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Electronic Supplementary Information

Ni–Fe hybrid nanocubes: An efficient electrocatalyst for non-enzymatic glucose sensing with a wide detection range

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Materials and methods

Materials: Glucose, L-glutamate, cytosine, thymine, adenine, Vitamin C, Glycine, lysine, were purchased from Aladin Ltd. (Shanghai, China). Nickel acetate (II), sodium citrate, potassium ferricyanide (III), sodium hydroxide (NaOH), sodium chloride, sodium sulfate, were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NaH_2PO_4, Na_2HPO_4 and ethanol were purchased from Beijing Chemical Reagent (Beijing, China). The above-mentioned reagents were used instantly without whatevera pretreatment. The water used throughout all experiments was purified through a Millipore system. Phosphate buffer solution (PBS) was prepared by mixing stock solutions of NaH_2PO_4 and Na_2HPO_4. Human blood samples were kindly provided by the Shuozhou Modern Hospital (Gubei Street, Shuocheng District, Shuozhou, Shanxi, China). The human serum was separated from the blood samples by centrifugation. Human serum samples were diluted to different concentrations with a PBS solution, and each sample was analyzed for three times.

Instruments: Transmission electron microscopy (TEM) measurements were made on a JEM-2100 (JEOL, Japan) with an accelerating applied potential of 200 kV. The sample for TEM characterization was prepared by placing a drop of the dispersion on carbon-coated copper grid and dried at room temperature. Fourier Transform Infrared spectroscopy (FT-IR) measurements were made on a FT-IR Spectrometer TENSOR 27 (Bruker Optik GmbH, Ettlingen, Germany). Scanning electron microscopy (SEM) measurements were made on a JSM-7500F SEM (JEOL, Japan) at an accelerating applied potential of 20 kV. The sample for SEM characterization was prepared by placing a drop of the dispersion on a bare Si substrate and air-dried at room temperature. Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments Ins., Shanghai). A conventional three electrode cell was used, including a glassy carbon electrode (GCE) (geometric area = 0.07 cm^2) as the working electrode, a Ag/AgCl (3 M KCl) electrode as the reference electrode, and platinum foil as the counter electrode. All potentials given in this work were referred to the Ag/AgCl electrode. All the experiments were carried out at ambient temperature.

Synthesis of Ni-Fe hybrid nanocubes: Ni-Fe hybrid nanocubes are synthesized according to a previous method with a little modification [Adv. Mater. 29 (2017)

1703870]. 0.6 g of nickel acetate and 0.82 g of sodium citrate dihydrate are dissolved in 80 mL ultrapure water to forming a mixed precursor solution. An aqueous solution of 0.528 g potassium ferricyanide (III) dissolved in 120 mL ultrapure water is added to the above mixed solution slowly and stirred for 1 min. The acquired mixture is placed at indoor temperature for 24 hours. Finally, the obtained precipitate is centrifuged filtered and washed with ultrapure water and ethanol and dried at 70℃ to obtain the final products (Ni-Fe hybrid nanocubes). To prepare Fe-PBA, 1.352 g of ferric trichloride (III) is dissolved in 50 mL ultrapure water to forming a uniform solution under stirring for 10 min. An aqueous solution of 1.584 g potassium hexacyanoferrate (II) dissolved in 50 mL ultrapure water is added to the above solution under stirring for 20 min and dried at 60℃. The Ni-PBA is prepared in a similar way.

