Electronic Supplementary Information

Conversion of Waste Egg-shell ~~*in situ* to Hierarchically Structural~~ Hydroxyapatite for Highly-sensitive Detection of ~~Environmental~~ Endocrine Disruptor Bisphenol A

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Experimental

Conversion of egg-shell to hydroxyapatite under hydrothermal conditions:

The $NH_4H_2PO_4$ was purchased from Alfa Aesar and used without any purification. Typically, the egg-shell was cleaned of macroscopic impuritites in tap water using a brush, and the adherent membrane was peeled off. Then, the shell was sonicated for 30 min, washed with ultra-pure water (Millipore) and anhydrous ethanol. After air-dried at 40 ºC for 2 hours, the shell was ground in a mortar and sieved to obtain egg-shell powders. 0.5 g of this powder was added into an autoclave filled with 40 mL of $NH_4H_2PO_4$ solution (0.12 g/mL). The autoclave was then sealed and heated at the temperatures of 80-160 ºC for 2 days. After this, the hydrothermal treatment products were filtered, alternately washed with ultra-pure water and anhydrous ethanol for three times, and then air-dried at 60 ºC for 12 hours.

The commercial $CaCO_3$ (Alfa Aesar) was used in control experiment. 0.5 g of this reagent was added into an autoclave filled with 40 mL of $NH_4H_2PO_4$ solution (0.12 g/mL). After hydrothermally treated at 110 ºC for 2 days, the product was filtered, alternately washed with ultra-pure water and anhydrous ethanol for three times, and then air-dried at 60 ºC for 12 hours.

The phases of the products were indentified by powder X-Ray Diffraction meter (XRD; D/ruax 2550PC) using CuKα radiation (λ=1.5418Å). The diffractometer was operated at 40 kV and 100 mA at a 2θ range of 5-75º with a step size of 0.02º. The microstructures of the original egg-shell and converted shell powder samples were observed by Field Emission Scanning Electron Microscope (FESEM; NOVA NANOSEM 230).

Characterization of original egg-shell powders

Figure S1 displays the morphology of the original egg-shell powders. It can be observed that there are some gaps and pores existing in certain areas; most pores are circular in shape with diameters of 200-400 nm (**Figure S1A**). Additionally, many small particles with sizes of 100-500 nm are adhered at the surface. The enlarged view of the rectangular area in **Figure S1A** (**Figure S1B**) identifies the tiny mammillas on the surface. These mammillas are supposed to supply nucleation points for the consequently conversion.

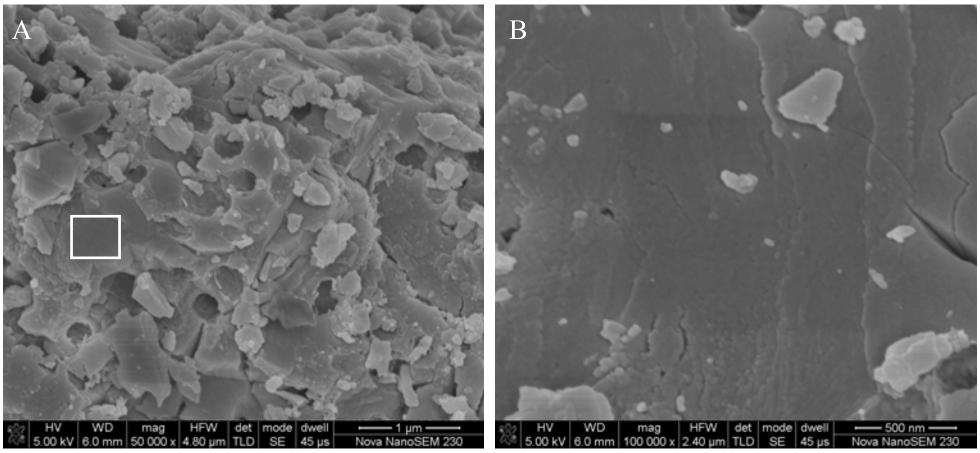

Figure S1 (A) Morphologies of the original egg-shell powders. (B) the enlarged view of the rectangular area in panel (A).

