

*Electronic Supplementary Information for*

**Synergetic adsorption and catalytic oxidation performance originated from leafy graphite nanosheets anchored iron(II) phthalocyanine nanorods for efficient organic dye degradation**

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**Preparation of FePc@LGNS Hybrid**

The FePc@LGNS hybrid was synthesized by a facile acid intercalation-thermal expanding-ultrasonic exfoliation-spontaneous adsorption method. Briefly, flake graphite was mixed with the concentrated sulfuric acid and nitric acid mixture with volume ratio of 4:1 at room temperature. After vigorous stirring for 16 h, the acid-treated natural graphite was filtered and washed with 0.1 mol L<sup>-1</sup> NaOH and distilled water to remove the remaining acid until the solution pH reached ~6.6. After being dried at 100 °C overnight, the resultant graphite intercalation compound was heat-treated at 900 °C in tube furnace for 3 min, then cooling down to room temperature in air stream to form exfoliated graphite (EG). In next stage, 5.0 g EG powder was added in 70% alcohol-water solution for 24 h ultrasonic irradiation with a power of 400 W to effectively fragmented into the leafy (nanosheets) graphite. Then, the foliated graphite dispersion was filtered and centrifugated, and finally dried in a vacuum drying oven at 105 °C for further testing and using.

The FePc@LGNS hybrid was prepared by using a simple adsorption/deposition method. Under stirring condition, 30 mg of FePc was dissolved in 50 mL chloroform. Subsequently, 5.0 g

of LGNS was slowly added. The mixture was stirred for 24 h followed by dilution and washing with deionized water. After the mixture was evaporated to dry in oil bath at 60 °C, the solid products were washed thoroughly with ethanol-water solution and dried at 60 °C for 24 h, and thus the FePc@LGNS hybrid was obtained. For comparison, the FePc@Graphite hybrid was also synthesized by using the same way just substituting LGNS for Graphite.

### **Characterizations of Solid Catalysts**

The morphology and microstructure of the resultant samples were performed on Scanning Electron Microscopy (SEM, FEI Quanta 200 FEG). X-ray diffraction (XRD) pattern was recorded on a Rigaku D/MAX-2400 powder diffractometer using nickel filtered copper radiation (Cu K $\alpha$ ) as monochromatic detector at 40 kV and 100 mA over a 2 $\theta$  range of 20–80° with a scanning rate of 2° min<sup>-1</sup>. Fourier transfer infrared (FTIR) spectrometer was carried out on Shimadzu 8400S with KBr-pellets to investigate the chemical structures of the resultant samples. X-ray photoelectron spectroscopy (XPS) was performed with a VG ESCALAB-MKII spectrometer using a nonmonochromatized Al K $\alpha$  X-ray source (1486.6 eV). The binding energies were calibrated by using the carbonaceous C1s line (284.8 eV) as reference. N<sub>2</sub> adsorption/desorption isotherms were recorded on a Micromeritics ASAP 2020 Surface Area/Pore Distribution analyzer (Micromeritics Instrument Corp.) at 77 K. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the pore size distributions were determined from desorption branches by the Barrett-Joyner-Halenda (BJH) method.

### **Adsorption and catalytic oxidation experiments**

The sorption experiment was carried out in 500 mL conical flask at room temperature. Firstly, 200 mL, 0.1 mM CR was added into the flask, and allowed the CR aqueous solution for

ultrasonication for 2 min. The sorption experiment was performed in the lucifugal shaker (ZWY-240) and subsequently started by adding 0.2 g LGNS, FePc@LGNS or FePc@Graphite hybrids. The residual CR concentration was determined at given time interval.

The catalytic oxidation of CR was conducted in a 300 mL glass beaker. First, 200 mL, 0.1 mM CR aqueous solution was added and adjusted to the desired pH with H<sub>2</sub>SO<sub>4</sub> and NaOH under magnetic stirring in a constant temperature (30 °C) water bath. The desired dosages of FePc@LGNS catalyst and H<sub>2</sub>O<sub>2</sub> were added successively into the solution to induce the catalytic oxidation reaction. During the oxidation process, the beaker was enclosed with aluminum foils and covered with caps to block the light.

