Supporting information

Pickering Emulsion Catalysis in a Continuous Flow System for Methyl Orange Degradation

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Materials

Graphite and Chloroform were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). $Ni(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). H_2SO_4 and HCl were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). $KMnO_4$ and $FeSO_4$ were purchased from Adamas Reagent Co., Ltd (Shanghai, China). MO and $NaNO_3$ were purchased from Tianjin City Guang Fu Tech Development Co., Ltd (Tianjin, China). The Ar (99.9%) used in the experiment is from Yihong Gas. All reagents were obtained from commercial sources at the highest purity available and were used without further purification. Deionized water was used in every aqueous phase of the experiments.

Methods

Preparation of GO.

Graphene oxide was synthesized via the Hummers method. Specifically, 5 g of graphite and 2.5 g of $NaNO_3$ were dissolved in 130 mL of H_2SO_4 at 0−5 ^oC, and the mixture was stirred for 2 hours. Then, 15 g of K_2MnO_4 was gradually added over 3 hours, followed by the gentle addition of 230 mL of deionized water at 35 ^oC; the reaction was allowed to proceed for 1 hour before the mixture was heated to 98 ^oC and held at this temperature for 30 minutes. Subsequently, 400 mL of deionized water, 20 mL of 30% H_2O_2, and 50 mL of 5% HCl were added to the system in the specified order. The resulting product underwent three rounds of repeated precipitation to replace the deionized water, and was finally centrifuged to achieve neutralization.

Preparation of NiAl-LDH-GO.

The NiAl-LDH-GO composite was prepared as follows: First, a mixed alkali solution (0.15 mol/L NaOH, 0.1 mol/L Na_2CO_3) and a salt solution were prepered —

the latter by dissolving 0.582 g $Ni(NO_3)_2$ and 0.375 g $Al(NO_3)_3$ in 10 mL deionized water. Next, 72.48 mg GO was added to 30 mL of the mixed alkali solution, sonicated for 30 min, then 10 mL of the salt solution was added; the pH was adjusted to 10.5 and the mixture was stirred continuously for 30 min. After that, it underwent hydrothermal reaction at 100 ^{o}C for 16 h, followed by centrifugation and washing with deionized water until neutral. It was then vacuum-dried at 80 ^{o}C for 16 h, ground into powder, and thermally expanded at 200 ^{o}C for 2 h under Ar atmosphere to obtain the NiAl-LDH-GO composite.

Preparation and Characterization of Emulsions.

Chloroform was used as the oil phase, and the deionized water was used as the water phase. A specific amount of NiAl-LDH-GO was added as an emulsifier. The emulsion was prepared through 60 min of ultrasonic treatment followed by 2 min of stirring at 10,000 rpm. To analyze the emulsification process, the oil–water ratio was adjusted to 2:1 1:1, 1:2, and 1:3. Additionally, the emulsifier concentration was varied at 3, 4, 5, 6, and 7 mg/mL. The optimal conditions for emulsion preparation were determined to be an oil-water ratio of 1:3 and an emulsifier concentration of 5 mg/mL. Under these conditions, the emulsion achieved 100% emulsification. Subsequent characterization of the emulsion was conducted under these optimal conditions. First, the morphology and size of the emulsion particles were observed using a metallurgical microscope. Next, the oil phase was dyed with Nile red, and the emulsion type was identified using a fluorescence microscope.

Materials characterization.

First, the sample's Fourier transform infrared spectroscopy (FT-IR) was analyzed using the JASCO FT/IR-430. The photoelectron spectroscopy (XPS) of graphite oxide and NiAl-LDH-GO was recorded using a Thermo ESCALAB 250 photoelectron spectrometer. To examine the basic morphology and EDS spectra of NiAl-LDH-GO, the sample was placed on a JSM-7900F scanning electron microscopy (SEM) tray. The thermal stability of the samples was evaluated using a ZRT-B thermogravimetric analyzer (TGA) over a temperature range of 0−700 °C. Finally, the three-phase contact angle was measured using the CSCDIC-100 contact angle measuring instrument.

