

# **A Simple and Industry-Scale Strategy to Prepare Flexible Graphene Tape Electrode**

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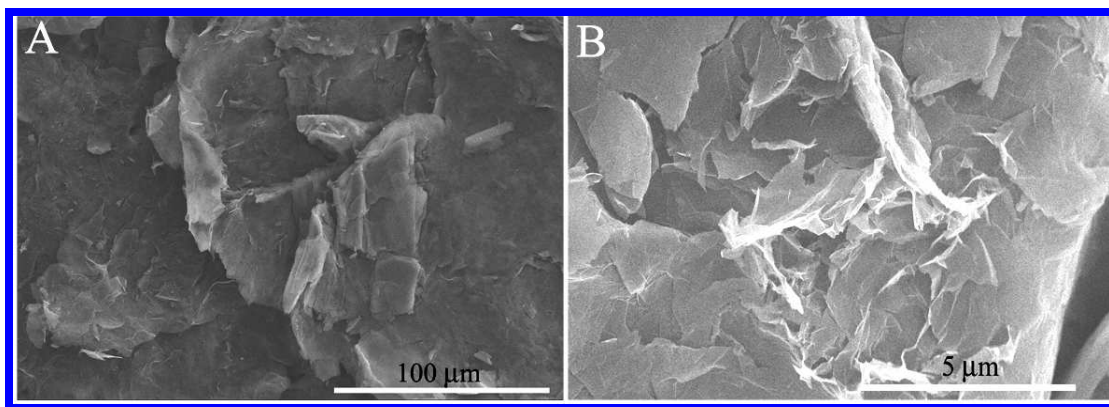
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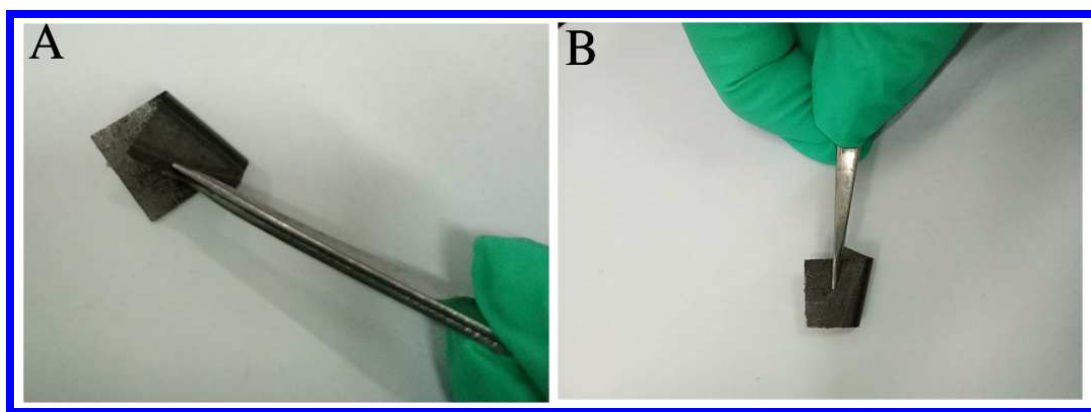
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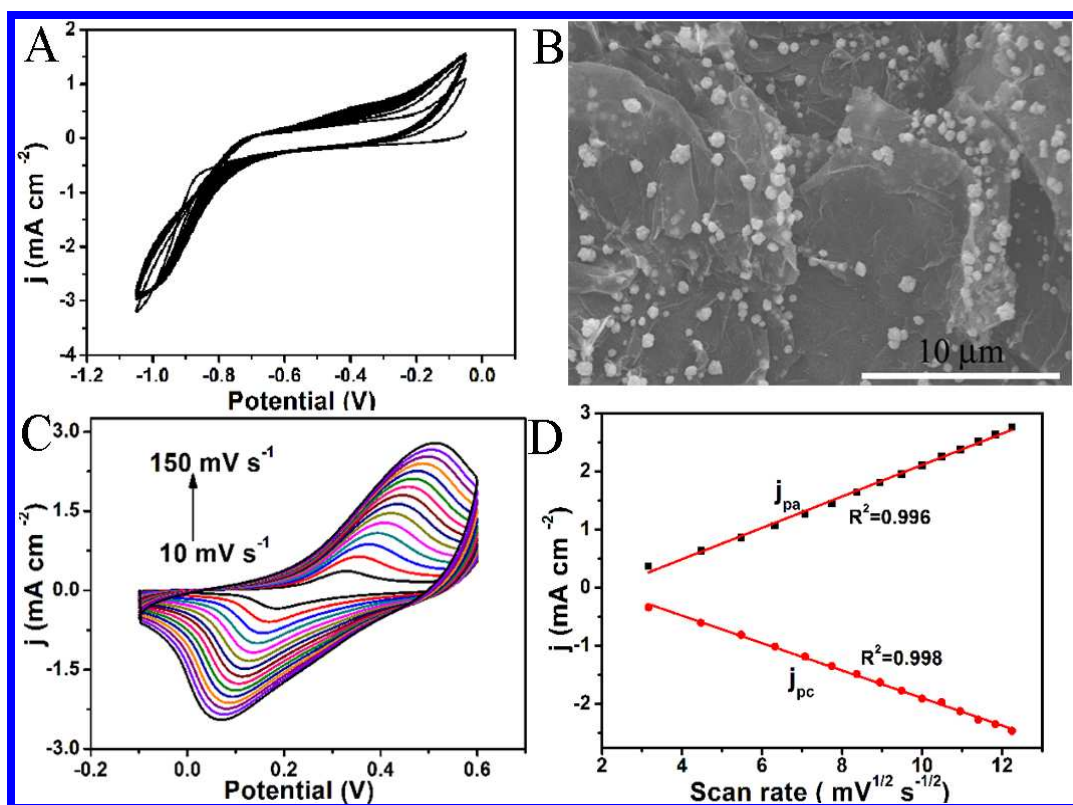
**Figure S1.** The installation process of flexible GTE working electrode.



