Supporting Information

Synthesis of water-dispersible molecular imprinted electroactive nanoparticles for the sensitive and selective paracetamol detection

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In our work, a series of PNEA copolymers with different compositions (Table S1) have been synthesized by changing the feeding ratio of NVC:EHA:AA to establish the optimum copolymer compositions in obtaining the best MIP film for PCM sensing. The NMR and FTIR spectra provided in Fig. S1 confirmed the successful synthesis of these copolymers. The size distribution of self-assembled nanoparticles of PNEA copolymers with different composition was shown in Fig. S2. It was found that the mean diameter of the imprinted nanoparticles increased from 44 nm (PNEA-5) to 100 nm (PNEA-16) with the increasing amount of acrylic acid (AA) monomer, which is attributed to the swollen of the nanoparticles triggered by the increasing electrostatic repulsion. It has been observed from our previous works that smaller size of imprinted nanoparticles was advantageous to accommodate more template molecules and thus to enhance the sensing performance of the resulted MIP sensor (Biosensors and Bioelectronics 2011, 26, 2607–2612; Electroanalysis 2013, 25, 1907 – 1916). So imprinted nanoparticles prepared from PNEA-3, PNEA-5 and PNEA-8 are more appropriate to be used for the preparation of MIP film. It was also found that the imprinted nanoparticles prepared from PNEA-3 are relatively not so stable during the electrodeposition process, possibly owing to the limited number of hydrophilic acrylic acid groups in PNEA-3. To find the best polymer composition for sensing PCM, the peak response of prepared MIP sensors from PNEA copolymer (PNEA-5, PNEA-8, PNEA-12 and PNEA-16) were compared. And a higher signal response was observed for the MIP sensor prepared from PNEA-5, which is attributed to the larger amount of electroactive NVC groups in PNEA-5, resulting in higher conductivity of the resulted MIP film. So considering the size, stability of the MIENPs and electrochemical property of the resulted MIP film, PNEA-5 with NVC:EHA:AA feeding ratio of 3:5:5 was chosen as the optimized copolymer to prepare imprinted nanoparticles and MIP sensor.

Table S1

Copolymer sample	Feeding ratio of NVC:EHA:AA	Actual ratio of NVC:EHA:AA in PNEA copolymer
PNEA-3	3:5:3	3:4.7:2.8

PNEA-5	3:5:5	3:4.8:4.8
PNEA-8	3:5:8	2.7:4.7:8
PNEA-12	3:5:12	2.8:5:11.4
PNEA-16	3:5:16	2.8:5:15

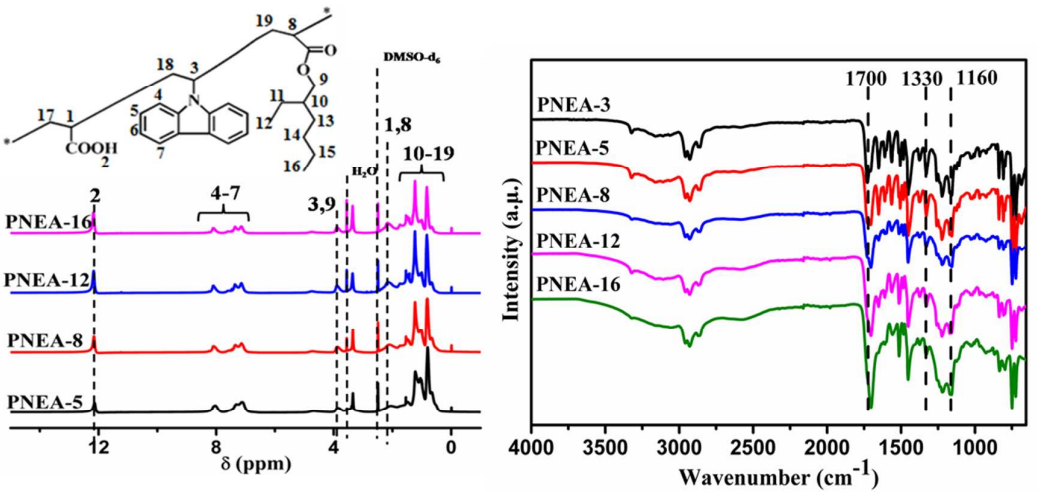

Fig. S1 1H NMR (left) and FT-IR (right) spectra of PNEA copolymers with different feeding ratios of monomers

