Electronic Supplementary Material (ESI) for Analyst
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Electronic Supplementary Information

Copper@carbon coaxial nanowires synthesized by hydrothermal carbonization process from electroplating wastewater and their use as an enzyme-free glucose sensor

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1. Experimental details of Cu@C-graphite NWs and Cu@C-amorphous NPs/MWCNTs.

1.1 Fabrication of vertical arranged Cu@C-graphite composite nanowires through metal organic chemical vapor deposition (MOCVD) approach for comparison. In a typical procedure, the CVD chamber was first cleaned using aqueous 1.0 M HCl solution, followed by repeated rinsing with distilled water. After dried under a Ar gas flow the copper(II)-acetylacetonate as the precursor was evaporated and pumped into quartz tube within CVD cavity using Ar as a carrier gas with flow rate of 30 sccm at a temperature of 450°C under 0.01 bar, and deposition performed onto a blank silica substrate in the coming process. During this synthetic process Cu(acac)2 acts as both the copper and carbon source. The furnace was heated up to growth temperature with a rate of 5°C/min and lasted for 1 h. Ultimately, the furnace was cooled to room temperature. Cu@C-graphite NWs of similar quality could be grown on the surfaces of silicon substrate.

1.2 Preparation of Cu@C NPs/MWCNTs through MOCVD approach for comparison. MWCNTs (~95% purity) with the diameters ranging from 3 to 50 nm and length are over 50 μm were purchased from Chengdu Organic Chemicals Co. Ltd., CAS. To eliminate metal oxide catalysts within the nanotubes, MWCNTs was dispersed in 5.0 M HCl for 3 h with the acid of ultrasonic agitation, rinsed thoroughly with distilled water to neutrality, and finally dried. The deposition was carried out within the same CVD chamber by using the copper(II)-acetylacetonate ($Cu(acac)_2$) as the precursor, which was first mixed with the same molar quantities CNTs and placed in quartz tube at a temperature of 600°C under 0.01 bar, the

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duration time is 3 h. After a deposition process, it was stopped by rapidly cooling the reactor to room temperature using compressed Ar flow.

1.3 Preparation of the modified electrodes. For comparison, the Nf/Cu@C-G NWs/GCE, Nf/Cu NWs/GCE, Nf/Cu@C-A NPs/CNTs/GCE and blank Nf/GCE were prepared with the same procedures as described in preparation of Cu@C-A NWs/GCE. Bare glassy carbon electrode (GCE, 3-mm diameter) were polished before each experiment with emery paper and alumina slurry (CHI Instrument, Shanghai, China) in sequence, then rinsed successively with nitric acid, ethanol, distilled water using bath sonication for 10 min, followed by drying at room temperature. Subsequently, 12 mg various as-obtained nanomaterials were dispersed in 1.0 ml of ethanol suspension and 5 μL drop on the surface of GCE. After drying, 5 μL of Nafion (Nf, 0.4 wt%) was then cast on the layer of these nanocomposites for the purpose of entrapment.

2. Supporting figures.

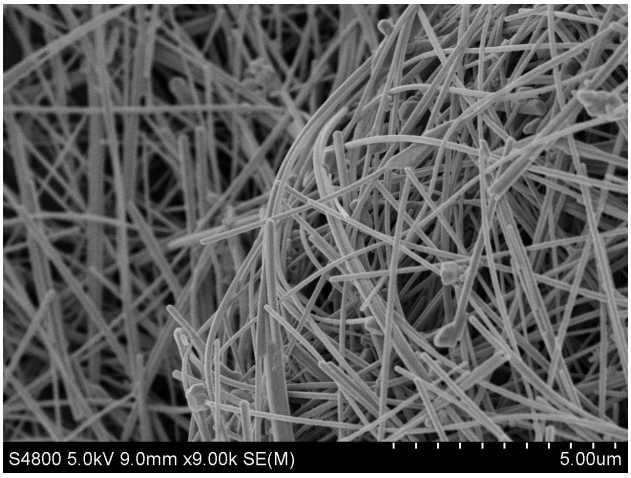

Figure S1. SEM image of as-prepared Cu@C NWs after centrifugation at a rotation speed of 4500 rpm.

