Supporting Information

# Fast synthesis of $Cu_2O$ hollow microspheres and their application in DNA biosensor of hepatitis B virus

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## ELECTROCHEMICAL EXPERIMENT

### Regents and materials

All the DNA sequences were supplied by the Beijing SBS Gene Technology Limited Company. Their base sequences were as below:

Probe DNA: 5'-AAT GTG CTC CCC CAA CTC CTC-3'

Target DNA: 5'-GAG GAG TTG GGG GAG CAC ATT-3'

3 base mismatch to Probe DNA: 5'-GAC GAG TTG CGG GAG CTC ATT-3'

Non-complementary to Probe DNA: 5'-AAA AGG TGT AAG CGT TTG CCG-3'

The target DNA for DNA biosensor is the HBV gene sequences: 21-base target DNA sequences (target ssDNA, namely a 21-base fragment of HBV gene sequences). The probe DNA is the sequences completely complementary with the target DNA. The mismatch DNA is shown with 3-mismatched bases underlined. Methylene blue (MB) and other chemicals were of analytical reagent grade.

### Electrode fabrication and modification.

Carbon paste was prepared by hand mixing of graphite powder with solid paraffin at a ratio of 4/1 (w/w) in a mortar at 65□. The homogeneous carbon paste was packed into a glass tube ($\Phi$ = 3.5 mm) and cooled down to the ambient temperature. The electrical contact was got with a copper wire connected to the paste in the tube (Figure S1a). After the surface of electrode was polished, carbon paste electrode (CPE) was obtained. Hollow $Cu_2O$ suspension (typical sample) was dropped onto the glossily surface of inverted CPE and air-dried at room temperature. A film of hollow $Cu_2O$ hollow spheres was formed on the surface of CPE, and the modified electrode was denoted as $Cu_2O$/CPE (Figure S1b). The electrode was rinsed with B-R buffer solution (a mixture of H3PO4, HOAc, and H3BO3 (each of 0.04 mol/L) adjusted by 0.2 mol/L NaOH to pH of 7).

### Immobilization of ssDNA probe on modified CPE.

20 μL of probe ssDNA ($5\times10^{-6}$ mol $L^{-1}$) was dropped onto the $Cu_2O$/CPE surface. The probe DNA droplet was air-dried at room temperature for 1 h and then rinsed with B-R buffer solution to remove the

un-immobilized DNA. The ssDNA probe modified CPE denoted as ssDNA/$Cu_2O$/CPE (Figure S1c). After that, the electrode was washed with water and rinsed with B-R buffer solution before hybridization.

**Hybridization of the electrode and electrochemical detection**

Hybridization reaction was carried out by immersing the ssDNA/$Cu_2O$/CPE electrode into 2×SSC hybridization buffer solution (0.3 mol·$L^{-1}$ sodium chloride-0.03 mol·$L^{-1}$ sodium citrate) with different concentration of the target DNA for 40 min at 40 °C. Then the electrode was washed with B-R buffer to remove the un-hybridized DNA, and used as working electrode. The response signal of MB was measured by using differential pulse voltammetry (DPV) after the working electrode was immersed in B-R buffer (pH 7.0) containing $2.0\times10^{-5}$ mol $L^{-1}$ MB with 0.02mol $L^{-1}$ NaCl. Similar procedures were also repeated using the 3-base-mismatched DNA sequences and Non-complementary DNA sequences, respectively. The principal steps for the immobilization, hybridization and detection of DNA are showed in Figure 1.

