiO₂/HM-HAP achieves a higher degradation degree with a lower TiO₂ content, highlighting its superior efficiency compared to the other composites. This comparison emphasizes the potential of 10% TiO₂/HM-HAP as a more efficient and cost-effective photocatalyst.

Section 2: Hydroxyapatite (HAP) has a hexagonal lattice structure consisting of calcium ions, phosphate groups, and hydroxyl groups. HAP possesses a substantial surface area and is rich in hydroxyl groups, which contribute to its negative charge and render it an exceptional adsorbent material.

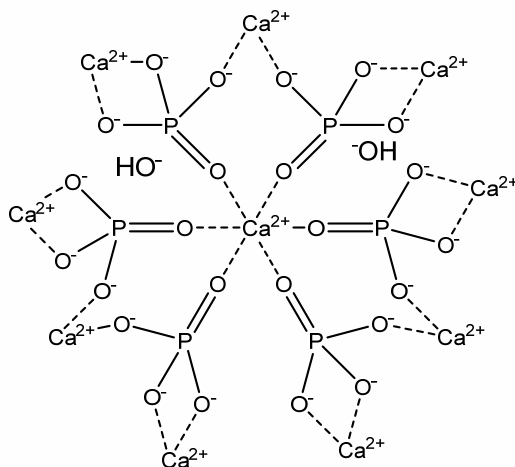


Fig. S7 Structure of hydroxyapatite (HAP).

Titanium dioxide (TiO_2), on the other hand, typically exists in anatase form for photocatalytic applications, with a tetragonal structure that provides active sites for photocatalytic reactions.

In the TiO_2 /HM-HAP composites, the interaction between TiO_2 and HAP occurs through the coating process. The TiO_2 nanoparticles are applied to the surface of HM-HAP, forming TiO_2 -coated HM-HAP composites. This interaction improves the stability and distribution of TiO_2 particles, while the hydroxyl groups on HAP offer additional sites for the pollutants to be adsorbed. As a result, the composite material takes advantage of the photocatalytic properties of TiO_2 and HAP's high surface area and adsorption capacity. The combined effect of TiO_2 and HAP in the composite material greatly enhances the process of breaking down contaminants, such as methyl red dye, using UV light.