The catalytic stability of FePc@LGNS hybrid was evaluated by five consecutive cycles under the typical conditions of pH 6.98, 30 °C, 1.0 g L<sup>-1</sup> FePc@LGNS, and 50 mM H<sub>2</sub>O<sub>2</sub>. At the end of each run, the catalyst was separated by centrifugation, washed with pure water to remove residual H<sub>2</sub>O<sub>2</sub>, and then dried in a vacuum drying oven at 60 °C for the next run.

#### **Analysis methods.**

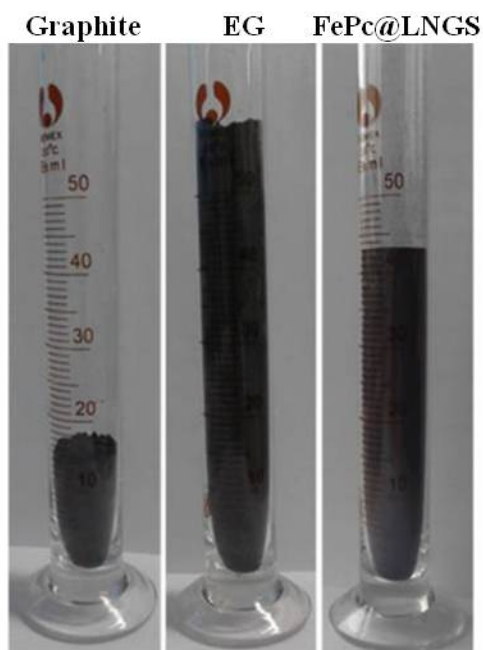
During the course of adsorption and catalytic oxidation experiment, samples were collected with syringe at various time intervals, and then were measured quickly by the spectrophotometric method (UV-1700 spectrophotometer, Shimadzu) at 488 nm to determine CR concentration. Decolorization rate was calculated according to the following equation:

$$\text{Decolorization rate(\%)} = \frac{A_0 - A}{A_0} \times 100$$

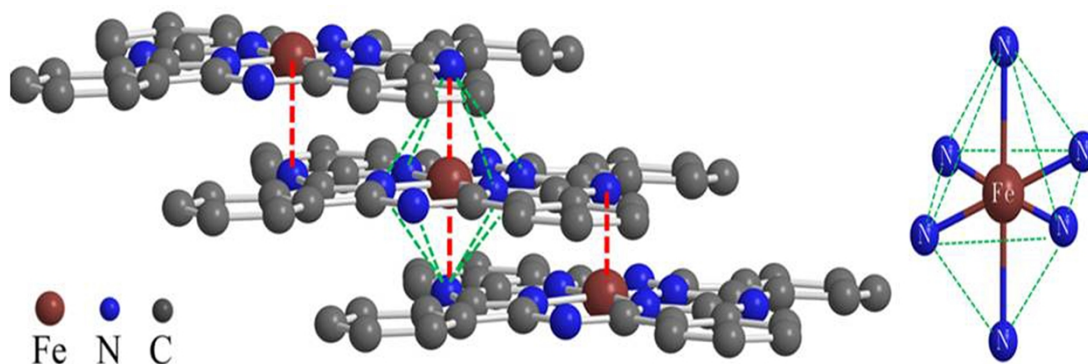
where the  $A_0$  and  $A$  were the absorbance of the sample at time 0 and  $t$ , respectively.

The degradation products were analyzed by LC-MS (Agilent 6224). Acetonitrile was adjusted to pH 5.9 with ammonium acetate, and then was used as the mobile phase at a flow rate of 0.3 mL min<sup>-1</sup>. Nitrogen was used as the drying gas (5 L min<sup>-1</sup>) at 350 °C. Electrospray ionization

(ESI) source was employed in negative ion mode. Leached iron ion in aqueous solution after catalytic oxidation was detected by an atomic absorption spectrophotometer (Shimazu type AA-630-01). All the samples aliquots withdrawn from treated solutions were filtered with 0.45  $\mu\text{m}$  PTFE filters before each analysis.



