

**Three-dimensional electro-Fenton oxidation of N-heterocyclic compounds with a novel catalytic particle electrode: High activity, wide pH range and catalytic mechanism**

Table S1 Properties of the as-synthesized CPEs

Parameters	SAC	SAC-Fe
$S_{\text{BET}}$ (m <sup>2</sup> /g)	388.9	351.6
$V_{\text{meso}}(\text{macro})$ (cm <sup>3</sup> /g)	0.282	0.258
$V_{\text{micro}}$ (cm <sup>3</sup> /g)	0.133	0.122
Pore size (nm)	3.711	3.614
Ash (wt%)	16.94	19.32
Fe	1.28	15.43
Si	6.89	5.99
Al	3.29	2.86
Zn	1.31	1.26
Mg	0.83	0.73
Ca	0.367	0.322
C	60.84	59.49
O	20.17	19.25
N	2.11	1.89
pH <sub>pzc</sub>	6.2	7.8

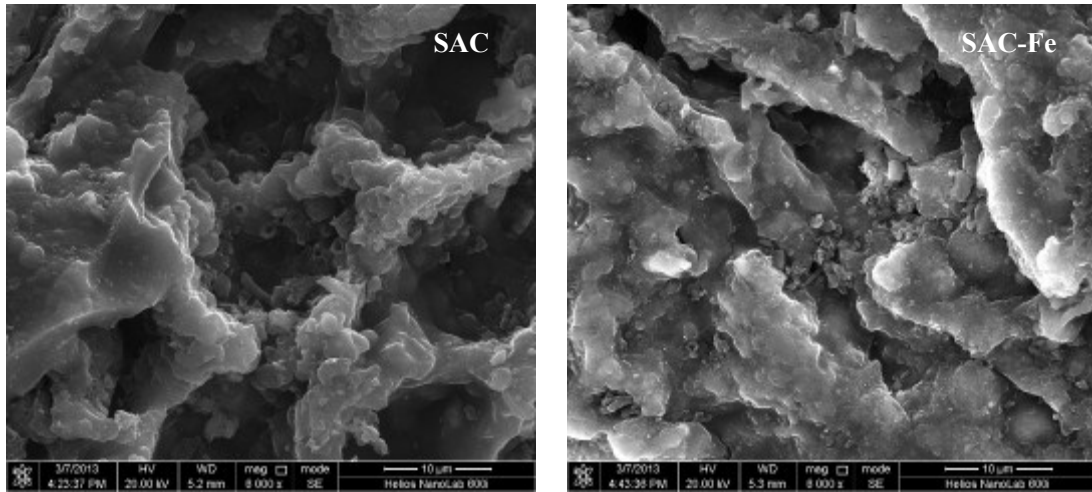


Fig. S1 SEM of the prepared CPEs

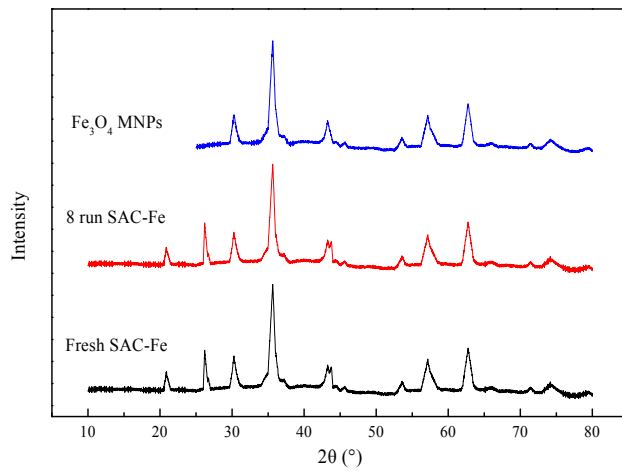


Fig. S2 XRD patterns of the prepared CPEs

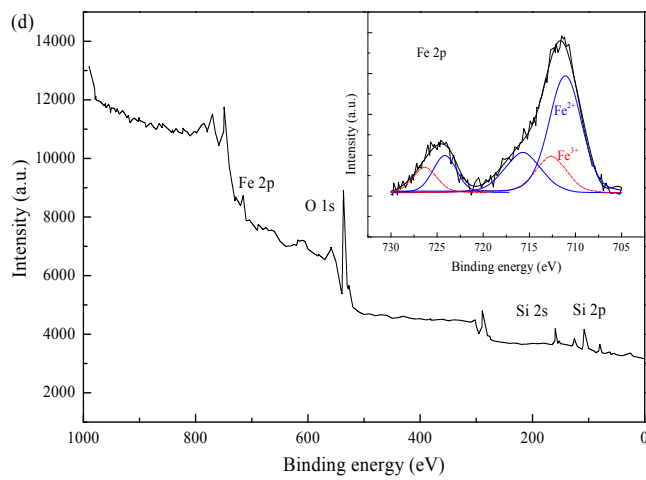


Fig. S3 XPS spectra of the prepared CPEs

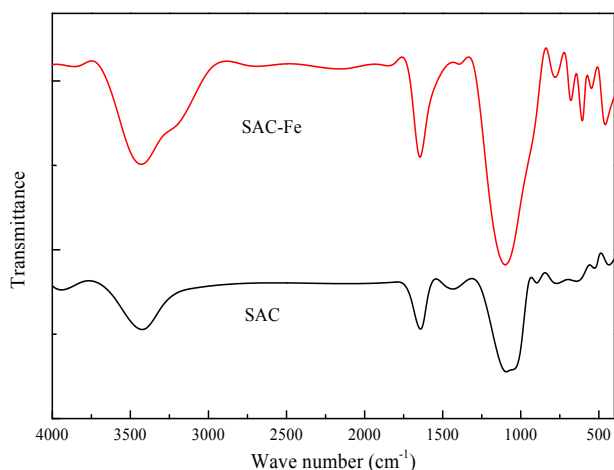


Fig. S4 FTIR analysis of the prepared CPEs

### FTIR analysis

Both the spectra of SAC and SAC-Fe exhibit a prominent peak located at 3451 and 1638  $\text{cm}^{-1}$ , associating with the stretching vibration and bending vibration of -OH. Strong and asymmetrically shaped bands centred at 1041-1070  $\text{cm}^{-1}$  were of Si-O-Si and Si-O-C groups. Peak at 1611  $\text{cm}^{-1}$  is believed to arise from aromatic C=C bonds which are polarized by oxygen atoms bond near one of the C atom. The region near 1522  $\text{cm}^{-1}$  is commonly associated with carbonyl (C=O) and alkene (C=C) bonds, which normally come from the vibration of small molecule organics. The broad high intensity band at 1080  $\text{cm}^{-1}$  relates to the asymmetric stretching vibrations of Si-O-Si, evidencing the presence of  $\text{SiO}_2$ . The intense absorption peaks