Electrode preparation: Before modification, the GCE surfaces were polished with 3 μm and 0.05 μm alumina slurry on a microcloth polishing pad successively, washed with water and sonicated for a few minutes in twice distilled water and ethanol respectively. The electrode modification was accomplished with freshly prepared solutions using a drip method, that is, the uniformly dispersed material was directly dropped onto the surface of the GCE and dried under infrared light. A series of characterizations of the modified GCE were carried out by cyclic voltammetry (CV) and other electrochemical testing techniques.
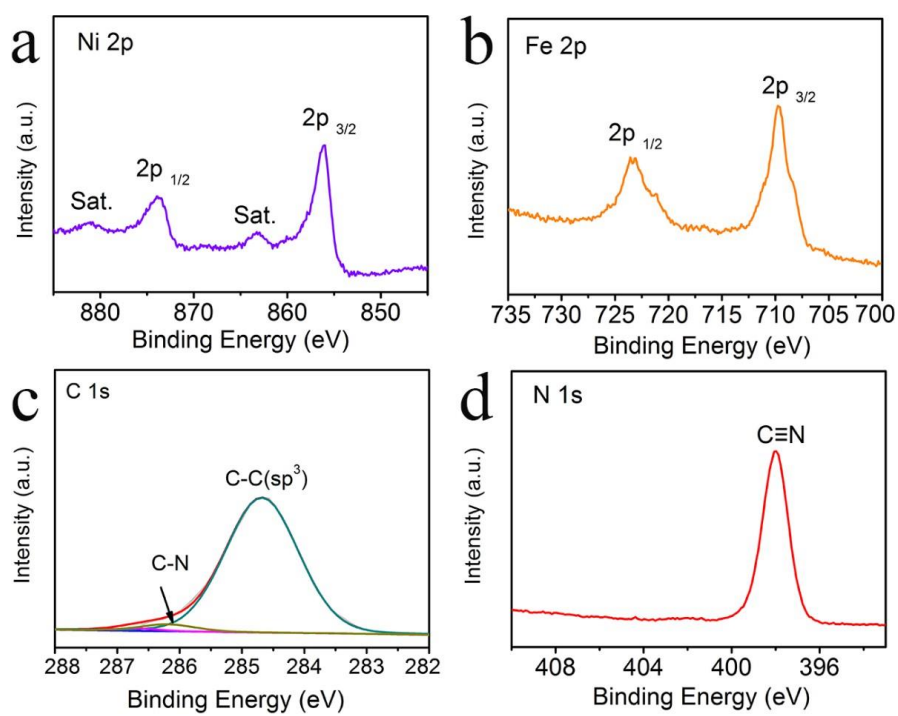
Fig. S1. XPS spectrum for Ni-Fe PBA nanocube in the (a) Ni 2p, (b) Fe 2p, (c) C 1s, and (d) N 1s regions.
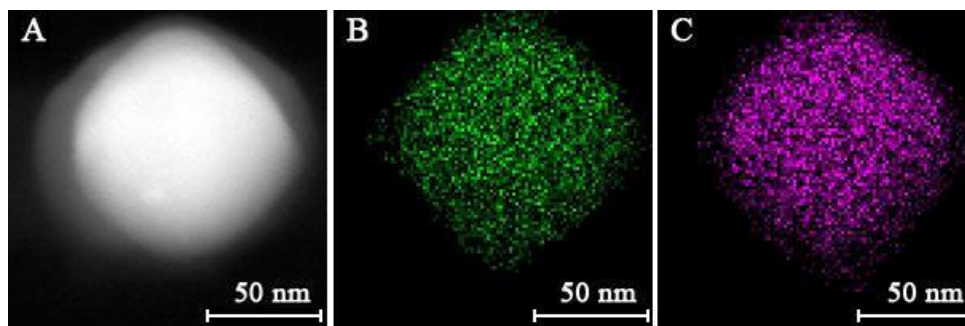