**Fig. S1.** The photographs of 5.0 g of Graphite, EG and FePc@LGNS powder filled in 50 mL measuring cylinder, respectively.



**Fig. S2.** Presumed crystal structure of FePc nanorods (left picture). The right picture shows a proposed pseudo-octahedral system composed of the square planar system and two nearest nitrogen atoms.

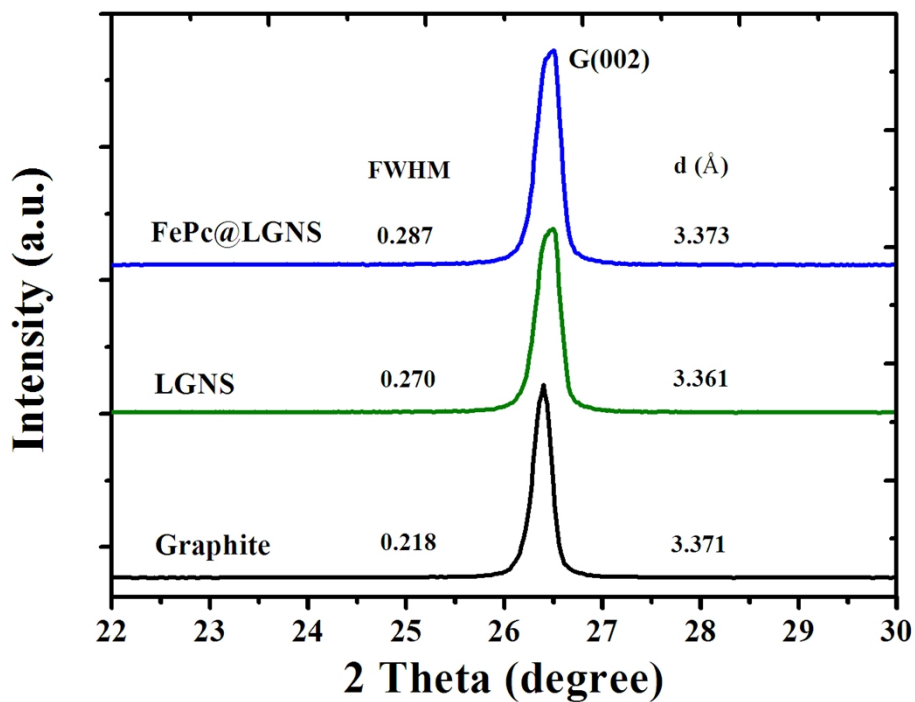


Fig. S3. XRD patterns in the angular range of 22–30°.