**Figure S2.** (A) Low and (B) high magnification SEM images of GTE after it bent for 200 times.



**Figure S3.** The digital pictures of bending (A) Ni-CoNPs/GTE and (B) GOD/AuNPs-CHIT/GTE.

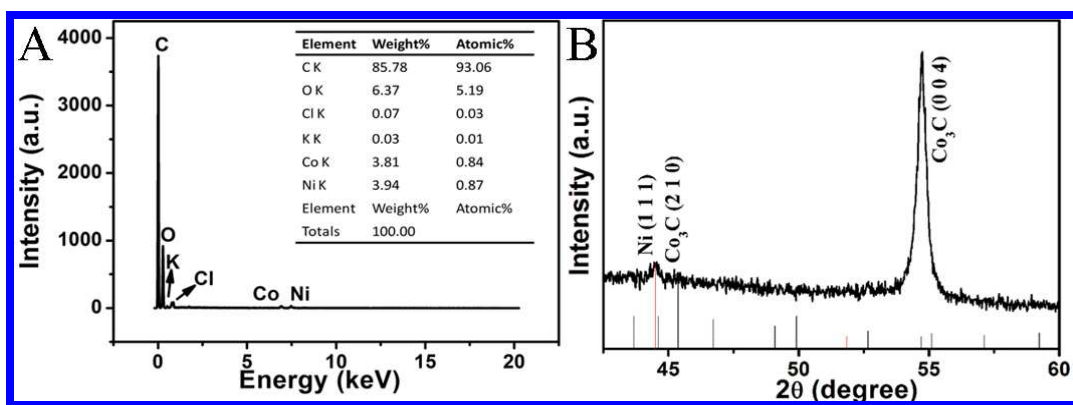


**Figure S4.** (A) CVs of GTE in 0.1 M KCl + 0.005 M NiCl<sub>2</sub> + 0.005 M CoCl<sub>2</sub> at 50 mV s<sup>-1</sup>. (B) Low and high (Inset) magnification SEM images of Ni-CoNPs/GTE. (C) CVs of Ni-CoNPs/GTE in 0.1 M NaOH at different scan rates by step of 10 mV s<sup>-1</sup>. (D) Plot of peak potential versus the root of scan rates. The CVs, EIS and LSV experiments were performed in a quiescent solution. EIS was carried out in 0.1 M KCl containing 5.0 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> at open circuit potential in the frequency range from 10<sup>5</sup> Hz to 0.01 Hz with a signal amplitude of 5 mV.

