Supplementary Material

Poly-(3-thiopheneacetic acid) coated Fe_3O_4@LDHs magnetic nanospheres as photocatalyst for efficient photocatalytic disinfection of pathogenic bacteria under solar light irradiation

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1. Preparation of Fe_3O_4@LDHs nanospheres

1.35 g $FeCl_3 \cdot 6H_2O$ was dissolved in 40 mL ethylene glycol to form a clear solution, followed by the addition of 3.6 g NaAc and 1.0 g polyethylene glycol. The mixture was stirred vigorously for 30 min and then sealed into an autoclave pressure vessel. The autoclave was heated to and maintained at 180 °C for 6 h, and allowed to cool to room temperature. The black products were washed several times with ethanol and dried at 60 °C for 6 h [1].

In the next step, 0.20 g Fe_3O_4 particles were ultrasonicated for 30 min in 0.1 M HNO_3, followed by washing twice with deionized water. Then, the treated Fe_3O_4 particles were redispersed in 100 mL aqueous solution containing 0.5 M aqueous glucose. After ultrasonicated for 30 min, the suspension was transferred to an autoclave and kept at 180 °C for 3 h. After reaction, the autoclave was cooled naturally in air. The suspensions was isolated with the help of a magnet and washed with deionized water and alcohol for three times, respectively, resulting in the product Fe_3O_4@C. Then, 0.10 g Fe_3O_4@C particles were dispersed into a 60 mL methanol solution containing 0.420 g NaOH then ultrasonically agitated for 30 minutes to obtain a uniform suspension. Another 60 ml methanol solution containing 0.769 g $Mg(NO_3)_2 \cdot 6H_2O$ and 0.563 g $Al(NO_3)_3 \cdot 9H_2O$ was added dropwise into the above suspension with vigorous stirring. The resulting slurry was aged at 60 °C under N_2 atmosphere for 48 h to obtain LDHs@Fe_3O_4.

2. Characterization of Fe_3O_4@PTAA-LDHs

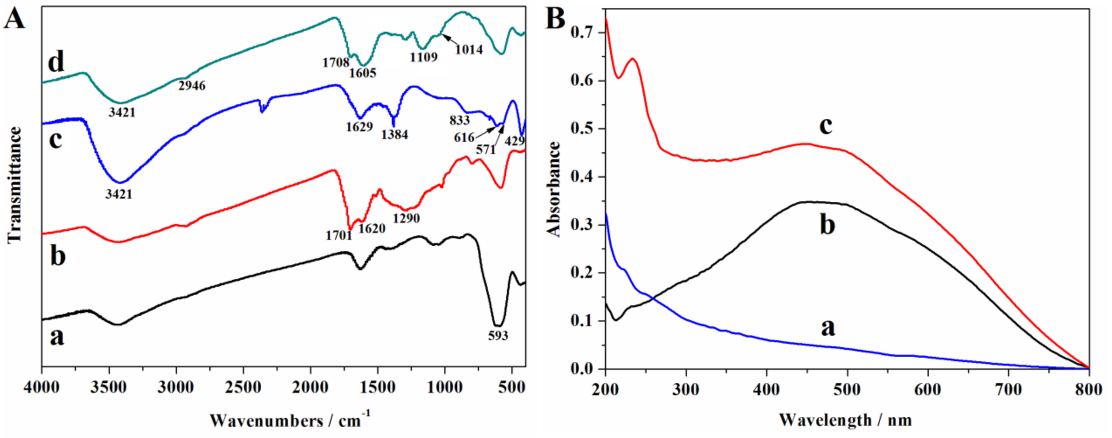

Fig. S1. (A) FT-IR spectra of Fe_3O_4 (a), Fe_3O_4@C (b), Fe_3O_4@LDHs (c) and Fe_3O_4@PTAA-LDHs (d). (B) UV-vis spectra of PTAA (a), Fe_3O_4@LDHs (b) and Fe_3O_4@PTAA-LDHs (c).