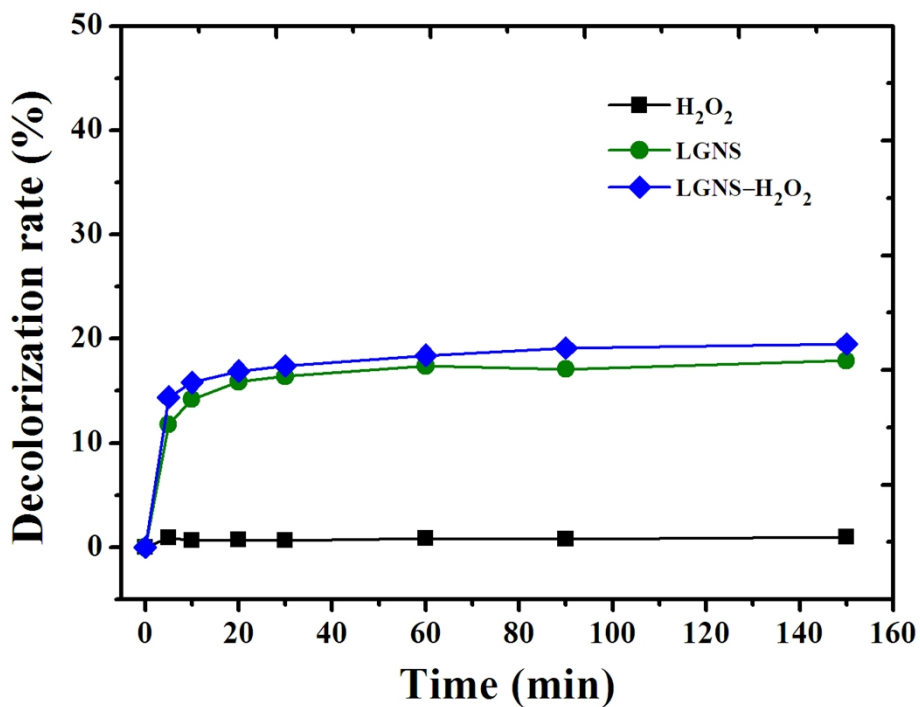
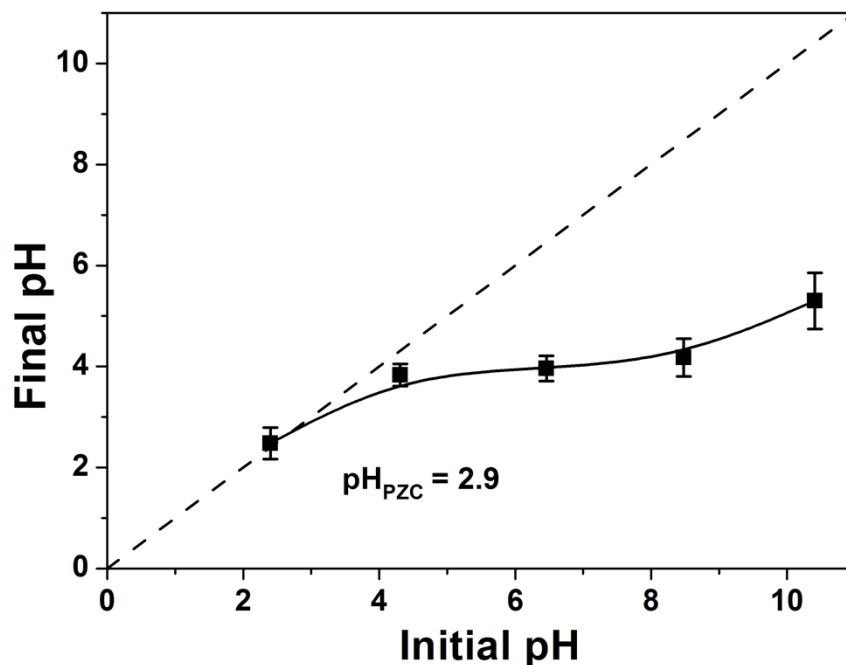