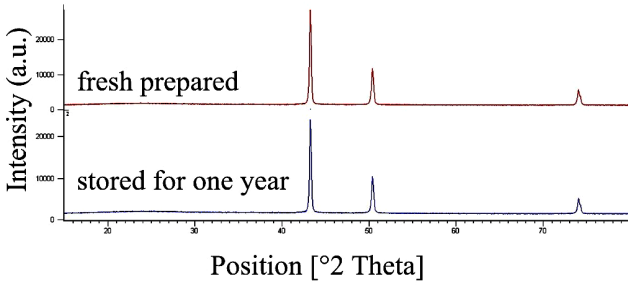

Figure S2. XRD patterns of fresh fabricated Cu@C-A NWs and the same samples stored for one year..

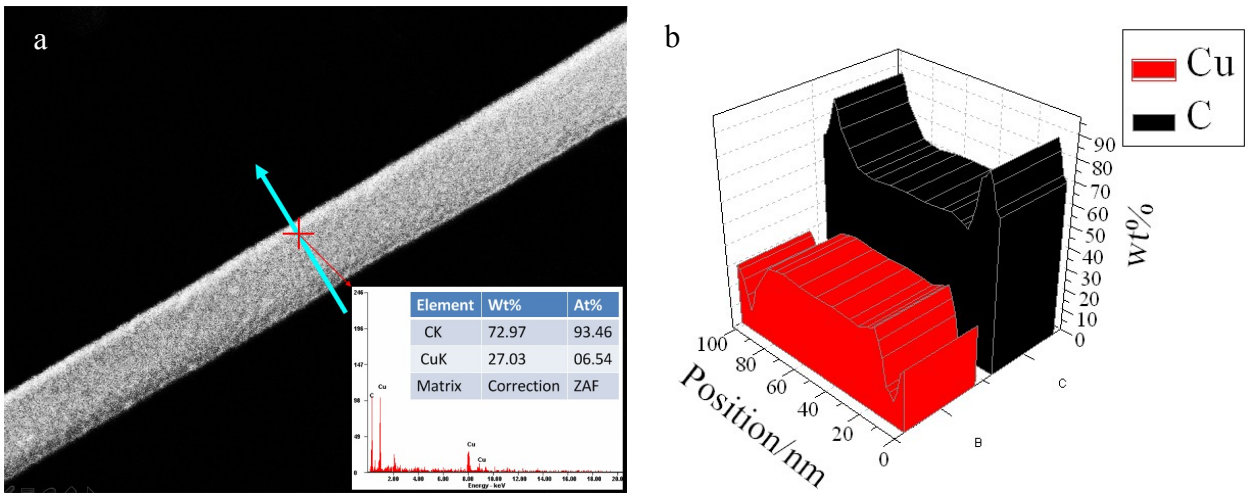

Figure S3. a) EDX spectra of selected area and b) Cu and C-distribution across the axis of a Cu@C nanowire synthesized via hydrothermal process by EDX-analysis.