Figure S4A showed the CVs curves of the flexible GTE scanned at the voltage window between -0.05 V to -1.05 V at 50 mV s<sup>-1</sup>. A cathodic peak appeared at -1.05 V which might be ascribed to the reduction of Ni<sup>2+</sup> and Co<sup>2+</sup> to form Ni-CoNPs on the GTE surface and the corresponding anodic peak was observed at -0.49 V which might originate from the oxidation of the Ni-CoNPs. The cathodic peak current decreased with the increasing of the CVs numbers, which indicated

that  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  were reduced and deposited on the surface of GTE gradually.

The CVs carried out in 0.1 M NaOH solution was used to explore the electrochemical behaviors of Ni-CoNPs/GTE. As shown in Figure S4C, a pair of redox peaks with cathodic peak at 0.2 V and anodic peak at 0.3 V related to the Ni-CoNPs oxidation and reduction was observed. Obviously, with the increasing of the potential scan rate, the peak current enhanced gradually. The peak current density increased linearly with the square root of potential scan rate, suggesting a diffusion-controlled process (Figure S4D).

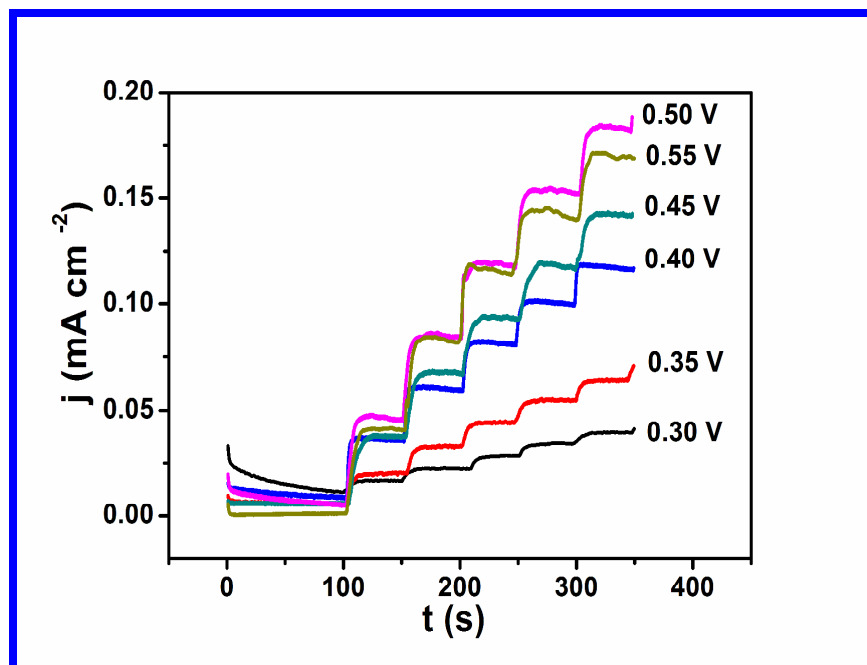


**Figure S5.** (A) EDX and (B) XRD of Ni-CoNPs/GTE.

EDX was used to study the composition of the Ni-CoNPs/GTE (Figure S5A). The peaks corresponding to Ni, Co, C, O, K and Cl were observed in which C-related peak in the EDX data came from the graphene, and the K<sup>+</sup>, Cl<sup>-</sup>, and O-related peaks originated from the electrolyte. The ratio of the Ni/Co was calculated to be about 1:1, which was in accordance with the ratio of Ni<sup>2+</sup> and Co<sup>2+</sup> in the electrodepositing solution. The results clearly revealed that the Ni-CoNPs were successfully modified on the flexible GT electrode.

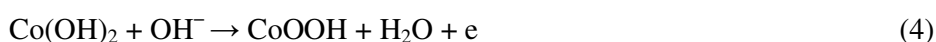
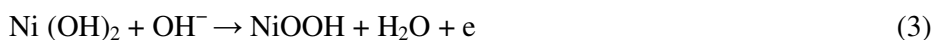
The Ni-CoNPs/GTE was also characterized by XRD (Figure S5B). As can be seen in the XRD pattern, the peak at 44.4° was assigned to the (111) planes of Ni.<sup>1,2</sup> The peaks at 44.6° and 54.7° were assigned to the (210) and (004) planes of Co<sub>3</sub>C, respectively (JSPDS card NO. for Ni is 04-0850 and for Co<sub>3</sub>C is 0450). The results were corresponding with the EDX results and confirmed the formation of Ni-CoNPs.