near 1000-1100  $\text{cm}^{-1}$  could be the structure of Si-O-C. Comparing with SAC, some new peaks were found in the spectra of SAC-Fe, such as the characteristic symmetric stretching vibration and bending vibration of Si-O-Fe (675 and 471  $\text{cm}^{-1}$ ). The shoulder at 930  $\text{cm}^{-1}$  corresponded to a Si-O-Fe linkage and a Si-O-Si symmetrical stretching was assigned at 800  $\text{cm}^{-1}$ . These results clearly indicated the chemical bonds between the inorganic

compound ( $\text{SiO}_2$ ) in the sewage sludge and the loaded Fe compound were formed during the carbonization process. The iron oxide was impregnated in the carbon matrix, which was beneficial from the mixture of sewage sludge and iron sludge (iron source).

### **Effect of CPEs dosage**

Increasing CPEs dosage heightened NHCs removal efficiencies (Fig. S5a). However, the promotion effect of NHCs removals induced by increasing CPEs dosage was slight when it increased from 5.0 to 10 g/L. eg. Indole removal efficiency increased from 81.8% to 99.1% when CPEs dosage rose from 2.5 to 5.0 g/L, while it just increased to 99.7% as CPEs dosage increasing to 10 g/L. Many microelectrodes formed with the addition of CPE. Both the electrode areas of the 3D system and the number of catalytic site increased with more amounts of CPEs addition, enhancing the generation and decomposition of  $\text{H}_2\text{O}_2$ . Therefore treatment efficiency was promoted with the increase of CPEs dosage. However, adverse effect occurred due to short circuit current by adding excessively high amount of CPEs between the anode and cathode, which resulted in the decrease of current efficiency and degradation efficiency. Thus 5.0 g/L CPEs was added in this study to form 3D EF system.