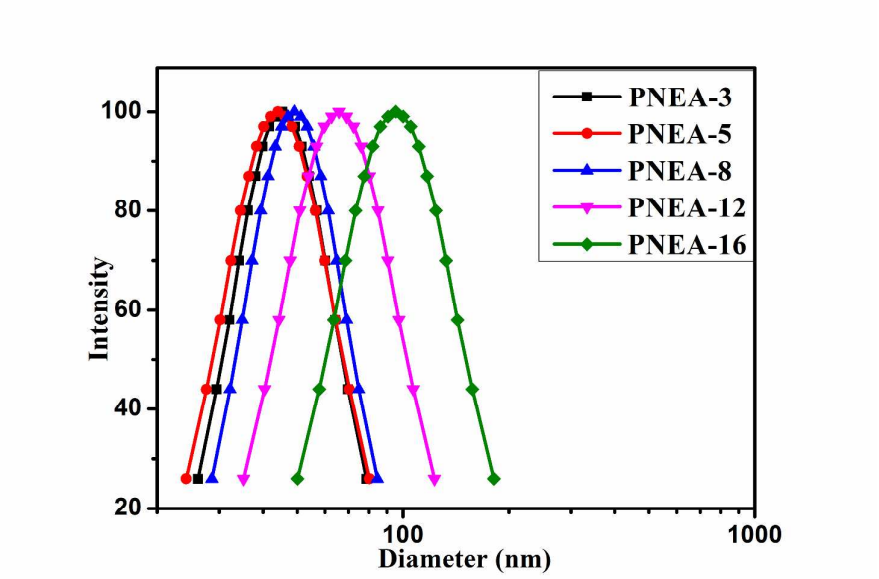

Fig.S2 Size distribution of imprinted nanoparticles from various PNEA copolymers

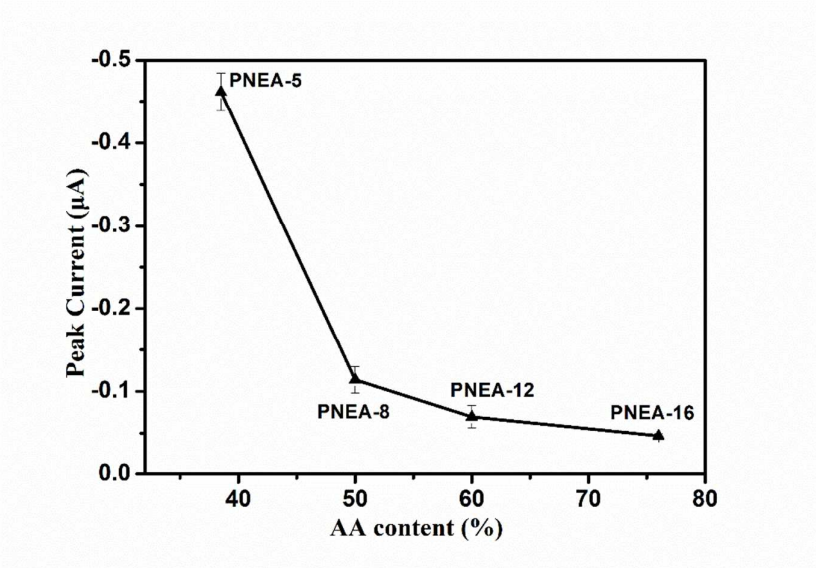

Fig.S3 The influence of the PNEA copolymers with different feeding ratios on the peak current of the resulted MIP sensors

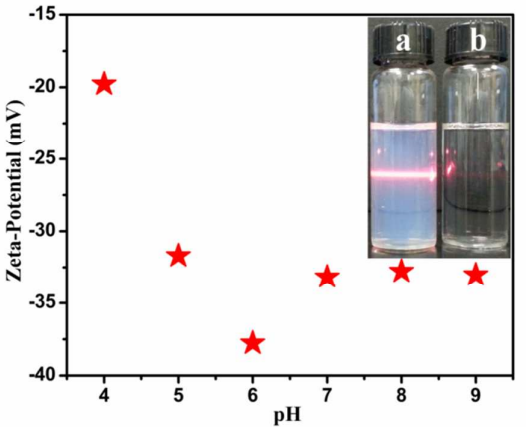

Fig. S4 Influence of pH on zeta-potential of imprinted nanoparticles

Inset: the photo of imprinted nanoparticles (a) and blank solution (b)