Fabrication of the CMCPE:

The chemically modified carbon paste electrode (CMCPE) was prepared by mixing the synthesised products and graphite powder

(99.8%, Alfa Aesar) to the chosen HAp/CP ratios of 10%, 20%, 30% and 40% by weight using paraffin oil as a binder. Then, the HAp-CPE was constructed by firmly packing a portion of the resulting paste into a commercial CPE shell with a PTFE cylindrical tube (geometric area = 0.1256 cm^2) utilising a copper wire to make electrical contact.

Determination of BPA:

The 0.2 M phosphate buffer solution (PBS) was used as supporting electrolyte and purged with pure nitrogen for 10 mins to remove the dissolved oxygen. A conventional three-electrode system consisting of the CMCPE working, SCE reference and platinum wire counter electrodes in a 50 mL glass sample cell which were utilized for the determination of BPA. BPA was purchased from YongDa Chemical Reagent Co., Ltd (China). The BPA stock solution (0.1 M) was prepared with anhydrous ethanol and kept in darkness at 4 ºC.

The detection of BPA by the proposed modified carbon paste electrode was carried out by cyclic voltammetry in the range of 0 to 1 V (vs. SCE), by using an Electrochemical Working Station (CHI-660d, China) under ambient conditions. The pH measurements were performed on PHSJ-3F digital pH meter (Shanghai Jingke Co., Ltd., China). All the measurements were carried out at room temperature (~20 ºC).

It was found that only a low background current was observed at CMCPE in the absence of BPA (**Figure S2**), indicating that the products converted from egg-shell powders were electro-inactive in the selected potential region of 0-1 V (vs. SCE).

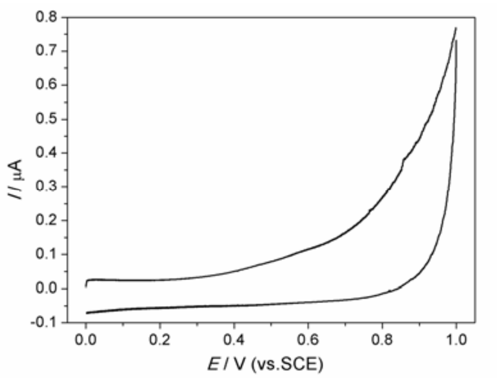

Figure S2 Typical CV curve of electrode modified with 20% of 160ºC -sample in pH 8 PBS.

Control experiment:

Figure S3 compares the patterns of the products hydrothermally converted from commercial CaCO$_3$ and egg-shell powder at 110 °C for 2 days. It can be found that the former product mainly consists of monetite (CaHPO$_4$, PDF 09-0080) (curve “a”), while the latter is composed of monetite with a small amount of whitlockite (Ca$_3$(PO$_4$)$_2$, PDF 09-0169) and HAp (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, PDF 54-0022) (curve “b”).

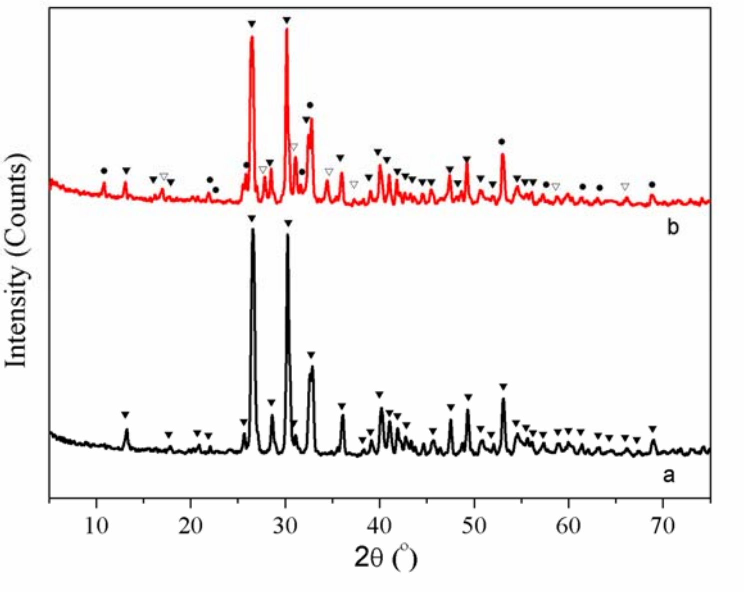

Figure S3 XRD patterns of the products hydrothermally converted from (a) commercial CaCO$_3$ and (b) egg-shell powder at 110 °C for 2 days (●Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ ▼CaHPO$_4$, Δ Ca$_3$(PO$_4$)$_2$)

In order to investigate the sensing performances towards BPA, the products mentioned above were used in CMCPEs and explored in a 0.2 M PBS. As can be seen in **Figure S4**, the peak current of curve "b" is obviously higher than that of curve "a", indicating the product converted from eggshell exhibits better sensing ability towards BPA than the product from commercial $CaCO_3$. It may be resulted from the difference of composite and micro-structure between them (**Figure S3**).