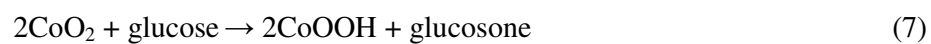
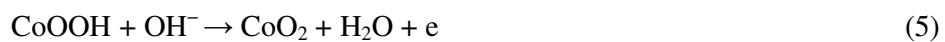




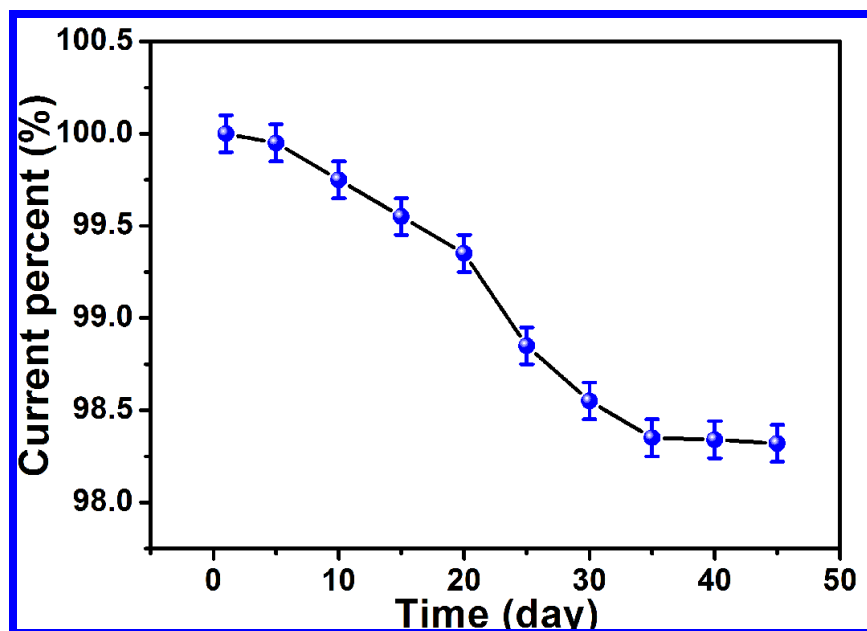
**Figure S6.** Electrocatalytic oxidation of 0.1 mM glucose on Ni-CoNPs/GTE at different applied potentials. The chronoamperometry experiments were carried out under a continuous stirring solution.

The performance of the nonenzymatic electrochemical glucose sensor based on the flexible Ni-CoNPs/GTE electrode was explored. Figure 3A showed the CVs of the flexible Ni-CoNPs/GTE electrode in 0.1 M NaOH solution in the absence (curve a) and presence (curve b and c) of glucose. It clearly showed that the oxidation peak at about 0.45 V was obviously increased and the corresponding reduction peak decreased, indicating the glucose was oxidized by Ni-CoNPs catalyst during the cyclic process. According to previous literatures, the proposed mechanism for the catalytic reaction can be described as followed:



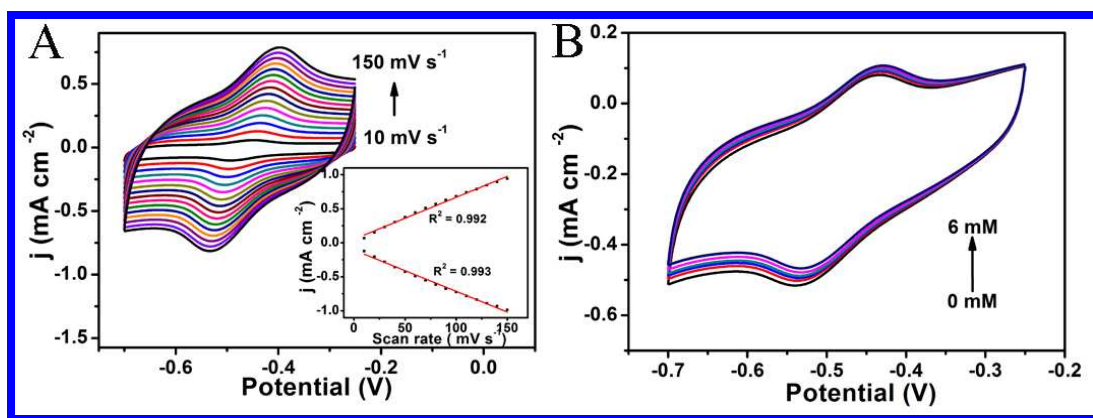


In the mechanism, the Ni (0) and Co (0) was firstly transformed into Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub> in the alkaline conditions, and then the oxides were further oxidized into NiOOH and CoOOH. The NiOOH can be used as heterogeneous catalysts and showed good chemical stability and electrocatalytic activity. At higher potential, CoOOH was further oxidized into CoO<sub>2</sub>. Then the glucose was oxidized to glucosone by the NiOOH and CoO<sub>2</sub>.

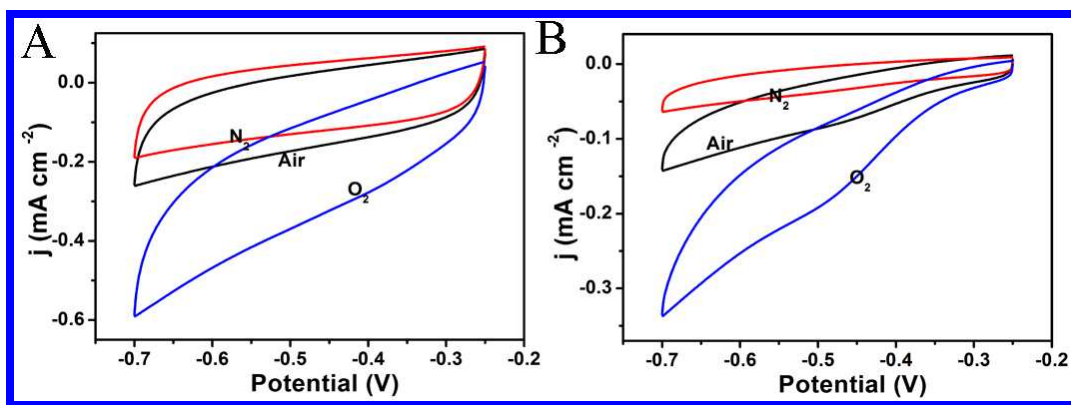


**Figure S7.** Stability test of the Ni-CoNPs/GTE.

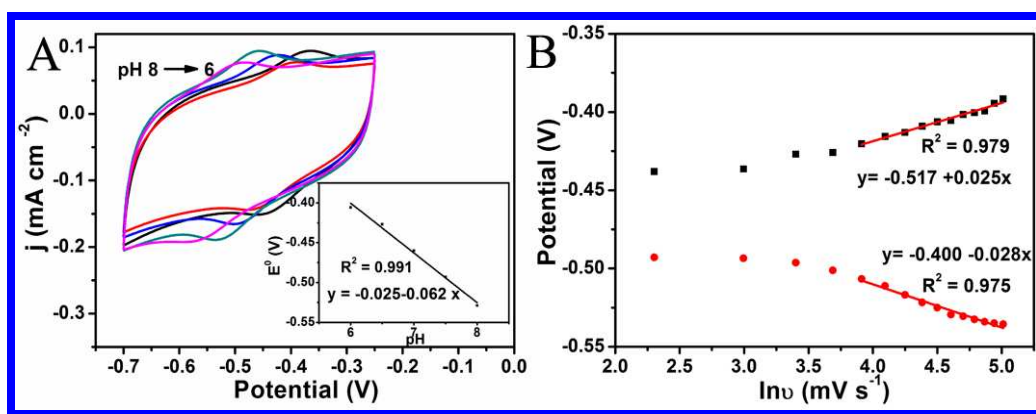
The stability of the Ni-CoNPs/GTE was also tested (Figure S7), after the Ni-CoNPs/GTE was stored in the inverted beaker at room temperature for 45 days, the current response to 1 mM glucose was decreased 1.68%, suggesting the good stability of the electrode.