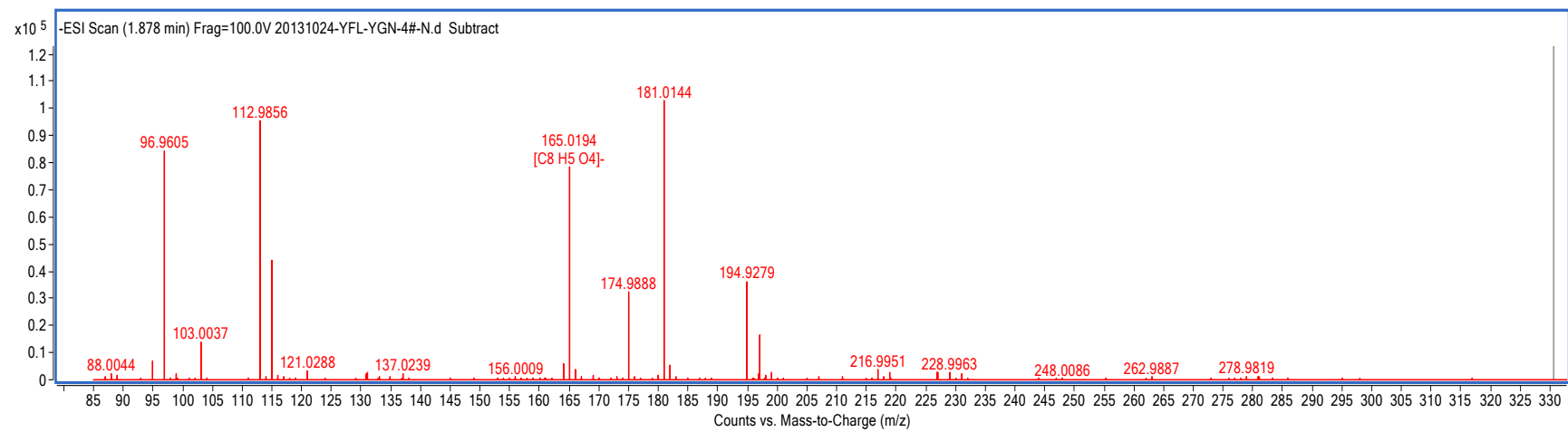
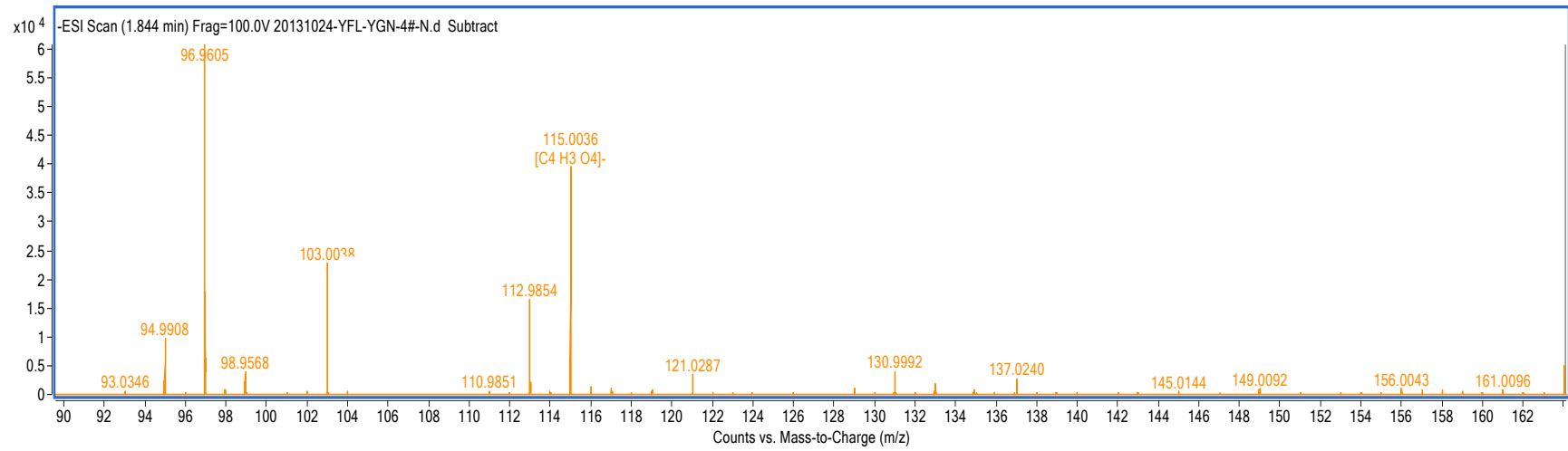
Fig. S4. Time-source evolution of CR decolorization rate under various conditions (pH 6.98, 30 °C, 50 mM H<sub>2</sub>O<sub>2</sub>, 1.0 g/L LGNS).