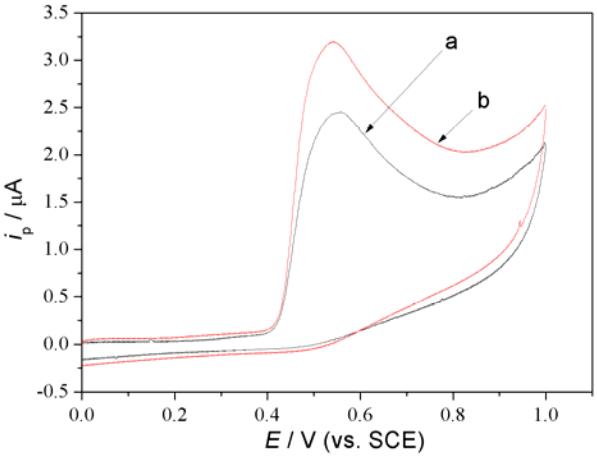

Figure S4 CV behaviour of CMCPE modified by the products hydrothermally converted from (a) commercial $CaCO_3$ and (b) egg-shell powder at 110 °C for 2 days. The measurement was performed in 0.2 M PBS containing 0.1 mM BPA with the scan rate of 100 mV/s.

Optimization of measurement conditions:

(i) Apatite loading:

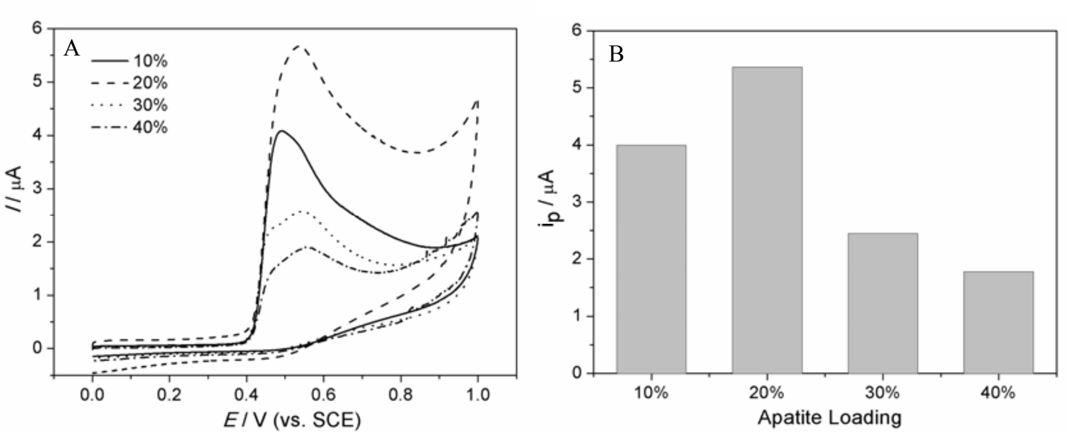

Figure S5 (A) CV curves of 0.1 mM BPA at the proposed electrode modified with 10%, 20%, 30% and 40% of powders obtained from hydrothermal treated egg-shell at 160 ºC for 2 days. (B) The relationship between the apatite loading and the peak current in (A).

Figure S5 indicates the effect of amount of 160 ºC-sample on the peak current of BPA. The peak current increases with the increasing of amount of modifier at first, because the concentration of HAp on the surface of the modified carbon paste electrode increases correspondingly. At 20% of HAp, relative to the mass of graphite powder, the largest peak current was obtained. However, the continuous increase of HAp causes a decrease of current response, due to the excessive HAp may result in the decrease of conductivity of the modified electrode. So the best ratio of the HAp-loading in carbon paste composition is 20% (w/w).