Fig. S2. (A–C) TEM image of Ni-Fe hybrid nanocube with the corresponding elemental mapping images of (B) Fe element and (C) Ni element.
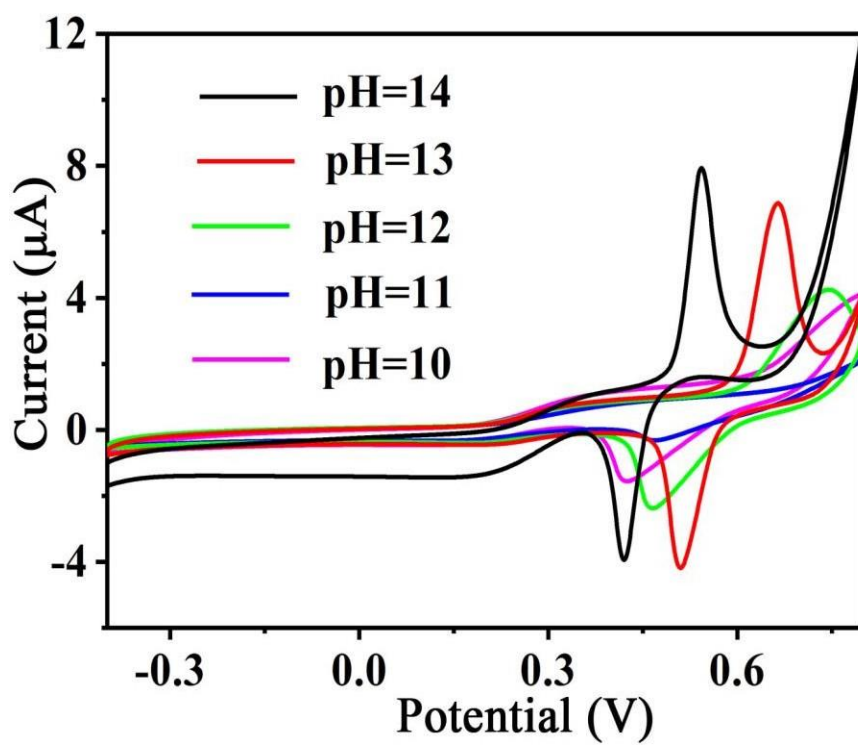
Fig. S3. The CV curves of influence of different pH on the current response of Ni-Fe hybrid nanocube/Nafion/GCE with 3 mM glucose at a scan rate of 50 mV/s.
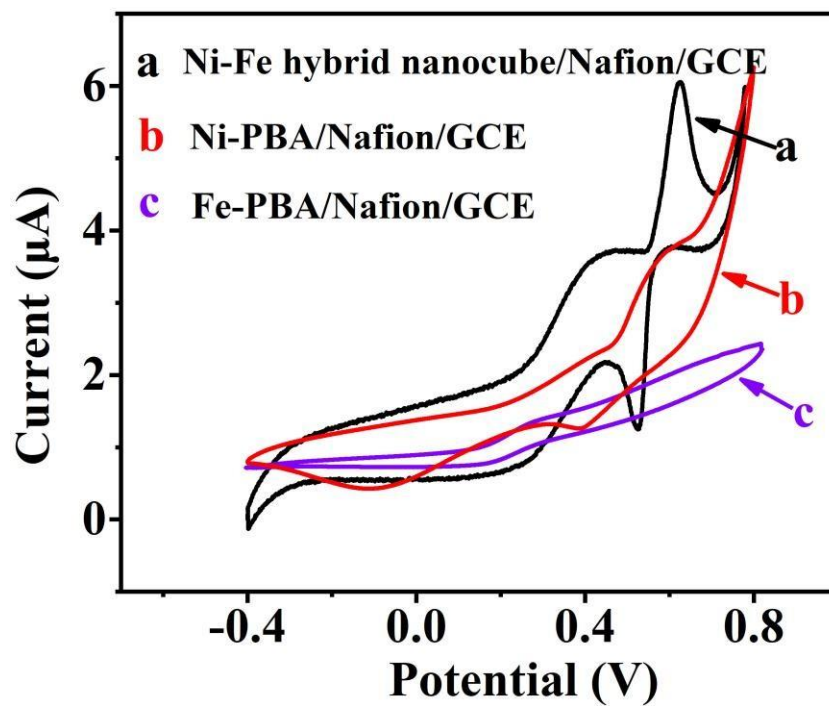
Fig. S4. The CV curves obtained from Ni-Fe hybrid nanocube/Nafion/GCE (a), Ni-PBA/Nafion/GCE (b) and Fe-PBA/Nafion/GCE (c) with 3 mM glucose in 0.1 M NaOH solution.
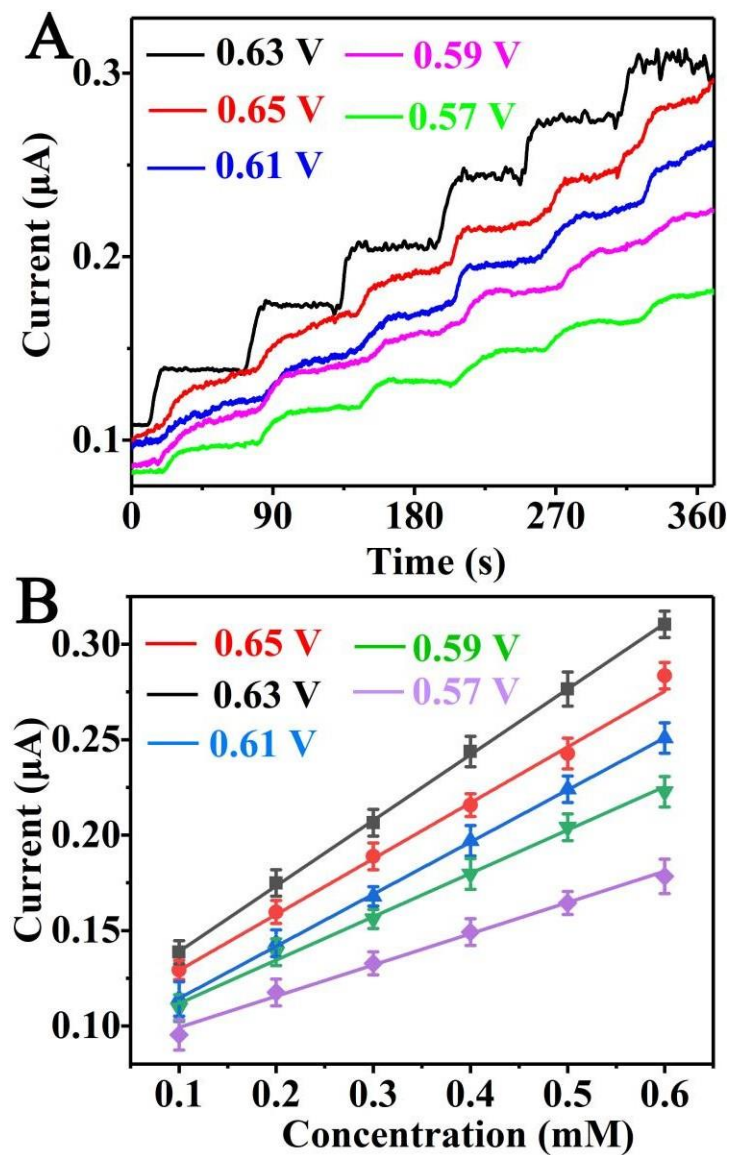
Fig. S5. (A) Amperometric response of Ni-Fe hybrid nanocubes electrode in 0.1 M NaOH solution towards addition the concentration of 0.1 mM glucose at different working potentials (0.57 ~ 0.65 V). (B) The calibration curves of the Ni-Fe nanocubes electrode at various potentials.
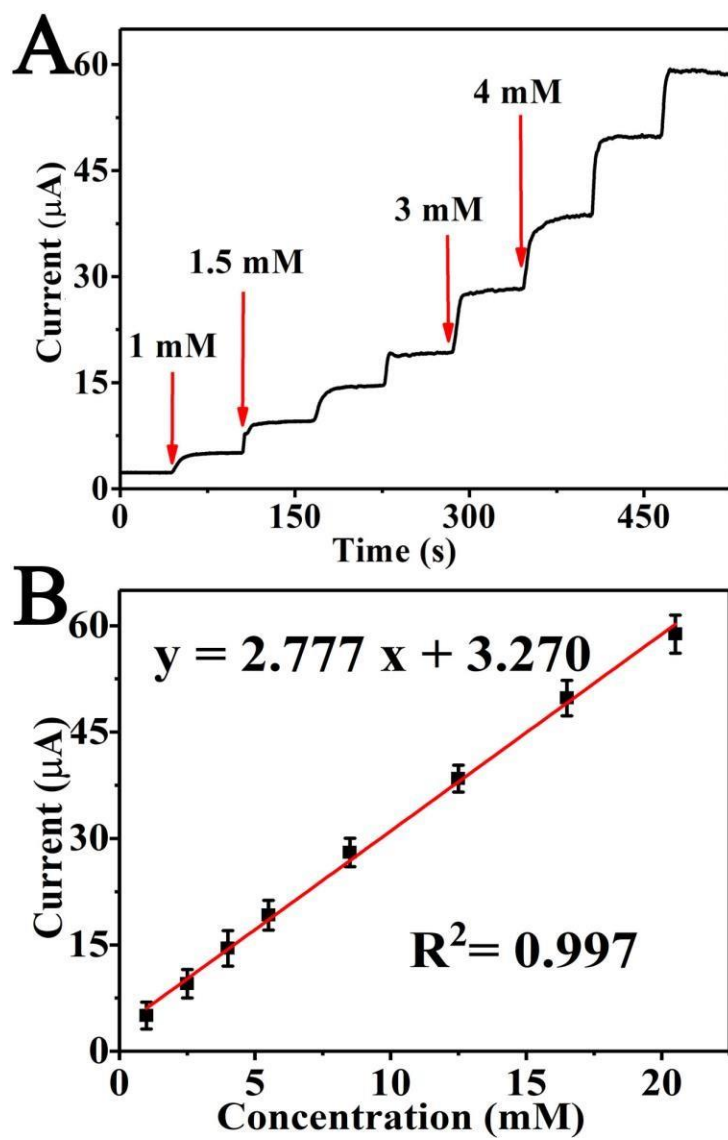
