# **Supporting Information**

# Fe<sub>2</sub>O<sub>3</sub> nanoparticles anchored on 2D kaolinite with enhanced antibacterial activity

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#### **Experimental Details**

**Materials.** Kaolinite was obtained from China Kaolin Clay Co.Ltd (Suzhou, China). The chemical composition of the sample in mass% was as follows: SiO<sub>2</sub>, 53.27; Al<sub>2</sub>O<sub>3</sub>, 42.46; Fe<sub>2</sub>O<sub>3</sub>, 0.476; MgO, 0.155; CaO, 0.09; K<sub>2</sub>O, 0.542; TiO<sub>2</sub>, 0.333; P<sub>2</sub>O<sub>5</sub>, 0.257. Potassium acetate (CH<sub>3</sub>COOK) and ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All reagents were used as received without further purification.

Synthesis of Kln<sub>KAc</sub>. A mixture containing 4 g kaolinite and 10 g potassium acetate was manually grinded for 0.5 h and a slurry obtained, followed by adding 10 wt.% deionized water under stirring for 10 min. Subsequently, the slurry was maintained at 30 °C for 72 h. The product was separated, washed three times with ethyl alcohol and dried at 60 °C, labeled as Kln<sub>KAc</sub>.

**Preparation of Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>**. 150 mL 0.4 mol L<sup>-1</sup> NaOH was added dropwise to 100 mL of 0.4 mol L<sup>-1</sup> FeCl<sub>3</sub> solution under vigorously stirring at 70 °C. Then, the mixture was cooled and aged for 24 h at room temperature, labeled as Fe(III) polyhydroxy cations. 1 g Kln<sub>KAc</sub> was dispersed in the prepared 50 mL Fe(III) polyhydroxycations solution and stirred at 60 °C for 72 h. The pH values were adjusted by 5 M NaOH solution. After separation and dry, the precipitate (FeOOH-Kln<sub>KAc</sub>) was calcined at 250 °C for 1 h, 350 °C for 1 h and 550 °C for 4 h in air with a heating rate of 5 °C/min, labeled as Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>.

**Characterization.** The crystal structure of the obtained samples were analyzed by X-ray diffractometer (RIGAKU D/max-2550 VB+) using Cu K $\alpha$  radiation ( $\lambda$ = 0.15406 nm) at a

scanning rate of 0.02°/s. The morphology of samples was observed by field emission scanning electron microscopy (FESEM, TESCAN MIRA3 LMU), transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) images (JEOL JEM-2100F microscope). The iron amount was measured by inductively coupled plasma atomic emission spectrometery (ICP-AES) on VISTAAX. Fourier transform infrared (FTIR) spectra of the samples were obtained between 4000 and 400 cm<sup>-1</sup> on a FTIR spectrophotometer (Nicolet Nexus 670). X-ray photoelectron spectroscopy (XPS) measurements of samples were conducted on a Thermo SCIENTIFIC ESCALAB 250Xi spectrometer. Nitrogen gas adsorption-desorption isotherms were measured using an ASAP 2020 Surface Area analyzer. Zeta potential of the samples was determined by a particle electrophoresis instrument using a Zeta sizer Delsa440sx. Static water contact angle (CA) measurement was performed using a Spinning Drop Interface tensiometer (TX500H).

Antibacterial activity. Escherichia coli Dh5 $\alpha$  (*E. coli*) was selected to evaluate the antibacterial properties of Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> samples by the colony count method. 150 mg Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> powders were added into 10 mL Luria-Bertani broth (LB), then well mixed with 100 µL bacteria dilutions (about 10<sup>5~6</sup> CFU/mL). The mixture was incubated under constant shaking at 37 °C, 220 rpm for 3.5 h. 100 µL of each dilution was dispersed onto LB agar plates. Colonies on the plates were counted after incubation at 37 °C for 16 h.

**Cell morphology observation with SEM.** A mixture of 10 mL of *E. coli* bacteria suspension (about  $10^{5-6}$  CFU/mL) and 1.5g Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> were incubated at 37 °C for 5 h. The bacteria treated with Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> were washed with 0.1 M phosphate buffer, and

then fixed and stained with 2.5% glutaraldehyde. Then the sample was dehydrated and dried. The dried sample was sputter-coated with gold for scanning electron microscopy (SEM) imaging by the HELIOS NanoLab 600i Electronic dual micro electron microscopy.