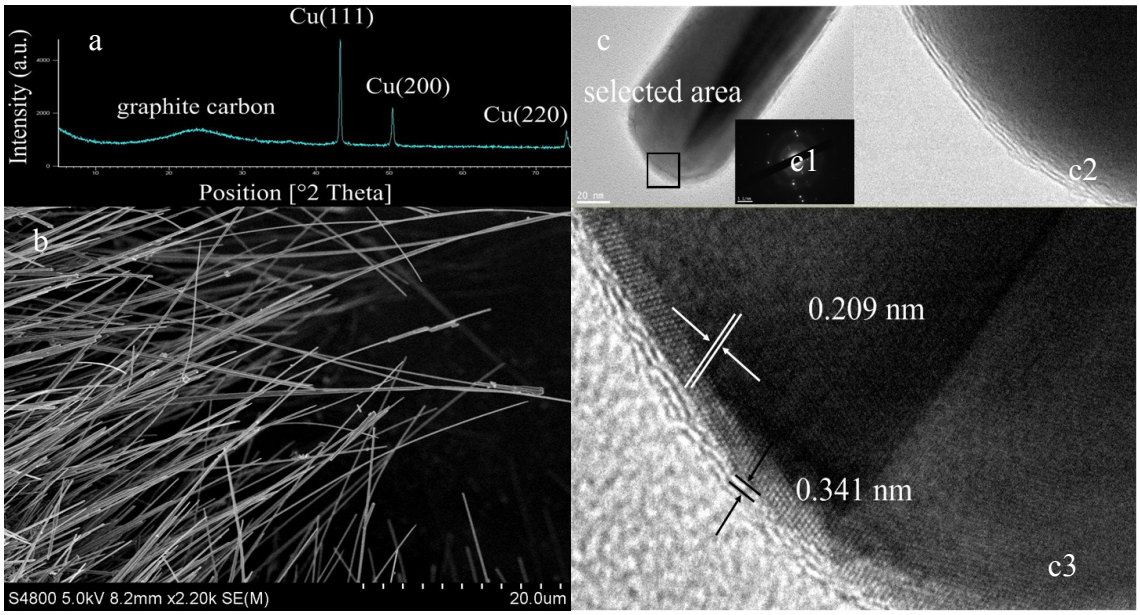

Figure S4. a) XRD-pattern of the as-obtained fresh products after dried in the atmosphere of nitrogen. b) SEM image with low magnification of the final products fabricated by MOCVD method. c) HRTEM characterizations of a single Cu@C NW: c1) TEM image of core-shell NW and its corresponding SAED pattern, taken along the [110] zone axis perpendicular to the long axis of the nanowire. c2) Copper/graphite carbon interface on the surface of Cu NW core, c3) HRTEM image of selected area from c1.