Fig. S6. (A) Amperometric response with the different concentrations of glucose (1 mM to 20.5 mM) were added continuously at 0.63 V in 0.1 M NaOH solution. (B) Plot of amperometric response to glucose concentration.

Table S1. Contrast of the prepared enzyme-free sensor with various glucose sensor reported previously.

Sensor	Linear range /M	LOD /μM	Ref.
(Ni-Co)(OH)$_2$	2.5×10^{-5} - 3.7×10^{-3}	-	1
Ni(OH)$_2$-Graphene	2.0×10^{-6} - 3.1×10^{-3}	0.6	2
Nickel electrode	0.1×10^{-3} – 2.5×10^{-3}	40	3
Fe$_3$O$_4$ nanoparticles/CPE	0.5×10^{-6} – 1.0×10^{-3}	0.21	4
Ni(OH)$_2$/3D graphene foam	1.0×10^{-6} – 1.2×10^{-3}	0.34	5
3D Ni$_3$S$_2$/Ni foam	5.0×10^{-6} – 3.0×10^{-3}	1.2	6
Fe$_3$O$_4$/Nafion/Pt electrode	6.0×10^{-6} – 2.2×10^{-3}	6	7
Fe$_2$O$_3$/n-FeGE	15×10^{-6} – 8.0×10^{-3}	-	8
NiFe PBA/Nafion/GCE	10×10^{-6} – 21×10^{-3}	0.64	This work

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