Supporting information

Constructing an Enzyme-free Highly Sensitive Blood Sugar Detection Platform Based on the Maillard Reaction Using Amino-functionalized Black Phosphorus Quantum Dot Hydrogels

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Experimental section

1. Materials

The black phosphorus (BP) crystals (99.98%) were purchased from Xian Feng Nano Company (China) and kept in a glove box filled with Ar before use. Urea, glucose, mannose, galactose, fructose and lactose were purchased from Shanghai Meryer Biochemical Technology Co., Ltd. (MERYER). The other analytically pure chemicals (e.g. Polyvinyl alcohol, DMF etc.) were purchased from Boer and used without further purification. Organic solvents were purified, dried, and distilled under dry argon. The human serum samples were obtained from Shanghai Minhang Hospital affiliated to Fudan University.

Measurements and Instruments: Ultraviolet/visible (UV/Vis) absorption spectra were measured on a Shimadzu UV-2540 spectrophotometer. A HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer was used to record the steady-state fluorescence spectra. All samples for the fluorescence measurement were dissolved in water and/or dry organic solvent, filtered, transferred to a long quartz cell, and then capped and bubbled with dry nitrogen for 15 min. Fourier transform infrared (FTIR) spectra were recorded by Spectrum 100 spectrophotometer (Perkin Elmer, Inc., USA). X-ray photoelectron spectroscopy (XPS) measurements were

carried out on a Kratos AXIS HSi spectrometer with a monochromatized Al KR X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and pass energy of 40 eV. The anode voltage and current were set at 15 kV and 10 mA, respectively. The pressure in the analysis chamber was maintained at 5×0^{-8} Torr or lower during each measurement. Raman spectra were recorded on an Invia/Reflrx Laser Micro-Raman spectrometer (Renishaw, England) with excitation laser beam wavelength of 532 nm. The field emission scanning electron microscope (FESEM) was measured on a JSM-IT800 microscope. The electrochemical impedance spectroscopy (EIS) was measured on CHI760E. All electrical measurements were performed on a Keithley 4200 semiconductor parameter analyzer in ambient condition without any device encapsulation.

Synthesis of black phosphorus quantum dots (BPQDs)： 100 mg of BP powder, which was obtained by grinding the BP crystals in the glove box filled with argon, was added to 150 mL of dry N-methyl-2-pyrrolidone (NMP), and then sonicated for 6h in an ice-bath at the power of 200W. The resultant dispersion was centrifuged for 120 min at speed of 9000 rpm. The supernatant containing BPQDs was decanted gently and kept in a dark bottle under argon atmosphere. The gained precipitate was re-dispersed in 50 mL NMP, re-sonicated to produce more BPQDs. The above cyclic process was repeated for at least three times. Before use, the above BPQDs dispersions, in which BPQDs in NMP shows very good stability, were centrifuged at high speed of 12000 rpm for 30 minutes. NMP is highly miscible with water and conventional organic solvents. To remove the residual NMP trapped in BPQDs, the collected solid BPQDs were added to anhydrous ethanol (200 mL) under an Ar-atmosphere and then sonicated for 30 minutes at the power of 200W, followed by centrifuging at high speed of 12000 rpm. This process was repeated for at least three times. After dryness under vacuum at 50^0C for several hours, the achieved solid BPQDs, which were weighed in the glove box, were directly used for the preparation of amino-functionalized BPQDs (BPQDs-NH_2) and BPQDs-based hydrogel (BPQDs-PVA).

Synthesis of BPQDs-NH_2: To an urea (57 mg, 0.95 mmol) in N,N-dimethylformamide (DMF, 200 mL) was added BPQDs (100 mg) in the argon atomosphere at room temperature and stirred for 10 minutes. Then, the reaction solution was heated at 160℃ for 14 hours under stirring and then was allowed to cool to room temperature. To the reaction mixture was added acetone (200 mL), followed by centrifuging at 13000 rpm for 20 minutes. The lower layer black solid was washed with acetone several times, and then freeze-dried for 16 hours. A black BPQDs-NH_2 (124 mg) was obtained.