(ii) pH value of PBS

Figure S6A shows a linear shift of the oxidation peak potential (E_o) towards negative potential with an increase in pH, indicating that protons were directly involved in the oxidation of BPA, and it obey the following equation (**Figure S6B**):

E_o (V)=−0.05776 pH+0.92246 (R=0.97482)

It can be found that E_o is linearly dependent on pH and the magnitude of the dE_o/dpH slopes is very close to the theoretical Nernstian value of 0.059 V, indicates the number of protons and electrons involved in the oxidation mechanism is the same. However, the background current obviously increased when pH was 10, though the current responds were the highest among the tested pH range. Then, the following measurement was carried out at the pH value of 8.

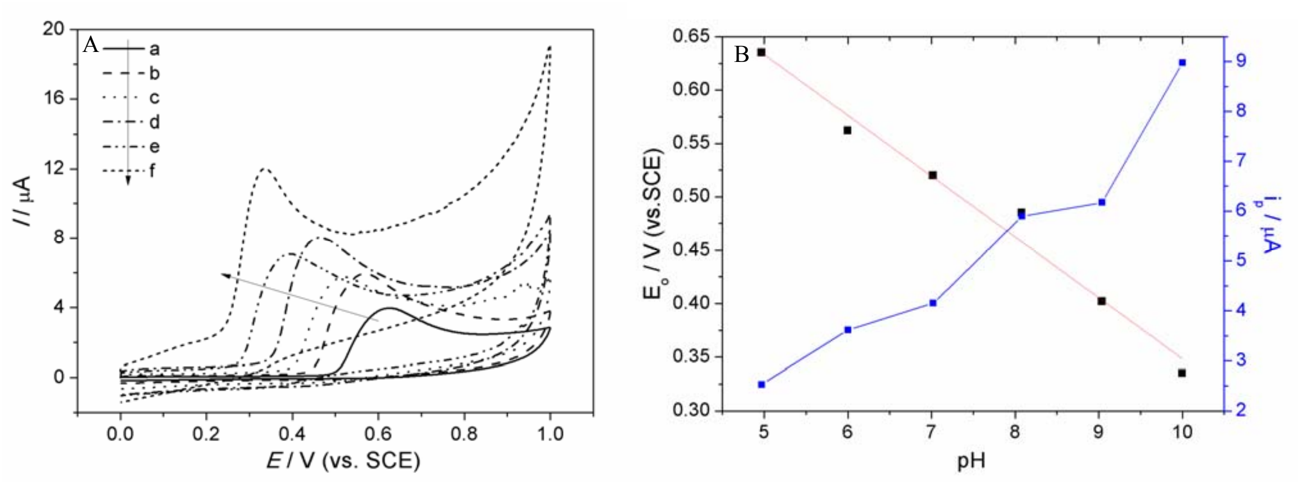

Figure S6 (A) CV curves of 0.1 mM BPA at the proposed electrode modified with 20% of apatite under different pH: (a-f) 5, 6, 7, 8, 9 and 10. (B) The relationship between the oxidation potential and peak current, respectively. Other conditions are the same as Fig.S3.