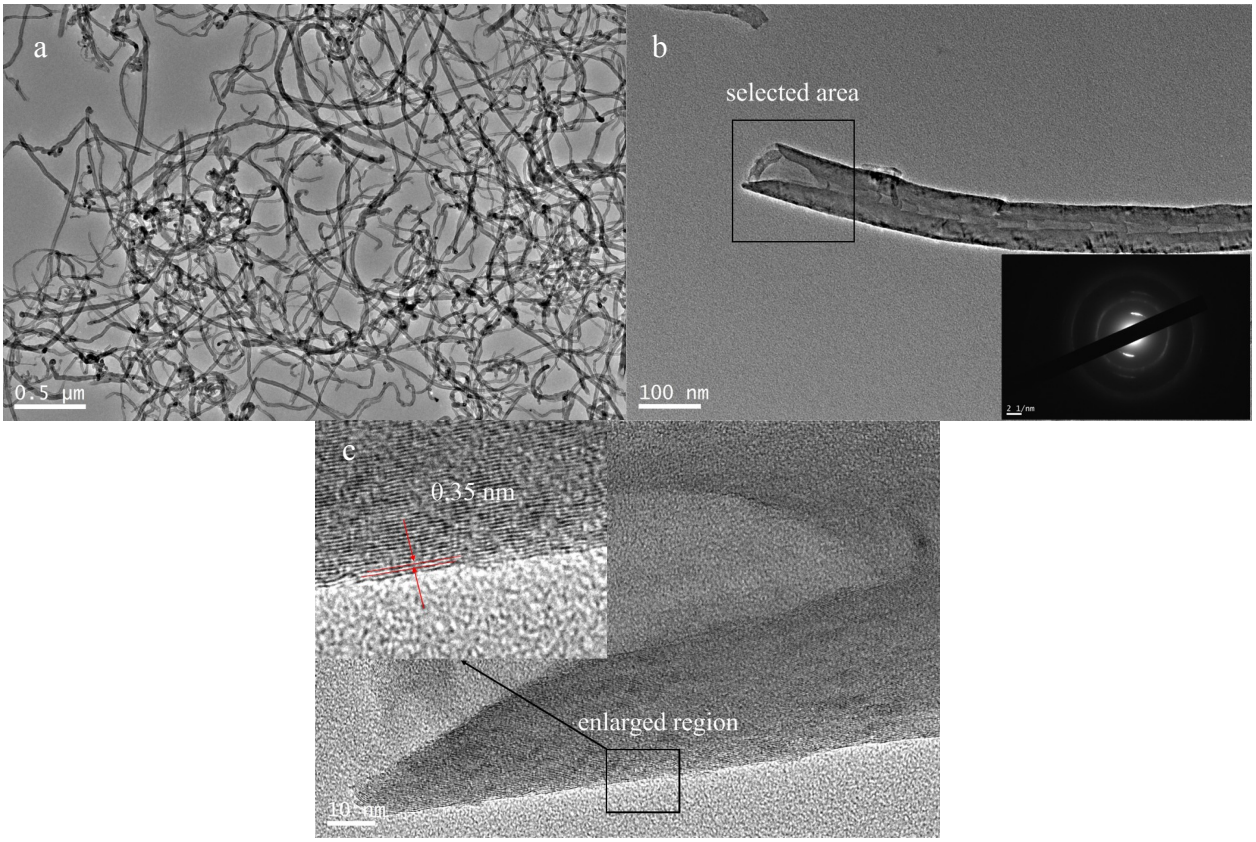

Figure S5. a) Low magnification TEM image of MWCNTs, b) TEM image of an individual MWCNT and inset is corresponding SAED pattern. c) High-resolution TEM image showing the multilayer sidewalls of a MWCNT and top left inset is enlarged region from edge area.

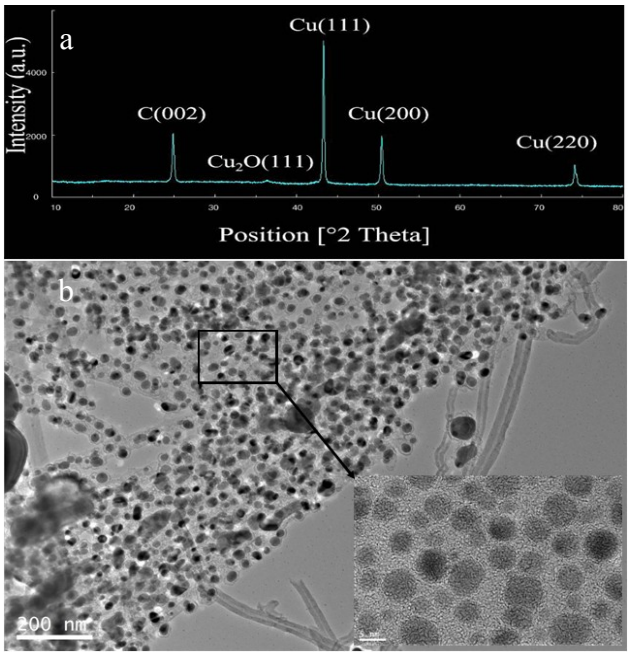

Figure S6. a) XRD pattern of as-prepared nanocomposites. b) Typical TEM micrographs of Cu@C-A NPs and their general size situation.