Preparation of BPQDs-NH_2/PVA hydrogels:

A mixture of BPQDs-NH_2 (100 mg) and polyvinyl alcohol (PVA，1g) in deionized water 110 mL) was heated at 90℃ for 2 hours. Then, the mixure solution was transferred to a suitable mold. Let it standed at -20℃ for 24 hours, then placed the frozen sample in a room temperature environment (around 25℃) to fully thaw. The freezing and thawing steps were repeated 3-5 times until hydrogels were completely formed. Similarly, we also prepared the pure PVA-based hydrogels for a reference according to the method described above.

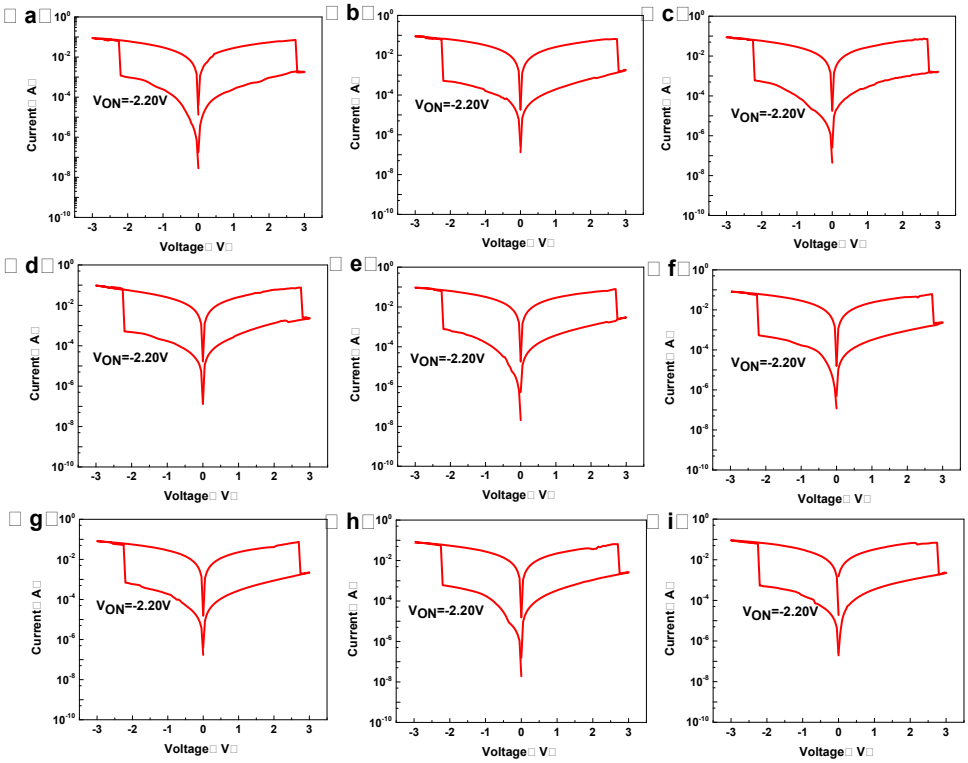

Figure S1. The current-voltage characteristics of the 9 randomly selected devices after being soaked in 5.4 mM blood sugar.

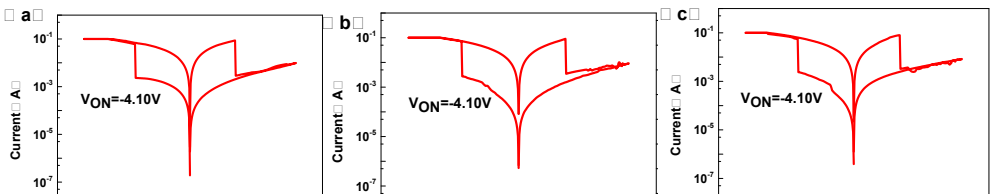

Figure S2. The current-voltage characteristics of the 9 randomly selected devices after being soaked in 12.6 mM blood sugar.