The interfacial area and per unit mass interface area of emulsion.

$$S = \frac{6a \cdot V_e}{D}$$

Where S is mass interfacial surface, D is emulsion diameter, V_e is the total volume of emulsion, a is the space utilization of hexagonal close-packed distribution.

MO Degradation Rate Test.

The degradation rate of the Fenton oxidation reaction for methyl orange (MO) was determined under both batch and continuous flow conditions. A UV-visible spectrophotometer was used for the measurement: the absorbance of the withdrawn solution (under batch condition) and effluent (under continuous flow condition) was measured at specific time intervals at a wavelength of 464 nm. Meanwhile, the absorbance of the initial MO solution was also determined, with distilled water serving as the blank control to calibrate the baseline. According to the Lambert-Beer law, the absorbance of methyl orange shows a linear relationship with its concentration within a certain concentration range. All solutions tested were diluted, so they meet the requirements of the Lambert-Beer law. The calculation formula is as follows:

$$\eta = \left(1 - \frac{A_t}{A_0}\right) \times 100\%$$

where η is the degradation rate, A_0 is the initial absorbance, and A_t is the absorbance of the withdrawn solution (under batch condition) or effluent (under continuous flow condition) at each time interval.

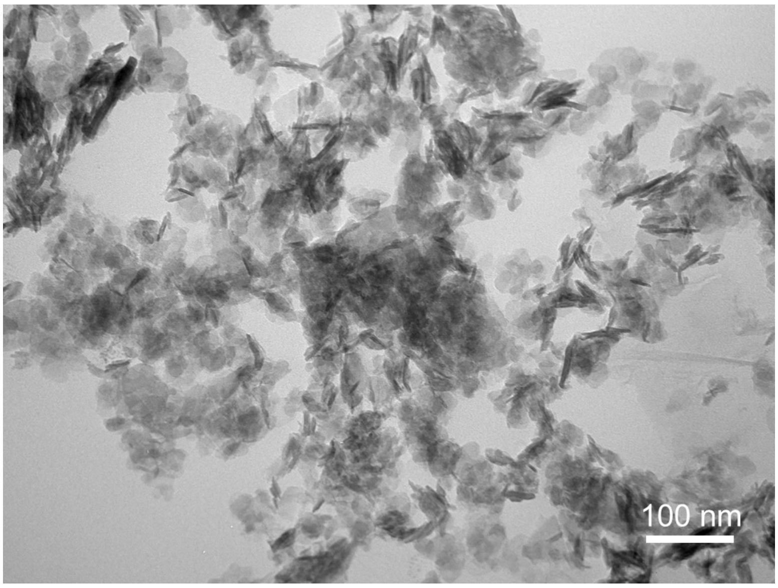

Fig. S1 TEM image of NiAl-LDH-GO

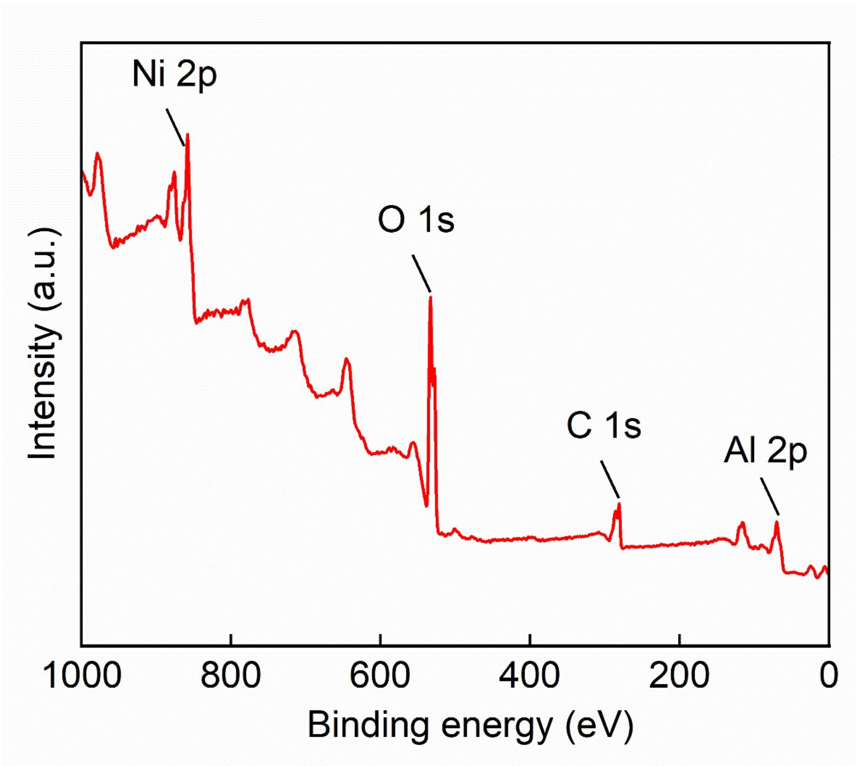

Fig. S2 The XPS survey spectra of NiAl-LDH-GO.

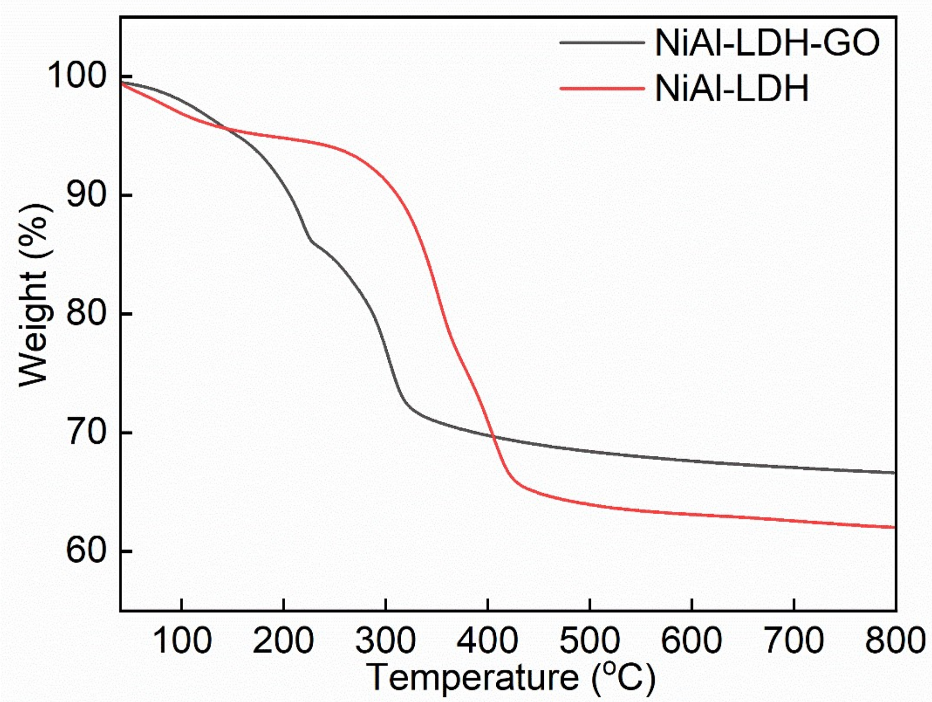

Fig. S3 TGA treatment of NiAl-LDH and NiAl-LDH-GO.