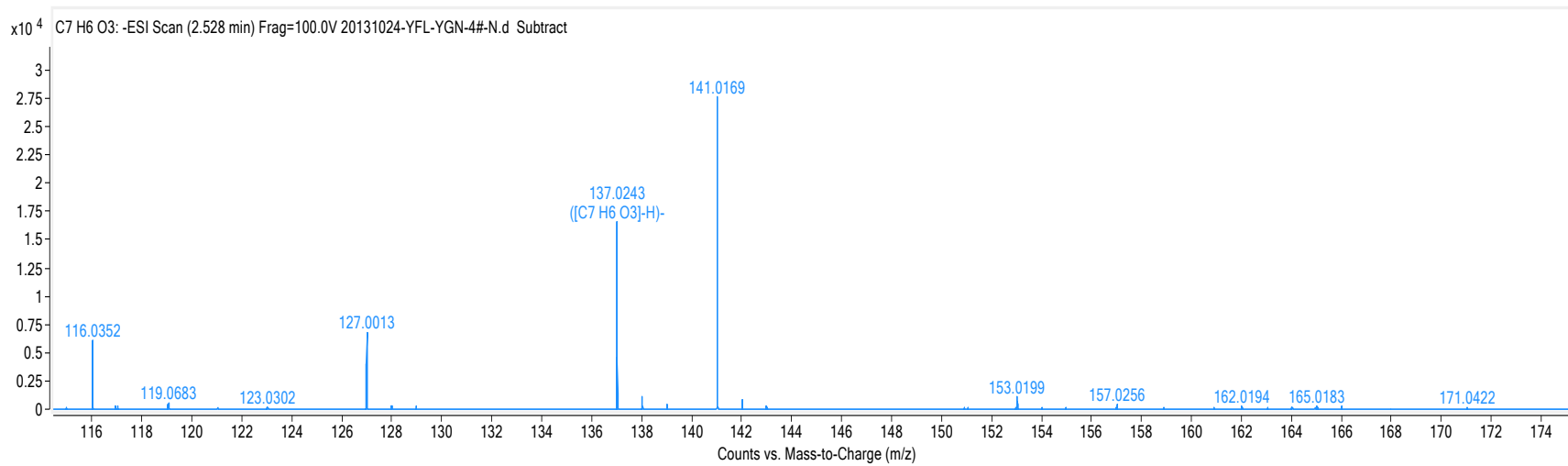
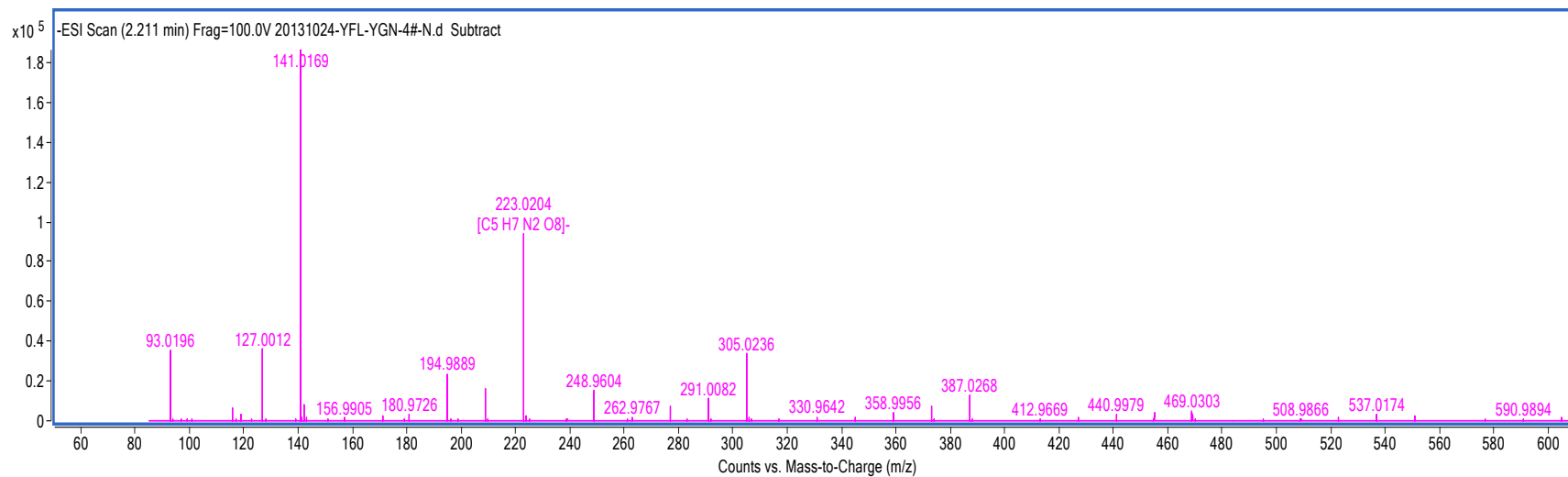