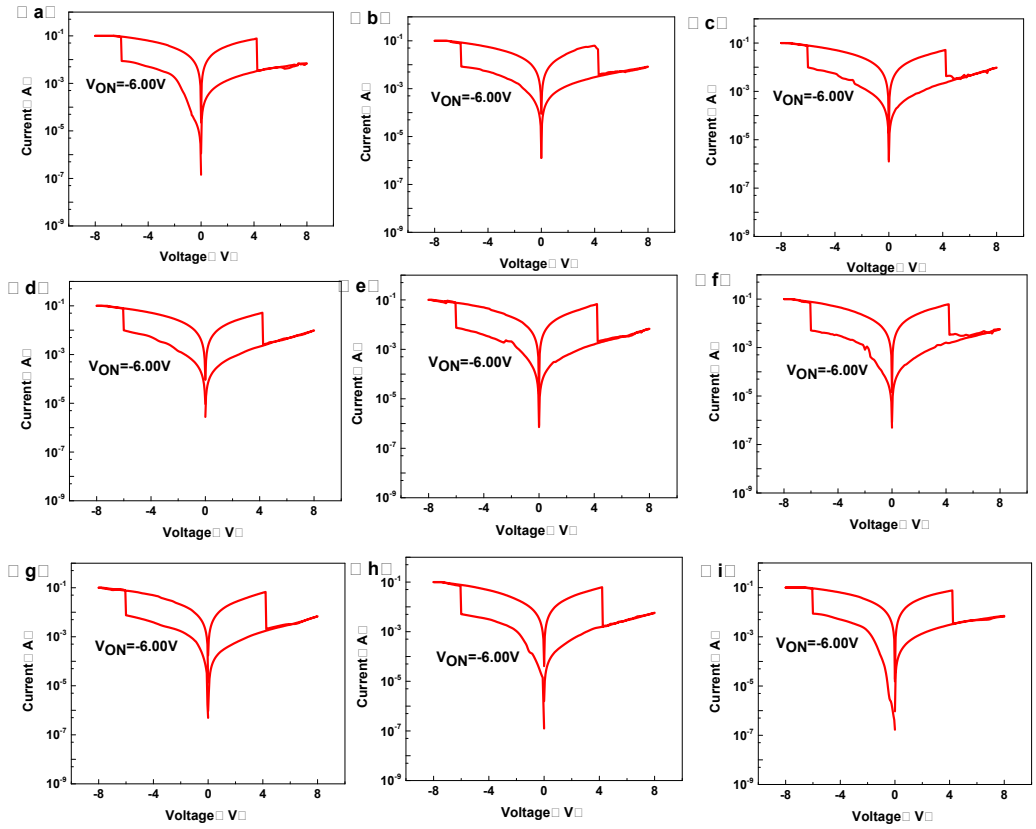

Figure S3. The current-voltage characteristics of the 9 randomly selected devices after being soaked in 19.8 mM blood sugar.

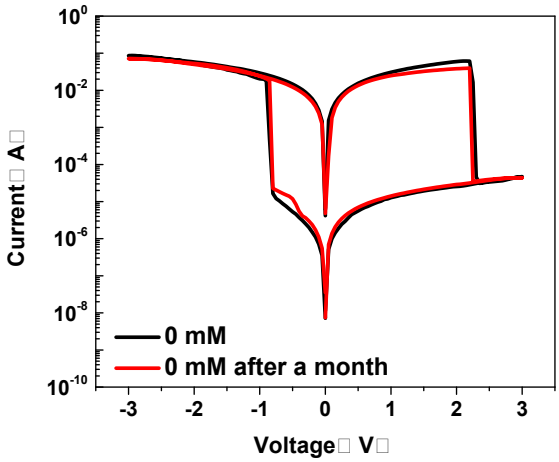

Figure S4. Stability of the as-fabricated memory device without glucose/blood sugar before and after exposure to the air.