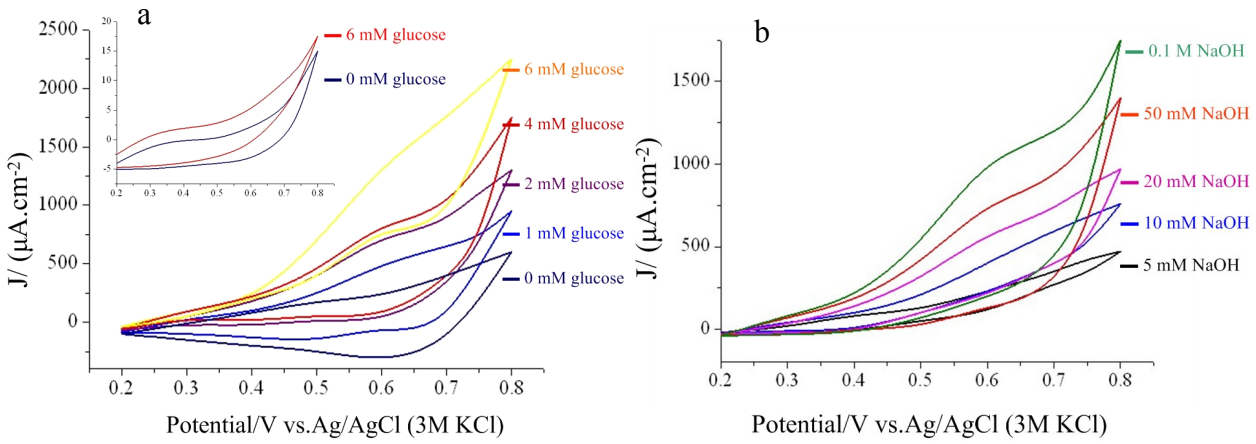

Figure S7. a) CVs of the Nf/Cu@C-A NWs/GCE and blank Nf/GCE (inset) in the presence of different concentrations of glucose from 0 to 6 mM, the electrolyte is 50 mM NaOH and the scan rate is 50 mV/s. b) Cyclic voltammograms of the Nafion/Cu@C NWs/GCE in different concentrations of NaOH from 5 mM to 0.1 M with 2 mM glucose concentration at a scan rate of 50 mV/s.

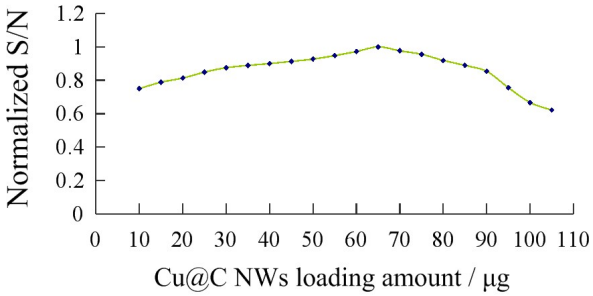

Figure S8. The signal-to-noise ratio (S/N) of the Nafion/Cu@C NWs/GCE in 50 mM NaOH to the injection of 50 μM glucose with increasing loading amount of Cu@C NWs.