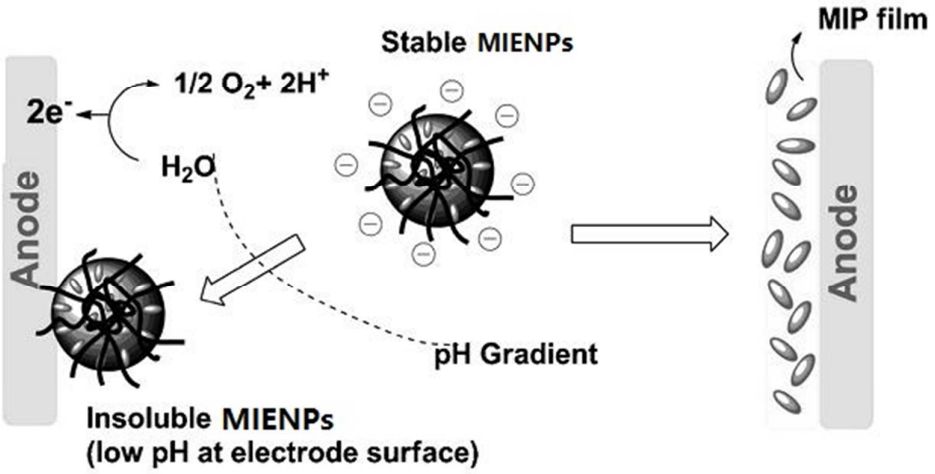

Fig. S5 Schematic illustration of the mechanism of MIENPs electrodeposition

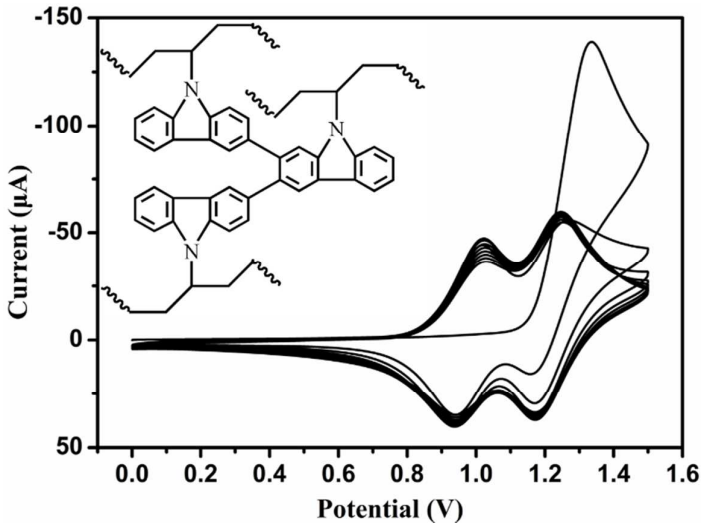

Fig. S6 CV curves for the electropolymerization of MIP film

The oxidation onset at about 1.35 V in the first cycle corresponds to the formation of the carbazolylium radical cations which allowed a subsequent start of electropolymerization of the carbazole units via 3,6 connectivity in the films. The anodic peak potential subsequently shifts to lower potential (1.25 V), which is related to an increase in conjugation as the chains grow which decrease the energy band gap between HOMO and LUMO, thus facilitating the oxidation reaction.

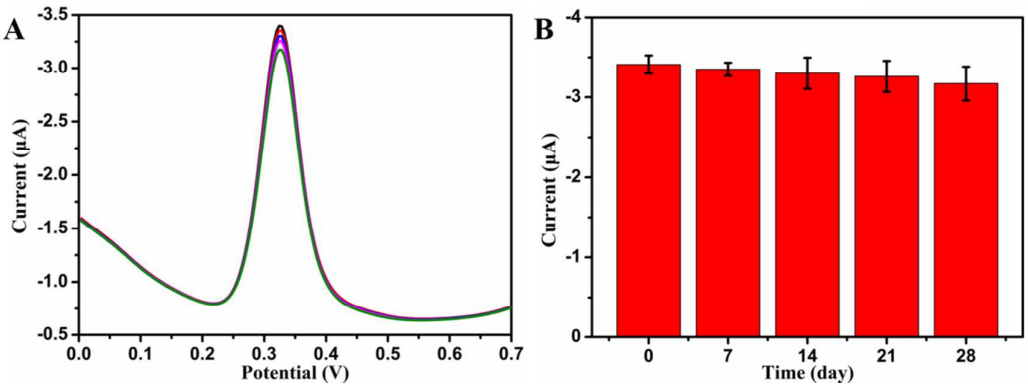

Fig. S7 (A) Different pulse voltammograms of one MIP sensor in 1 mM PCM measured every seven days; (B) Peak currents of one MIP sensor every 7 days