**Fig. S5.** The  $\text{pH}_{\text{PZC}}$  of FePc@LGNS hybrid obtained by pH drift method.

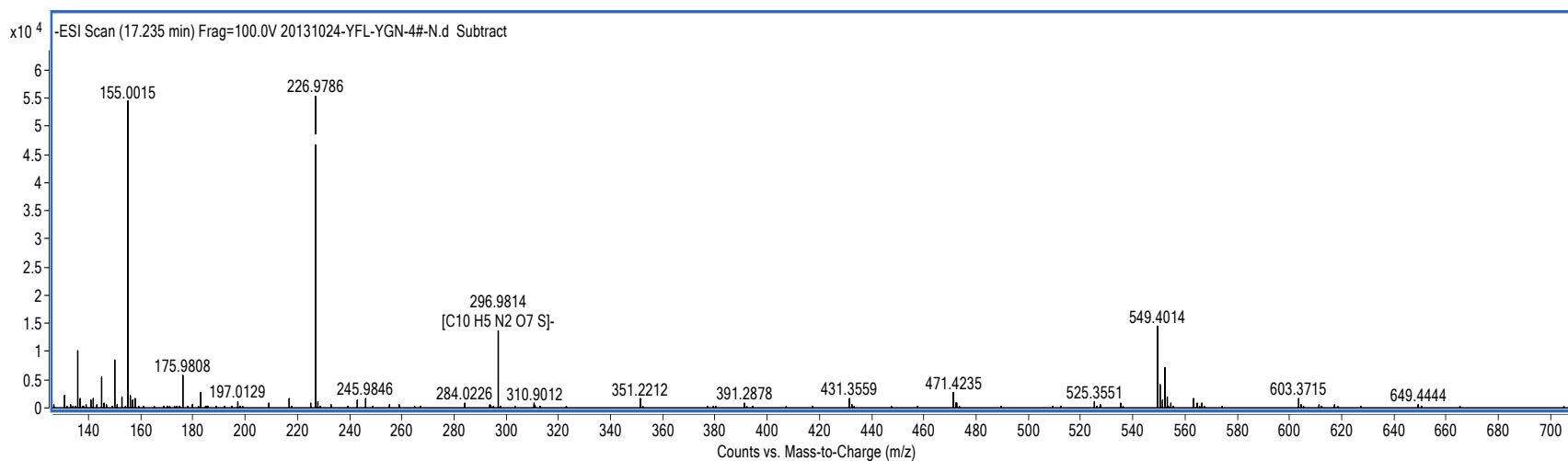
The  $\text{pH}_{\text{PZC}}$  of FePc@LGNS was measured on the basis of the literature [1]. Briefly, 50 mL, 0.01 M NaCl solution was added into a vessel at room temperature, and then  $\text{N}_2$  was bubbled into the solution to prevent the dissolution of  $\text{CO}_2$ . The initial solution pH was adjusted to consecutive values from 2 to 12 by using HCl or NaOH, and then 0.15 g FePc@LGNS was added. After 48 h the final solution pH was measured and plotted against the initial pH, as plotted in Fig. S5. The intersection point on the line of  $\text{pH}(\text{final})=\text{pH}(\text{initial})$  is taken as the  $\text{pH}_{\text{PZC}}$  of the FePc@LGNS hybrid

[1] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques. Carbon 37 (1999) 1215–1221.









**Fig. S6.** ESI mass spectra (negative ion mode) of the products during CR degradation process by FePc@LGNS-H<sub>2</sub>O<sub>2</sub> system (Reaction conditions: pH 6.98, 30 °C, 50 mM H<sub>2</sub>O<sub>2</sub>, 1.0 g/L FePc@LGNS hybrid, and 0.1 mM CR). The m/z value of 112.9856 is the signal of standard substance added into sample