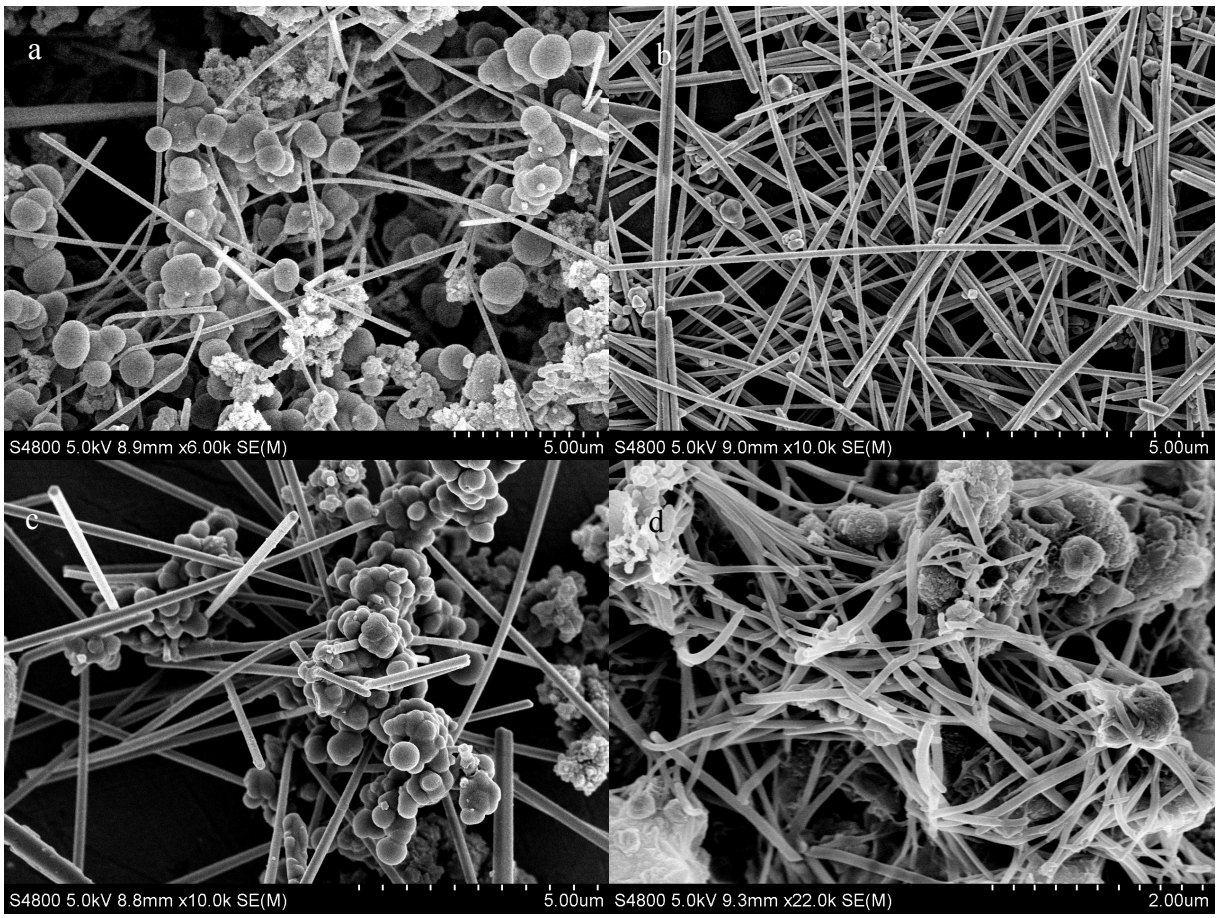

Figure S9. SEM images of Cu@C nanowires synthesized at different temperatures: (a) 140℃, (b) 150℃, (c) 160℃ and (d) 170℃.

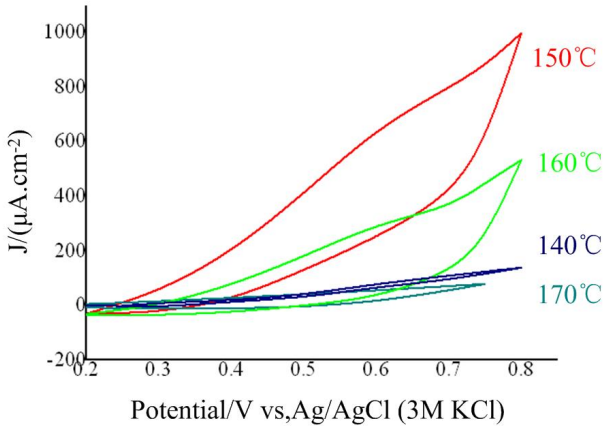

Figure S10. CVs of final products prepared under various temperature conditions modified electrodes with 2 mM glucose in 20 mM NaOH at scanrate of 50 mV/s.