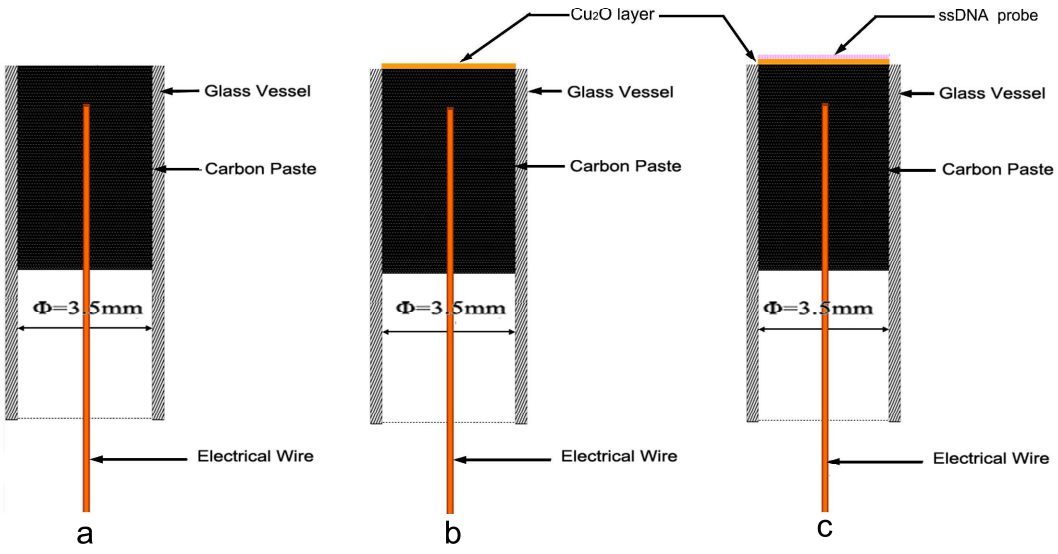


Figure S1. The schematic structure and SEM of CPE (a), $Cu_2O$/CPE (b), and ssDNA/$Cu_2O$/CPE (c)

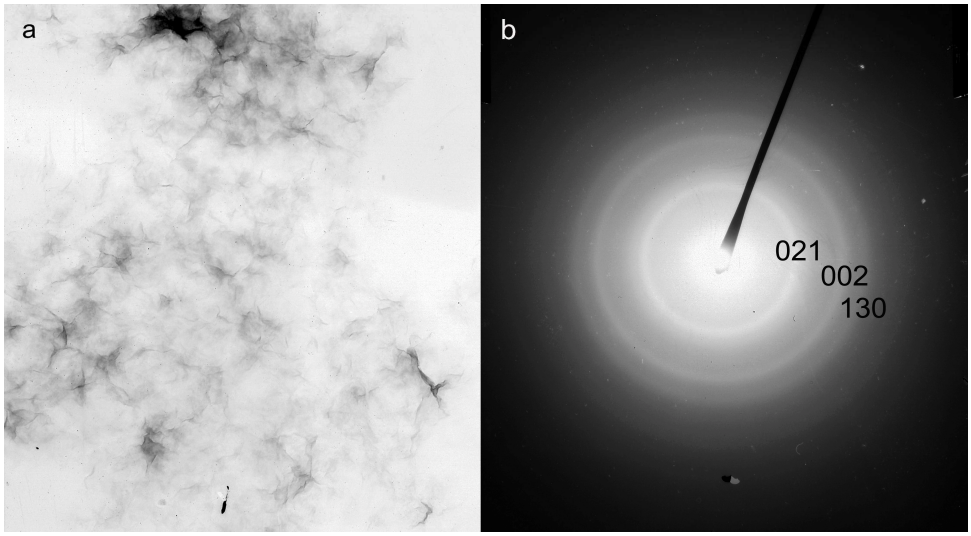


Figure S2. TEM image (a) and SAED pattern (b) of the interim product when NaOH solution with pH=12 was added and without adding $N_2H_4 \cdot H_2O$ solution. The three diffraction circles were indexed to 021, 002, and 130 of orthorhombic $Cu(OH)_2$ according to the literature (JCPDS, file no.35-0505).

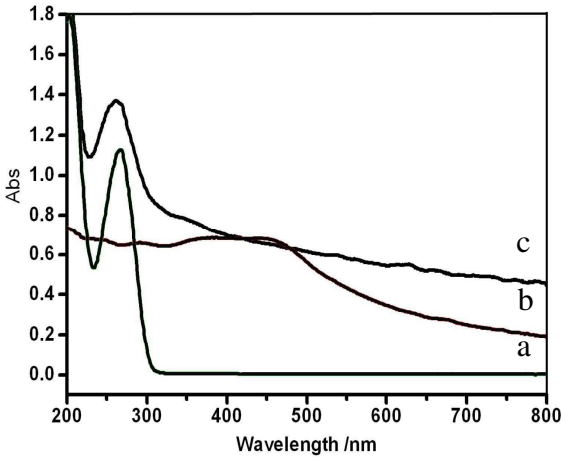


Figure S3. UV-Vis spectra of ssDNA (a), $Cu_2O$ hollow sphere (b) and the $Cu_2O$ labeled ssDNA (c). The absorption peak at about 260 nm in curve (a) was typical absorption of the ssDNA. The curve c was the sample obtained by centrifuging and washing with distilled water for twice after $Cu_2O$ hollow sphere were dispersed in ssDNA solution for 30 min. A new absorption band at about 260 nm appeared in curve (c) as compared with the unlabeled $Cu_2O$ hollow spheres (curve b), which was attributed to the typical absorption of DNA curve (a).