(iii) The relationship between scan rate and the peak current

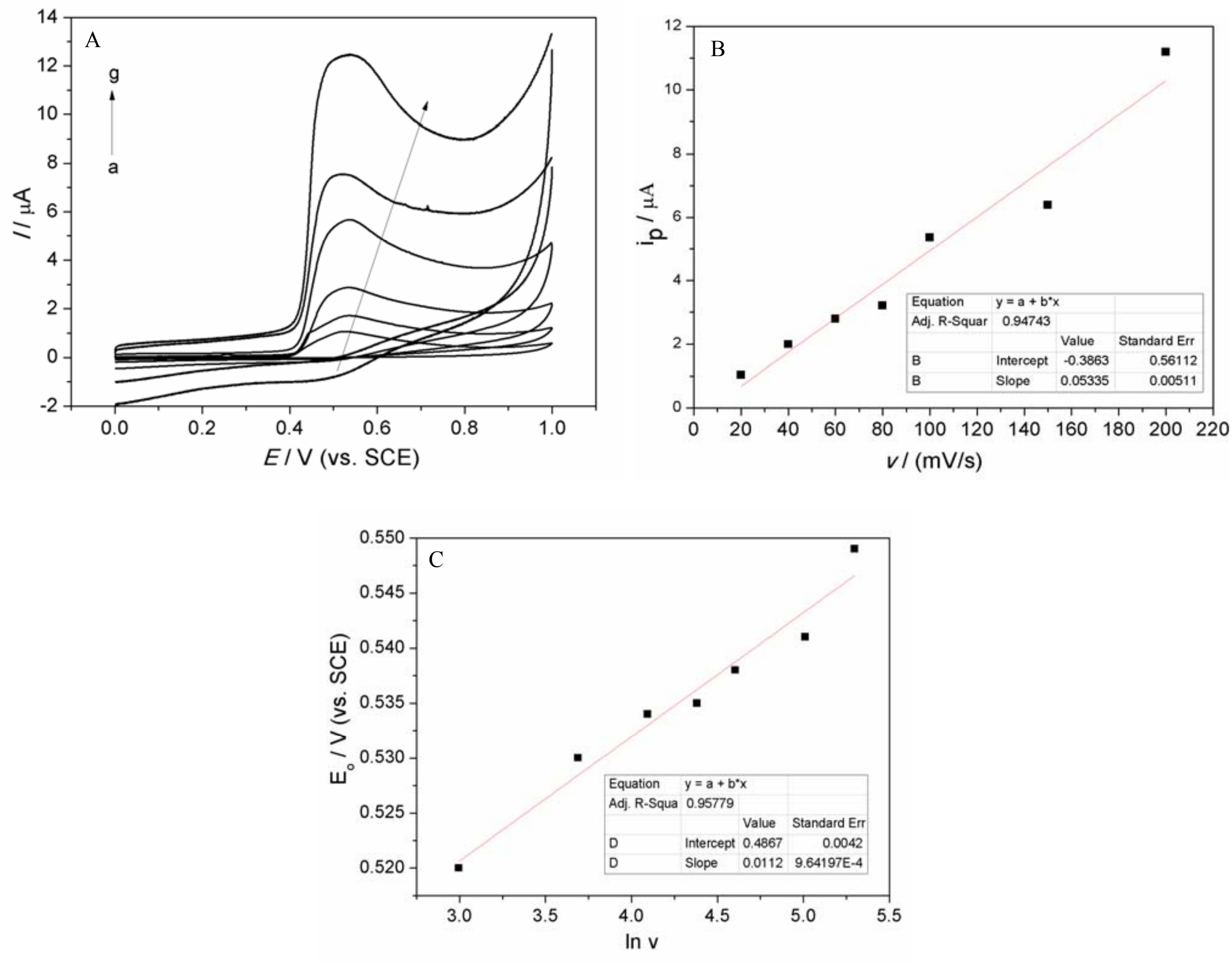

Figure S7 (A) CV curves of 0.1 mM BPA at the proposed electrode modified with 20% of apatite with different scan rates: (a-g) 20, 40, 60, 80, 100, 150 and 200 mV/s. (B) Dependence of the oxidation peak current on the scan rate. (C) The relationship between the oxidation potential and ln *v*. Other conditions are the same as Fig.S3.

Figure S7A shows cyclic voltammograms of 0.1 mM BPA at HAp-CPE with different scan rates. It can be seen in **Fig. S7B** that the peak current increased linearly with scan rate in the range of 20 to 200 mV/s, suggesting a typical adsorption-controlled process. In **Figure S7C**, the relationship between the peak potential and the natural logarithm of scan rate (ln*v*) clearly displays that E_o changed linearly versus ln$v$ with a linear regression equation of:

$$E_o = 0.0112 \ln v + 0.4867 \ (\mathrm{V, mV/s}, R=0.95779)$$

For a totally irreversible electrode process, the relationship between the potential (E_o) and scan rate (v) is expressed as follows:

$$E_o = E^0 + (RT/\alpha nF)\ln(RTk^0/\alpha nF) + (RT/\alpha nF)\ln v$$

Where α is cathodic electron transfer coefficient, n is electron transfer number, and R, T and F have their usual meanings. According to the slope of the E_o vs. ln$v$ plot, αn was calculated to be 2.293. Generally, α is assumed to be 0.5 in totally irreversible electrode process. So the electron transfer number (n) in electro-oxidation of BPA is 5. The pH effect on E_o demonstrate that the number of electrons and protons involved in BPA oxidation is equal. Therefore, the electro-oxidation of BPA at the proposed HAp-CPE is a five-electron and five proton process.