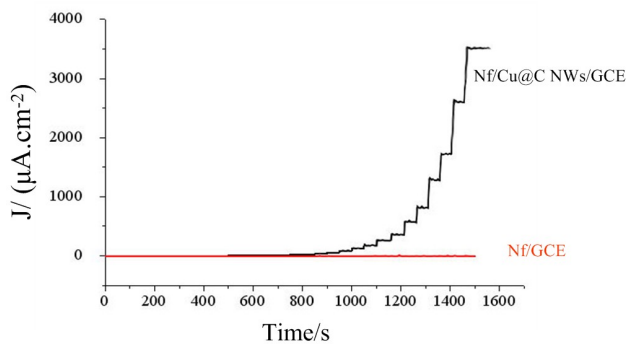

Figure S11. Amperometric responses of Nf/Cu@C NWs/GCE compared with blank Nf/GCE at 0.65 V to successive additions of glucose from 50 nM to 1 mM (double injections per concentration) in 50 mM NaOH.

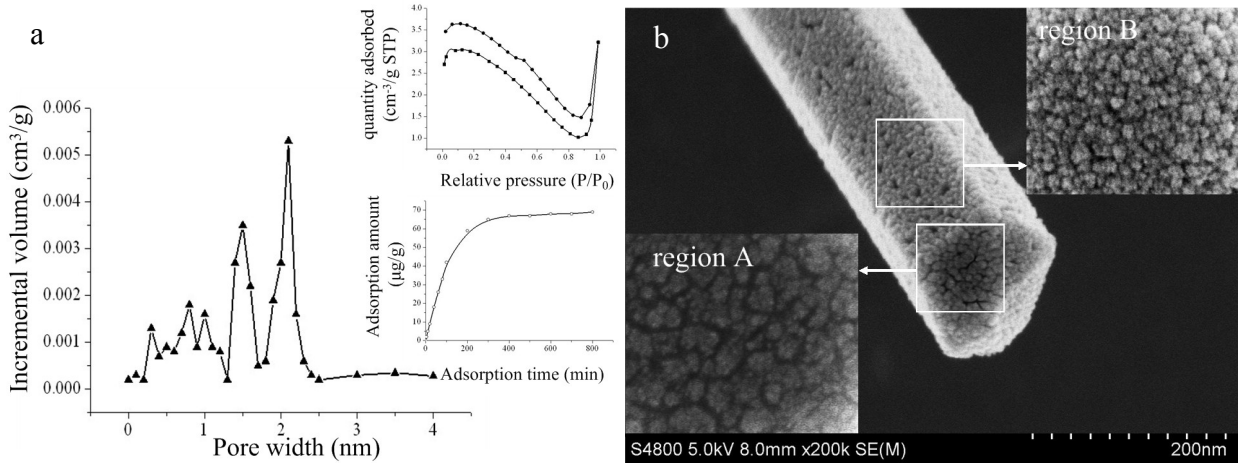

Figure S12. a) Nanopore size distributions within amorphous carbon shells coated on Cu NWs, top right inset shows nitrogen adsorption/desorption isotherms and bottom right inset is effect of adsorption time on glucose adsorption on Cu@C-A NWs. b) Partial enlarged view of a single Cu@C-A NWs which reveals surface of NW is rich in irregular voids and cracks.