**EPR measurements.** 15 mg  $Fe_2O_3$ -Kln<sub>KAc</sub> sample was added into a 1 mL solution containing 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) (0.02 M). The mixture was incubated for 20 min, filtrated for electron paramagnetic resonance (EPR) spectroscopy measurements using FA200 electron paramagnetic resonance spectrometer.

## FTIR Spectra and N<sub>2</sub> Adsorption/Desorption Isotherm Data

As shown in Fig. S4a, Kln<sub>KAc</sub> exhibits two types of hydroxyls which were assigned to Kln. The band at 3694, and two weak bands at 3667 and 3645 cm<sup>-1</sup> were ascribed to the inner surface hydroxyls, and the sharp band at 3618 cm<sup>-1</sup> was assigned to the -OH stretching of inner hydroxyl.<sup>1</sup> In the lower frequency region from 1600 to 400 cm<sup>-1</sup>, the bands corresponded to Si-O stretching vibration (1107, 1038 cm<sup>-1</sup>), Al-OH bending vibration (912 cm<sup>-1</sup>) and -OH translational vibration (698 cm<sup>-1</sup>), and Al-O, Si-O vibrations (540, 471 cm<sup>-1</sup>), respectively.<sup>1</sup> Two new bands belonging to acetate ion at 1605 cm<sup>-1</sup>, 1418 cm<sup>-1</sup> are detected, which is attributed to the stretching vibration of C=O and O-C-O, respectively. These variations in the stretching region, being consistent with the XRD results, implied KAc has been readily intercalate within the Kln structure. For Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> samples, the bands of -OH stretching at 3694, 3667, 3645, and 3618 cm<sup>-1</sup> all disappeared due to the calcination treatment of sample. The bands at 540 and 471 cm<sup>-1</sup>

corresponding to Al-O, Si-O vibrations became broadened due to the Fe-O of the loaded Fe<sub>2</sub>O<sub>3</sub> nanoparticles (Fig. S7c).

Kln<sub>KAc</sub> and Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> composites exhibited type-IV adsorption isotherms (Fig. S4b). The Kln<sub>KAc</sub> has a specific surface area of 28.6 m<sup>2</sup>/g, a total pore volume of 0.07 mL/g, and a average pore diameter 9.4 nm. The specific surface area of Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> composites increased sharply to 44.3, 57.8, and 156.0 m<sup>2</sup>/g with the total pore volume of 0.19, 0.26, and 0.41 mL/g, and average pore diameter 17.3, 18.1, and 10.4 nm for Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-3, Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-5, and Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-7, respectively. The specific surface area of Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> area of Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-8, Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-5, and Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-7, respectively. The specific surface area of Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-8, Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-8, and higher than that of pure Fe<sub>2</sub>O<sub>3</sub> sample (19.4 m<sup>2</sup> g<sup>-1</sup>) (Fig. S7d&e).

#### **XPS** Data

#### **XPS Data**

X-ray photoelectron spectra (XPS) measurements were taken to determine the surface elemental composition and chemical status of the  $Fe_2O_3$ -Kln<sub>KAc</sub> composites. The wide survey scan of XPS spectra were taken, and the peaks of Fe, O for  $Fe_2O_3$ , and O, Si, and Al for Kln are observed from the surface of the  $Fe_2O_3$ -Kln<sub>KAc</sub> composites (Fig. S5a, ESI†). The carbon peak could be attributed to adventitious carbon on the surface of samples. As shown in the high-resolution spectra of Fe 2p (Fig. 1b), the binding energies of  $Fe_2p_{2/3}$ ,  $Fe_2p_{1/2}$  and a satellite peak of pure  $Fe_2O_3$  were 710.8, 724.3 and 719.2 eV, respectively.<sup>2</sup> After the  $Fe_2O_3$  assembling on the Kln<sub>KAC</sub> nanosheets,  $Fe_2p_{2/3}$  and  $Fe_2p_{1/2}$  peaks shifted to 711.5 and 725.2 eV, respectively, higher than the corresponding values