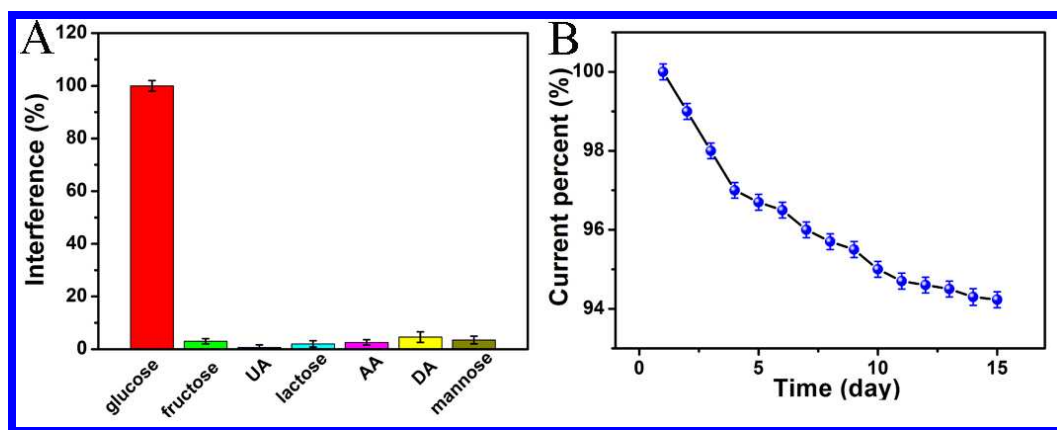
**Figure S8.** (A) CVs of GOD/GTE at different scan rates by step of  $10 \text{ mV s}^{-1}$  in  $0.1 \text{ M N}_2$ -saturated PBS. (B) CVs of GOD/GTE in  $0.1 \text{ M O}_2$ -saturated PBS (pH=7.0) in the presence of glucose with various concentrations.



**Figure S9.** CVs responses of GTE (A) and AuNPs-CHIT/GTE (B) under different oxygen partial pressures. The constant potential electrodeposition of AuNPs-CHIT/GTE was carried out with a three-electrode system by using a saturated calomel electrode (SCE) as the reference electrode, a platinum electrode as the counter electrode and the flexible GTE as the working electrode.



**Figure S10.** (A) CVs of GOD /AuNPs-CHIT/GTE in 0.1 M N<sub>2</sub>-saturated PBS at different pH at a scan rate of 50 mV s<sup>-1</sup> and (inset) plots of E<sup>0</sup> versus pH. (B) Plots of peak potential versus the natural logarithm of scan rate (lnv).



**Figure S11.** (A) The effects of some electroactive substance on glucose detection and (B) stability test of GOD/AuNPs-CHIT/GTE. Uric acid (UA), ascorbic acid (AA), dopamine (DA), fructose, galactose, sucrose and mannose were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China).

**Table S1.** Electrical conductivity of GTE and GCE.

	<b>GTE</b>	<b>GCE</b>
<b>Electrical conductivity</b>		
<b>(S cm<sup>-1</sup>)</b>	<b>47.62</b>	<b>188.7</b>



**Table S2.** The comparison of performance of various Ni-CoNPs-based glucose sensors.

Modified electrode	Detection limit	Linear range	Sensitivity	References
	$\mu\text{M}$	mM	$\mu\text{A cm}^{-2} \text{mM}^{-1}$	
3D-NF <sup>a</sup> -G-NiO	10	0.01-0.2	3230	3
Cu <sub>2</sub> O NCs <sup>b</sup> /Co <sub>3</sub> O <sub>4</sub> NHs <sup>c</sup>	0.63	0.001-5.330	280	4
Ni-Co nanosheets/RGO	3.79	0.01–2.65	1773.61	2
Porous Co nanobeads/RGO	47.5	0.15–6.25	39	5
Co <sub>3</sub> O <sub>4</sub> NFs-Nafion/GCE	0.97	up to 2.04	36.25	6
RGO-Ni(OH) <sub>2</sub>	0.6	0.002-3.1	11.43	7
NiO@Ag NWs <sup>d</sup> /GCE	1.01	0-1.28	67.51	8
CAT <sup>e</sup> -NiO	0.6	0.001-1	159	9
Ni-CoNPs/GTE	0.16	1.360-5.464	147	This work
		0.0006 - 0.26	0.4	

<sup>a</sup>Three-dimensional nickel foams; <sup>b</sup>Copper (I) oxide nanocubes; <sup>c</sup>Cobalt oxide nanohexagons; <sup>d</sup>NiO nanowires; <sup>e</sup>Catalase film