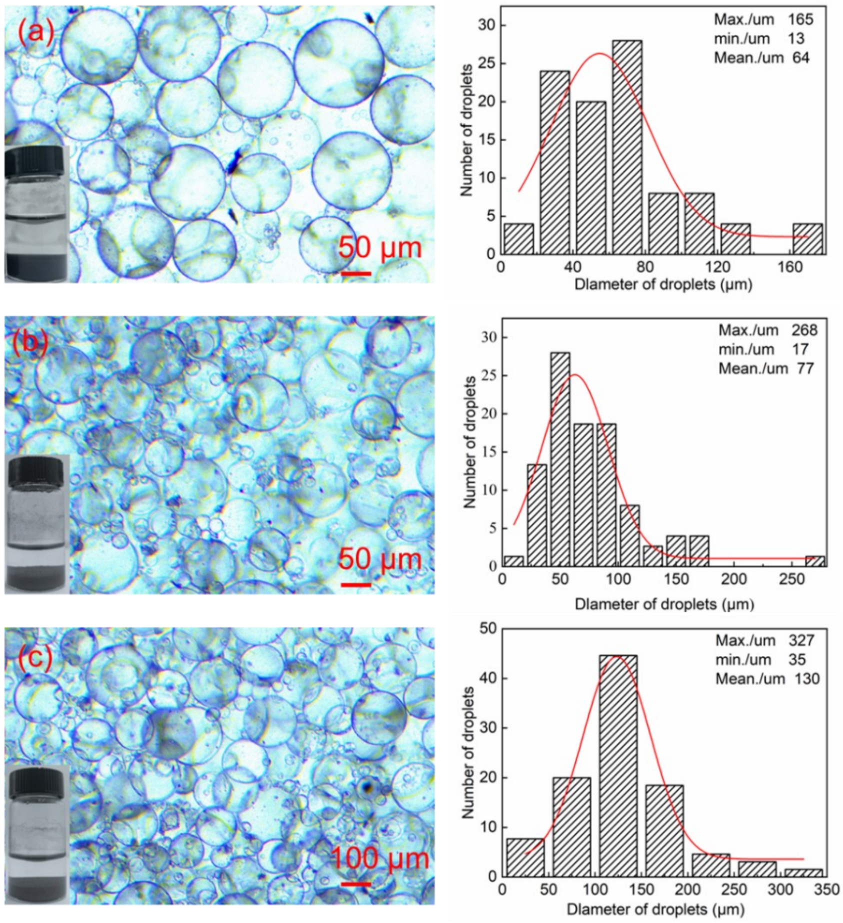

Fig. S4 Histogram of droplet size and particle size distribution of Pickering emulsion stabilized by NiAl-LDH-GO (emulsifier concentration: 3 mg/mL) under different oil–to–water ratios: (a) 1:1, (b) 1:2, (c) 1:3.

