Supporting Information

Experimental

Preparation of flower like HAp:

Typically, a polypropylene beaker with 30 mL of 0.1 M K_2HPO_4 solution was sealed with the egg-shell membrane, and inversely placed on a container which contains 30 mL of 0.1 M $Ca(CH_3COO)_2$ solution. The pH values of both solutions were adjusted to 6-11 by the addition of diluted hydrochloric acid or ammonia solution beforehand. The crystallization process was carried out at 37.5˚C without stirring. After holding for 10 days, the crystal formed on the lower surface of the membrane was carefully peeled off and dried in air for 12 h. The phase structure and morphology of the products were indentified by powder X-Ray Diffraction meter (XRD; D/ruax 2550PC) and Field Emission Scanning Electron Microscope (FESEM; NOVA NANOSEM 230), respectively.

Fabrication of the HAp-CPE:

The HAp modified carbon paste electrode (HAp-CPE) was prepared by mixing of synthesised flower-like HAp and graphite powder (CP) to the chosen HAp/CP ratios of 5%, 10%, 20%, and 30% by weight using paraffin oil as a binder. Then, the HAp-CPE was made up by firmly packing a portion of the resulting paste into commercial CPE shell with a PTFE cylindrical tube (geometric area = 0.1256 cm^2) utilising a copper wire to make electrical contact.

Determination of Pb^{2+} and Cd^{2+} ions:

The 0.2 M phosphate buffer solution (PBS) was used as supporting electrolyte and purged with pure nitrogen for 10 min to remove the dissolved oxygen. A conventional three-electrode system consisting of the HAp-CPE working, platinum wire counter and SCE reference electrodes in a 50 mL of glass sample cell was utilized for the determination. The Pb^{2+} and Cd^{2+} stock solution (5 μM) was prepared by dissolving the corresponding nitrate into Millipore ultra pure water, respectively. The square-wave voltammetry behaviour of proposed modified carbon paste electrode recorded from - 1.0 V to - 0.5 V was performed by using an Electrochemical Working Station (CHI-660d, China) under ambient conditions.

Optimization of measurement conditions:

Figure S1 indicates the effect of the amount of hydroxyapatite on the stripping signals of two kinds of metal ions. The peak current increases with the increasing of the amount of modifier at first, because the concentration of HAp on the surface of the modified carbon paste electrode increases correspondingly. At 20% (w/w) of HAp, relative to the mass of graphite powder, the largest peak current is obtained. However, the continuous increase of HAp causes a decrease of the current response, because an excessive amount of HAp may result in the decrease of conductivity of the modified electrode. So the best composition of the HAp in the carbon paste composition is 20% (w/w).

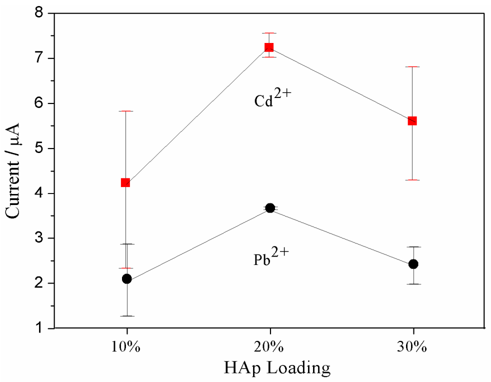

Figure S1 Effects of HAp-loading on the SWASV peak heights of 10^{-7} M Pb^{2+} and Cd^{2+} in 0.2 M PBS at HAp-CPE.

Then, the influence of the pre-concentration potential on the stripping currents of Pb^{2+} and Cd^{2+} ions was investigated in the range of -0.4 to -1.3 V, and the results are shown in **Figure S2**. It can be seen that the peak currents of Pb^{2+} and Cd^{2+} appear at a potential more negative than -0.4 V. The negative shifts of pre-concentration potential can obviously improve the reduction of these two ions on the surface of HAp-CPE and increase the peak current. However, the stripping peak current of Pb^{2+} does not enhance significantly when the potential is more negative than -1.1 V, and some other chemicals may be reduced at the potentials more negative than -1.2 V, which will interfere in the determination of Pb^{2+} and Cd^{2+}. So, at -1.2 V can be achieved a high sensitivity and better response.

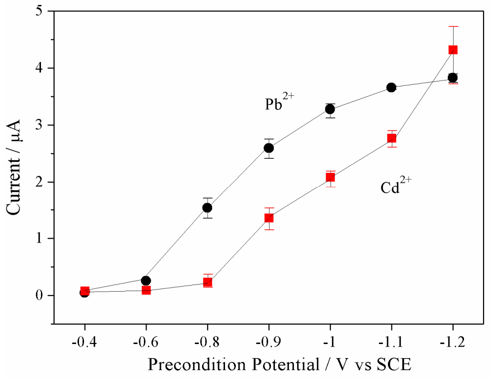

Figure S2 Effects of preconcentration potential on the SWASV peak heights of 100 nM Pb^{2+} and Cd^{2+} in 0.2 M PBS at HAp-CPE.

Figure S3 illustrates that when the pre-concentration time shifts from 90 s to 540 s, the stripping peak currents increase greatly. However, owing to the saturated loading of the electrode surface, the prolonged preconcentration time does not cause more metal ions to be reduced on the electrode surface. In the present work, the optimum preconcentration time can be determined as 540 s.

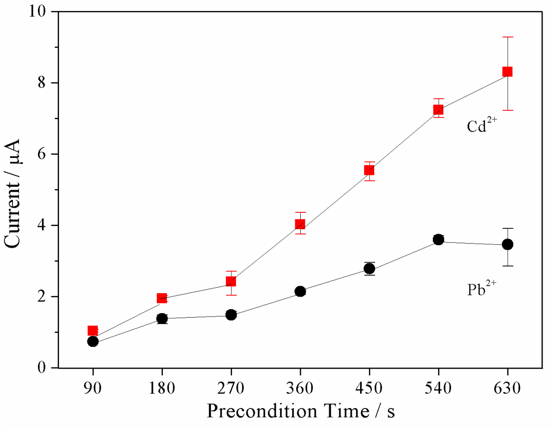

Figure S3 Effects of preconcentration time on the SWASV peak heights of 100 nM Pb^{2+} and Cd^{2+} in 0.2 M PBS at HAp-CPE.