Fourier transform Infrared (FT-IR) spectra of the as-made Fe_3O_4 (a), Fe_3O_4@C (b), Fe_3O_4@LDHs (c) and Fe_3O_4@PTAA-LDHs (d) were shown in Fig. S1A. The characteristic absorption peak of the Fe–O bond for Fe_3O_4 was observed at 593 cm^{-1} in Fig. S1A(a) [2]. In Fig. S1A(b), the Fe_3O_4@C microspheres showed bands at 1701 and 1620 cm^{-1} associated with the C=O vibration and C=C vibration, respectively, indicating the carbonization of glucose during hydrothermal reaction. The peaks at 1000-1300 cm^{-1} attributed to the C-OH stretching and O-H bending vibrations, suggesting the presence of large amount of hydrophilic groups. The presence of these hydrophilic groups not only endows Fe_3O_4@C microspheres with better dispersibility and stability than those of the as-synthesized Fe_3O_4 microspheres, but also significantly enhances the affinity between the microspheres and the LDHs [3]. The strong and broad band centered around 3421 cm^{-1} in Fig. S1A(c) with the O-H stretching vibrations of the hydroxyl groups in the LDHs layers and interlayer water molecules. The water deformation band was observed at 1629 cm^{-1}. Peaks corresponding to the v_3 and v_2 modes of interlayer nitrate ions appear respectively at 1384 and 833 cm^{-1}. The band at 616 cm^{-1} was assigned to metal-oxygen bending vibrations and the peaks at 571 and 429 cm^{-1} to metal-oxygen lattice vibrations [4]. In Fig. S1A(d), the characteristic band at 1014 cm^{-1} can be ascribed to C_β-H in the plane bending vibrations. The bands at 1605 cm^{-1} and 1109 cm^{-1} could be attributed to C=C symmetric stretching vibrations of thiophene ring and C-C resonance absorption. These results confirmed the presence of thiophene rings [5]. The bands at 3421 ($v_{O\text{–}H}$), 2946 ($v_{C\text{–}H}$) and 1708 ($v_{C=O}$) cm^{-1} were all attributed to the acetic acid groups at the "3" position of the thiophene ring. Fig. S1A(d) did not display a band at 720 cm^{-1}, associated with the C–H bond at the "2" position of thiophene ring and this result suggested that polymerization has occurred preferentially at the "2" position of TAA [6].

In order to investigate the response to solar light of the as-prepared photocatalysts, UV-vis spectrum was employed to evaluate the optic absorption. As demonstrated in Fig. S1B, the as-synthesized Fe_3O_4@PTAA-LDHs exhibited strong absorption both in the ultraviolet and visible spectral region (curve c). The maximum absorption band was around 235 nm and the weak and broad peak was found to be at about 450 nm. By contrast, PTAA (curve a) and Fe_3O_4@LDHs (curve b) presented the weak absorption in the spectra region. Based on the results from absorption spectra, effective excitation of Fe_3O_4@PTAA-LDHs would occur under solar light, followed by photophysical processes of energy transfer and further reactions. We can therefore predict that the photocatalysts could exhibit good photocatalytic behavior.

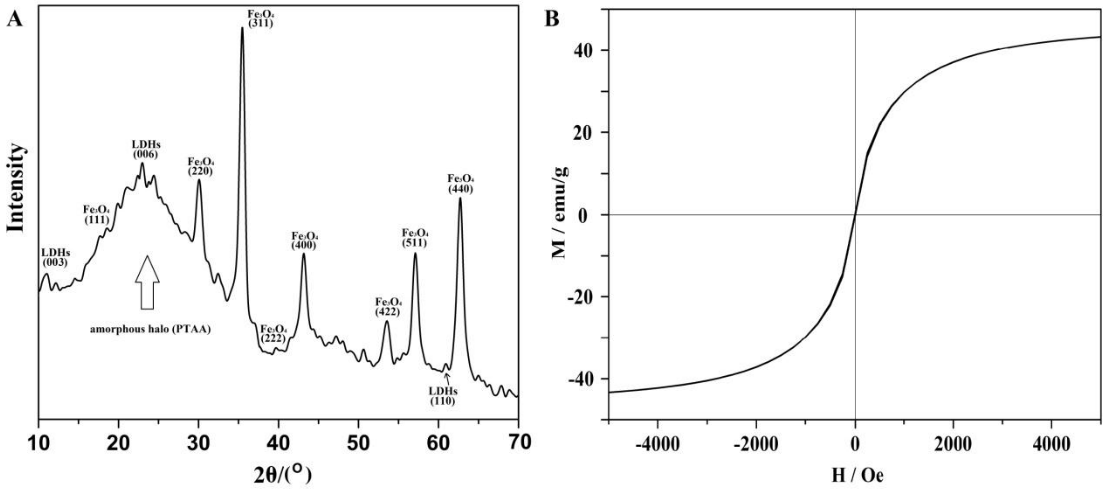

Fig. S2. (A) XRD pattern of Fe_3O_4@PTAA-LDHs. (B) Magnetic hysteresis loop of Fe_3O_4@PTAA-LDHs at room temperature.

In order to characterize the composition of Fe_3O_4@PTAA-LDHs X-ray diffraction (XRD) analysis was also carried out. As shownin Fig. S2A, characteristic peaks from the Fe_3O_4 core in an angular range of 18-65° remained intact in Fe_3O_4@PTAA-LDHs [7]. An amorphous halo from 15° to 30° was observed, which was attributed to the amorphous PTAA [8]. The two major peaks at 2θ values of 11° and 22°, which could be ascribed to the formation of NO_3-LDHs shell nanostructure. One additional new peak at 62° could be assigned to intra-sheet reflections of 110 peaks from a two-dimensional hexagonal cell, confirming that the LDHs nanosheet architecture remained intact in the layer-by-layer assembly process [7, 9]. Fig. S2B showed magnetic hysteresis loop of Fe_3O_4@PTAA-LDHs at room temperature, which indicated a superparamagnetic behavior of the as-prepared photocatalysts.

References

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