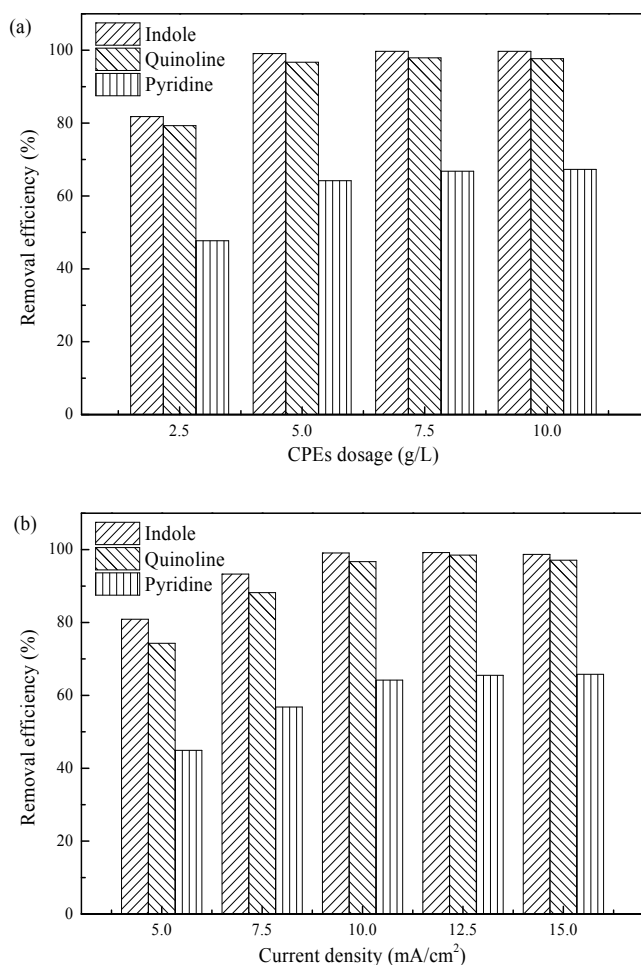


Fig. S5 Effect of CPEs dosage (a) and current density (b) on NHCs removals

### Effect of current density

Current driven electrochemical reactions to generate Fenton agents. Effect of current density on NHCs removals in the 3D EF was illustrated in Fig. S5b. Apparently, the removal efficiencies increased as the current density rose. eg. Indole removal efficiency increased from 80.9% to 99.1% when current density when the current density rose from 5 to 10 mA/cm<sup>2</sup>, while the removal efficiency increased slightly and even declined when further heightening the current density higher than 10 mA/cm<sup>2</sup>. The rise in current density promoted the degradation performance, accounted for the generation of more H<sub>2</sub>O<sub>2</sub> and radicals. However, exceeding high

current density enhanced the occurrence of side reaction, such as the oxidation and reduction of electro-generated  $\text{H}_2\text{O}_2$  at the surface of anode and cathode, four-electron reduction of oxygen. Exceeding higher current density even presented adverse effect on the degradation process due to scavenging radicals by excessive  $\text{H}_2\text{O}_2$ , which resulted in the decrease of pollutant removal efficiency. Thus,  $10 \text{ mA/cm}^2$  was selected in this study.

### **Stability and reusability**

Successive batch experiments using the recovered samples under identical reaction conditions were conducted to directly evaluate the stability and reusability of the prepared CPEs. Eight consecutive runs were conducted and between each trial, the CPEs were removed by filtration and then washed with deionized water for several times and dried at  $105^\circ\text{C}$ . Leaching tests were carried out to assess the stability of the CPEs as well as the contribution of homogeneous phase reactions by leached Fe ions. The indole solution with the addition of  $5.0 \text{ g L}^{-1}$  SAC-Fe was incubated at pH of 3.0 and 9.0 for 120 min, and then the supernatant after centrifugation was collected and divided into two parts. One part was for the measurement of dissolved ions, and the other was used to degrade indole in homogenous EF system.

The concentration of leached Fe-ion was  $1.78 \text{ mg L}^{-1}$  at pH 3.0 for 120 min reaction. While the concentration of leached Fe-ion was only  $1.02 \text{ mg L}^{-1}$  at pH 9.0. The concentrations of leached Fe-ion were lower than the EU discharge limits ( $<2 \text{ ppm}$ ). When the leaching solution was used in the homogenous EF system, about 7%

of indole removal was observed in 120 min at pH 3.0, being much lower than that in the corresponding heterogeneous system (99%). Only 3% of indole removal was achieved in 120 min at pH 9.0. The results indicated that the indole degradation was mainly induced by heterogeneous catalytic reaction of SAC-Fe and an almost completely surface-catalyzed process for H<sub>2</sub>O<sub>2</sub> decomposition. In successive batch experiments, no notable decrease (~5%) was observed in degradation efficiency after eight runs recycling utilization, which suggested that the reused CPEs remained high catalytic activity. In addition, as presented in the XRD patterns of reused CPEs (Fig. S2), there was no obvious change of characteristic peaks before and after the EF reactions, indicating superior stability of the CPEs. The high durability of the CPEs was mainly attributed to its embedded structure. The high content of iron impregnated in the carbon matrix not only prevented the iron oxides from being corroded, but also endowed numerous catalytic sites both for oxygen reduction and H<sub>2</sub>O<sub>2</sub> decomposition.