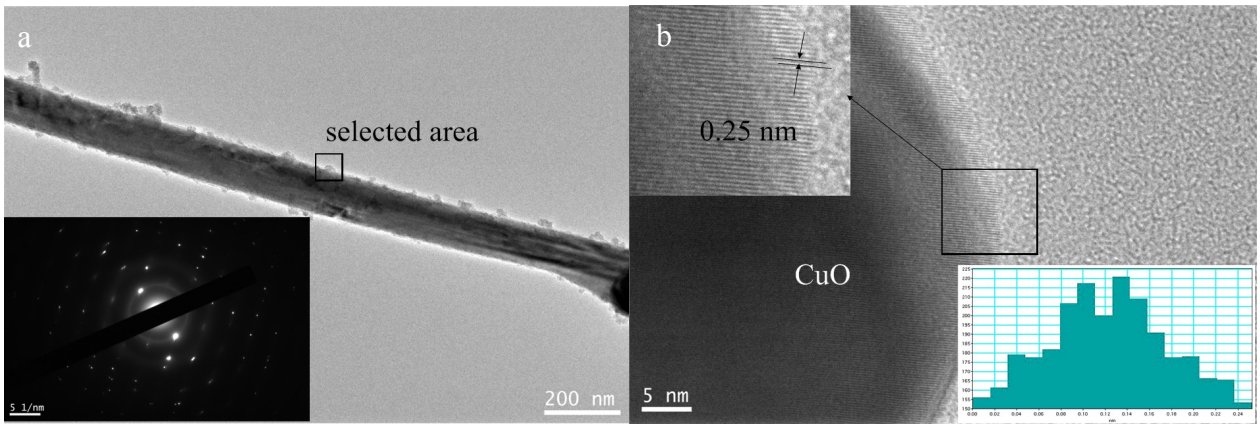

Figure S13. a) TEM images of as-prepared pure Cu NW sampleused for glucose detection stored at ambient conditions over two months, and inset is correponding SAED pattern. b) HRTEM image of a copper nanowire, the local enlarged image from the boxed region is also shown in this image, showing the latice spacing of 0.25 nm corresponds to a d spacing of [110] crystal planes.

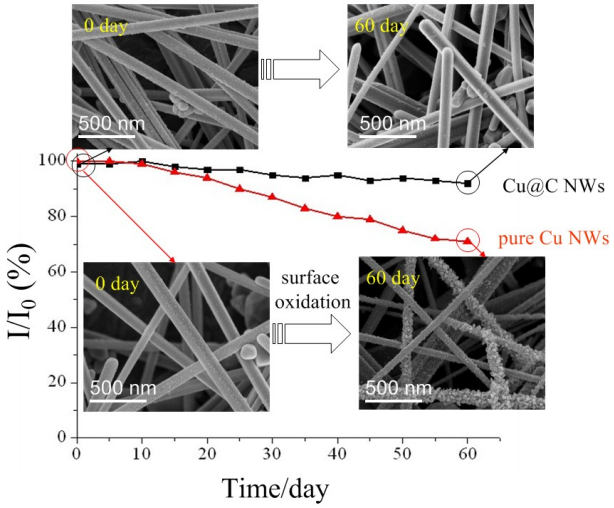

Figure S14. Long-term stability of the pure Cu NWs and Cu@C NWs modified sensors stored at ambient conditions over two months in 50 mM NaOH with addition of 1 mM glucose at 0.65 V.

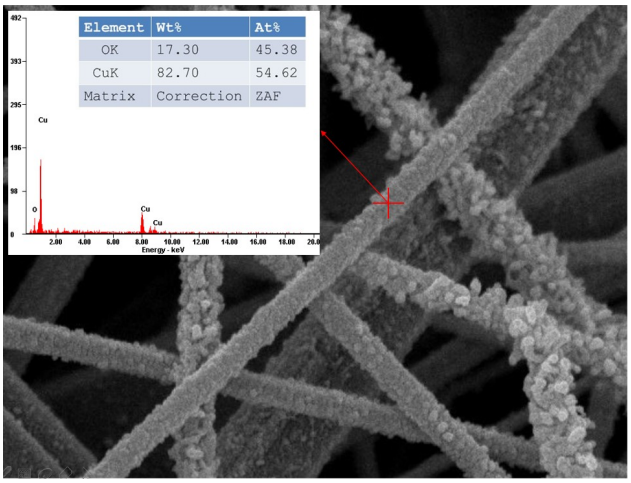

Figure S15. A typical SEM image and EDX spectrum of the CuO NWs stored in damp environment.