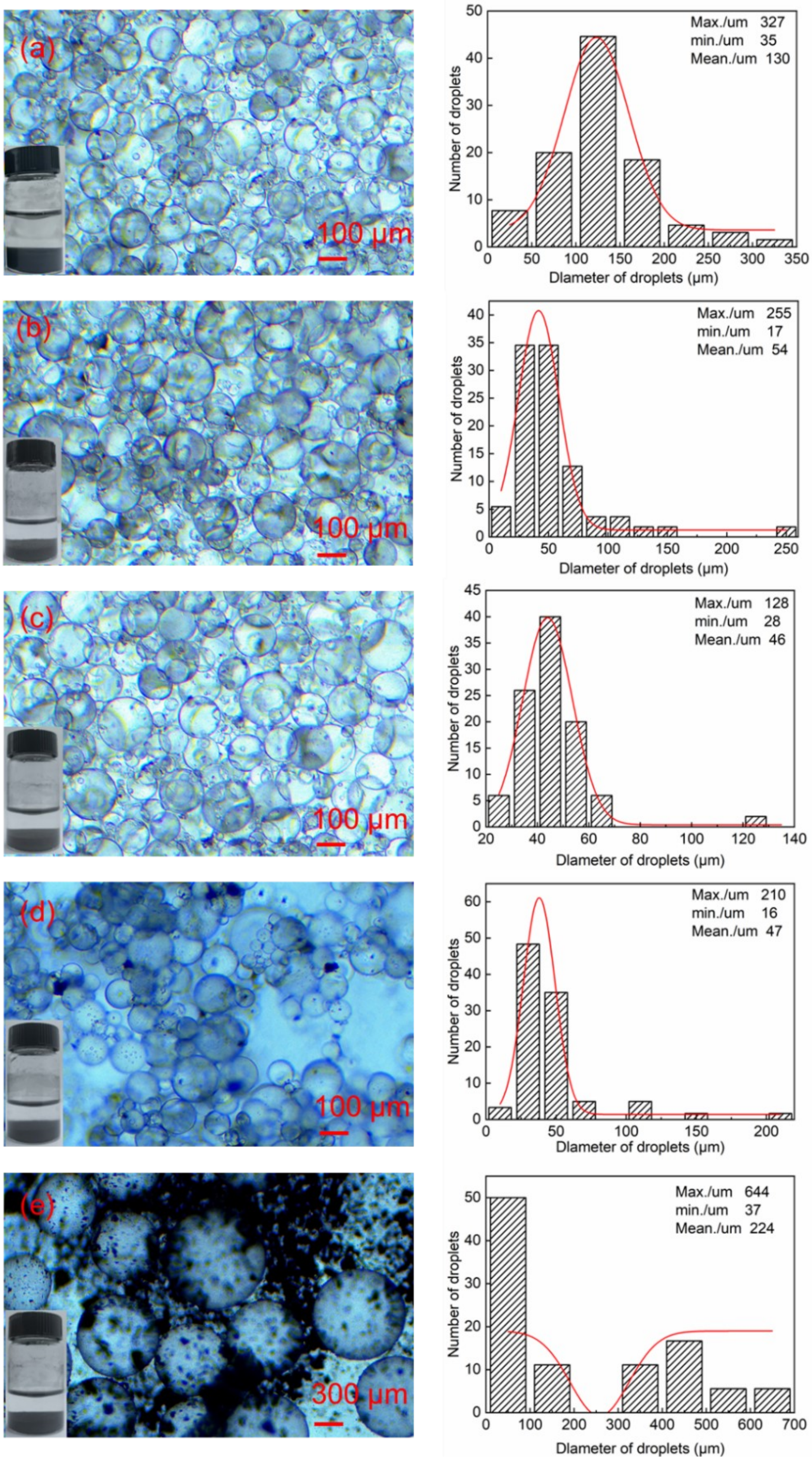

Fig. S5 Histogram of droplet size and particle size distribution of Pickering emulsion stabilized by NiAl-LDH-GO (oil–to–water ratio = 1:3) under different emulsifier concentrations: (a) 3 mg/mL, (b) 4 mg/mL, (c) 5 mg/mL, (d) 6 mg/mL, (e) 7 mg/mL.