of pure Fe<sub>2</sub>O<sub>3</sub>. The O component with a peak at 530.1 eV for Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> composite was attributed to the lattice oxygen species of Fe<sub>2</sub>O<sub>3</sub> (Fig. S5b, ESI<sup>†</sup>).<sup>2</sup> In addition, compared to the high-resolution spectra of Al 2p and Si 2p for raw Kln, the binding energy due to octahedral Al<sup>VI</sup> shifted from 74 eV to 74.6 eV in the Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> composite, while the Si 2p peak showed no obvious shift (Fig. 1b and Fig. S5c, ESI<sup>†</sup>).<sup>3</sup> Combined with the abundant Al-OH in the crystal structure of Kln, it could be concluded that Fe<sub>2</sub>O<sub>3</sub> nanoparticles might be immobilized on Kln<sub>KAc</sub> with the Al-O-Fe bond.

# SEM Images of Kln and Kln<sub>KAc</sub> Data

The pristine Kln had a typical pseudo-hexagonal morphology with mean diameter about 400 nm and mainly composed of large and irregular stacking particles (Fig. S5a). After intercalated by potassium acetate (Fig. S5b), The Kln<sub>KAc</sub> had a layered structure with larger diameter/thickness ratio compared to original Kln, which indicated that the original Kln agglomerates had been delaminated. Meanwhile, the individual sheets still kept a typical pseudo-hexagonal shape with regular edge and smooth surface.

### References

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	Reaction time (days)				Mass ratio of water		
Sample	1	3	5	7	0%	10%	20%
Intercalated rate (%)	87.0	92.0	90.4	95.6	90.3	92.0	86.4

 $\label{eq:stable} \textbf{Table S1} \quad \text{The intercalated ratio of } Kln_{KAc} \text{ composites with different reaction time or mass ratio of water.}$ 

 Table S2
 The statistical number of antibacterial properties for different samples.

Sample	Control	Kln <sub>KAc</sub>	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> -Kln <sub>KAc</sub> -3	Fe <sub>2</sub> O <sub>3</sub> -Kln <sub>KAc</sub> -5	Fe <sub>2</sub> O <sub>3</sub> -Kln <sub>KAc</sub> -7
CFU/Plate	400±13	390±16	240±37	140±33	204±27	260±32
Cell Viability (%)	100±3	97.5±4	60±9	35±8	51±6	65±8



Fig. S1 Zeta-potential at various pH of Kln<sub>KAc</sub>.



Fig. S2 XRD patterns of  $Kln_{KAc}$  with (a) different reaction time and (b) mass ratio of water.



Fig. S3 XRD patterns of the as-prepared FeOOH-Kln\_{KAc}-3 and Fe\_2O\_3-Kln\_{KAc}-3.



Fig. S4 (a) FTIR spectra, (b) Nitrogen adsorption/desorption isotherms and BJH pore size distribution (the insert graph) of  $Kln_{KAc}$  and  $Fe_2O_3$ - $Kln_{KAc}$  composites.



**Fig. S5** (a) XPS survey spectra of  $Fe_2O_3$ , Kln and  $Fe_2O_3$ -Kln<sub>KAc</sub> composites, and corresponding (b) O 1s and (c) Si 2p high-resolution XPS spectra.



Fig. S6 SEM images of (a) Kln, (b)  $Kln_{KAc}$  and (c)  $Fe_2O_3$ -Kln<sub>KAc</sub>-3.



Fig. S7 (a) SEM image, (b) XRD patterns, (c) FTIR spectroscopy, (d) Nitrogen adsorption/desorption isotherms and (e) pore size distribution, (f) Zeta-potential at various pH of  $Fe_2O_3$  nanoparticles obtained in the same conditions as the  $Fe_2O_3$ -Kln<sub>KAc</sub>-3.



Fig. S8 Photographs showing E. coli colonies grown on agar plates with Kln<sub>KAc</sub>, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub> composites.



**Fig. S9** (a) SEM images, (b) XRD patterns, (c) photographs showing *E. coli* colonies grown on agar plates, and (d) cell viability measurements of  $Fe_2O_3$ -Kln<sub>KAc</sub> composites prepared in different  $Fe^{3+}$  concentration at pH5.



Fig. S10 Wetting behavior of water droplets on Kln, Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-3, and Fe<sub>2</sub>O<sub>3</sub> nanoparticles.



Fig. S11 EPR spectrum of Fe<sub>2</sub>O<sub>3</sub>-Kln<sub>KAc</sub>-3 sample.