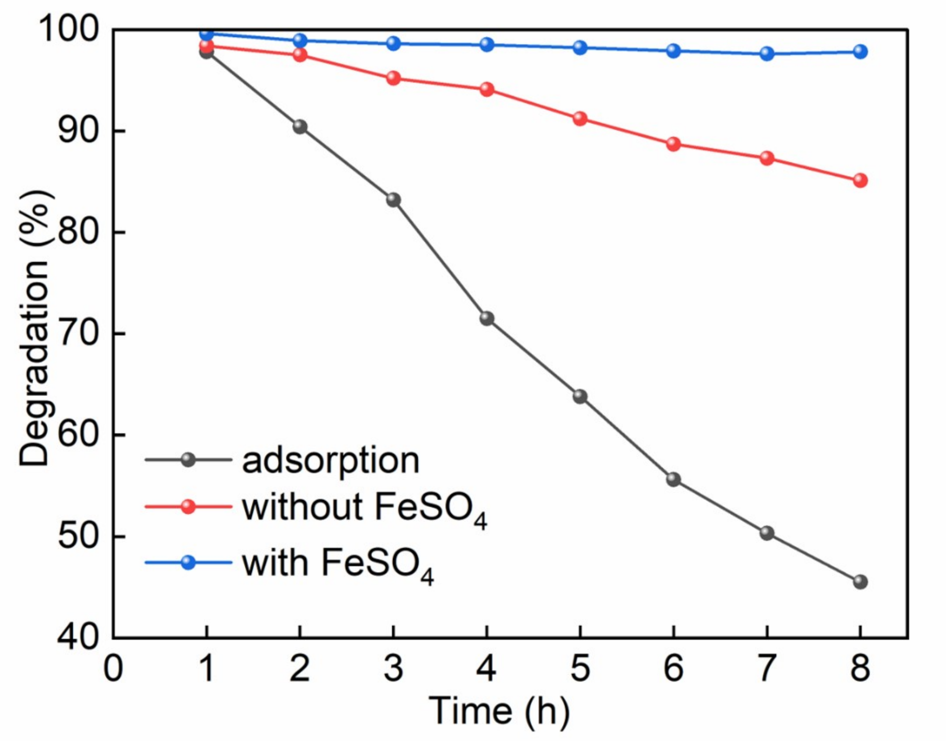

Fig. S6 Degradation curves of methyl orange (250 mg/L) with and without $FeSO_4$ when the concentration of H_2O_2 is 15 mmol/L.

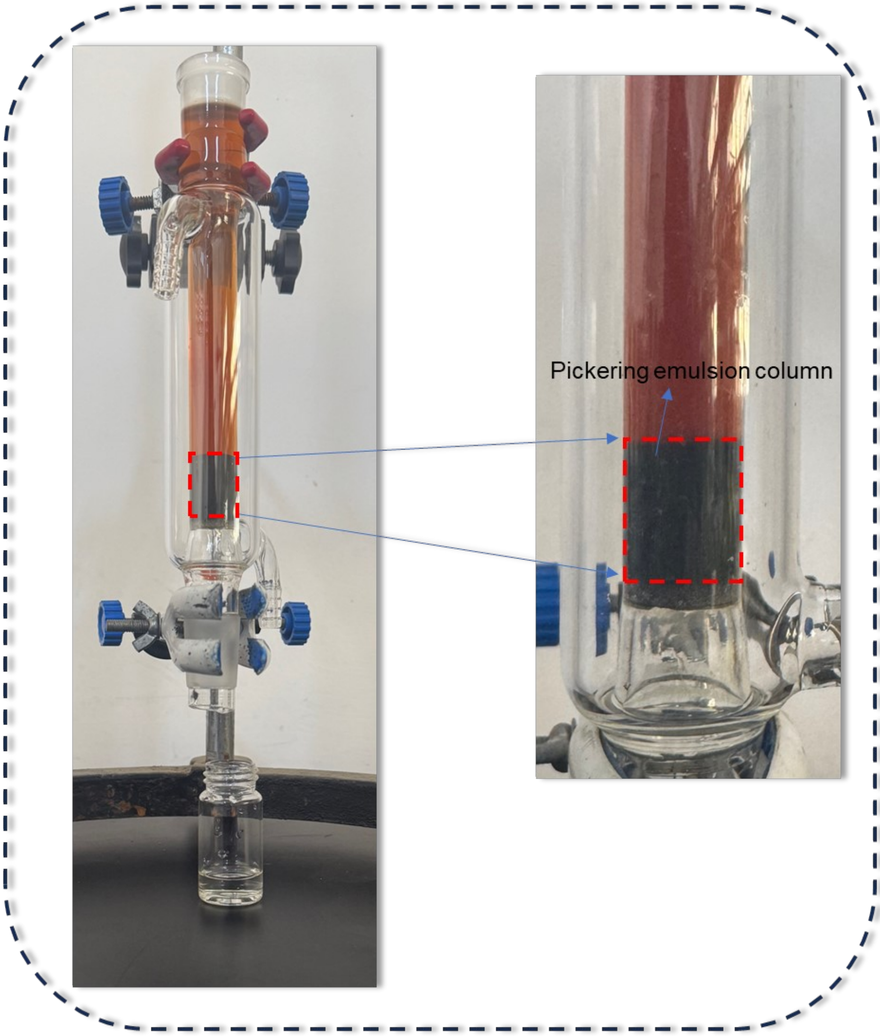

Fig. S7 Digital photos of methyl orange degradation in a continuous-flow emulsion column at room temperature.