**Table S3.** Determination of glucose by using the Ni-CoNPs/GTE in blood serum sample.

Samples	Diluted samples (mM)	Added (mM)	Founded (mM)	Recovery (%)	RSD (%,n=5)
1		1.00	2.73	101.49	4.21
2	1.69	2.00	3.72	100.81	3.94
3		3.00	4.67	99.57	3.32

**Table S4.** A comparison of the performance of various GOD-based glucose sensors.

Glucose sensors	Detection limit mM	Linear range mM	Sensitivity $\mu\text{A cm}^{-2} \text{mM}^{-1}$	Ref.
GOD/PVA <sup>a</sup> -Au-pphTEOS <sup>b</sup>	0.7	1.0–8.0	$4.905 \times 10^{-5}$ Amps $\text{cm}^{-2} \text{mM}^{-1}$	10
GOD/ERGO <sup>c</sup> -MWCNTs <sup>d</sup>	4.7	0.01–6.5	7.95	11
GOD@TiO <sub>2</sub> /FePc <sup>e</sup> -CNTs	0.03	0.05–4.0	$7.11 \mu\text{A mM}^{-1} \text{cm}^{-2}$	12
GOD/p-MAA <sup>f</sup>	0.01	0.009–8.26	$11.98 \text{ mA M}^{-1} \text{cm}^{-2}$	13
GOD/GR–CdS/GCE	0.7	2–16	0.2027	14
GOD/MGF <sup>h</sup> /GCE	0.25	1–12	0.124	15
GOD/Ag–RGO/GCE	0.16	0.5–12.5	0.27	16
GOD/Au–RGO/GCE	0.01	1–8	0.835	17
GTE/AuNPs-CHIT/GOD	0.202	0.616 - 14	9	This work

<sup>a</sup>Polyvinyl alcohol; <sup>b</sup>Partially prehydrolyzed tetraethyl orthosilicate; <sup>c</sup>Electrochemically reduced graphene oxide; <sup>d</sup>Multi-walled carbon nanotubes; <sup>e</sup>Iron phthalocyanine; <sup>f</sup>Poly-methacrylic acid; <sup>h</sup>Mesocellular graphene foam.

**Table S5.** Determination of glucose by using the GOD/AuNPs-CHIT/GTE in blood serum sample.

sample (mM)	Diluted samples (mM)	Added (mM)	Founded (mM)	Recovery (%)	RSD (%,n=5)
1		1.00	7.48	100.40	3.79
2	6.45	2.00	8.43	99.76	4.25
3		3.00	9.56	101.16	3.96

## REFERENCE

1. Rashid, M. H.; Raula, M.; Mandal, T. K. Polymer Assisted Synthesis of Chain-Like Cobalt-Nickel Alloy Nanostructures: Magnetically Recoverable and Reusable Catalysts With High Activities. *J. Mater. Chem.* **2011**, *21* (13), 4904-4917.
2. Wang, L.; Lu, X. P.; Ye, Y. J.; Sun, L. L.; Song, Y. H. Nickel-Cobalt Nanostructures Coated Reduced Graphene Oxide Nanocomposite Electrode for Nonenzymatic Glucose Biosensing. *Electrochim. Acta* **2013**, *114*, 484-493.
3. Zhao, B.; Wang, T.; Jiang, L.; Zhang, K.; Yuen, M. M. F.; Xu, J. B.; Fu, X. Z.; Sun, R.; Wong, C. P. NiO Mesoporous Nanowalls Grown on RGO Coated Nickel Foam as High Performance Electrodes for Supercapacitors and Biosensors. *Electrochim. Acta* **2016**, *192*, 205-215.
4. Velmurgan, S.; Devasenathipathy, R.; Chen, S. M.; Wang, S. F. A Facile Chemical Synthesis of Cu<sub>2</sub>O Nanocubes Covered with Co<sub>3</sub>O<sub>4</sub> Nanohexagons for the Sensitive Detection of Glucose. *Electroanalysis* **2016**, *28*, 1547-1552.
5. Song, Y. H.; Wei, C. T.; He, J.; Li, X.; Lu, X. P.; Wang, L. Porous Co Nanobeads/RGO Nanocomposites Derived from RGO/Co-Metal Organic Frameworks for Glucose Sensing. *Sens. Actuators, B* **2015**, *220*, 1056-1063.
6. Ding, Y.; Wang, Y.; Su, L. A.; Bellagamba, M.; Zhang, H.; Lei, Y. Electrospun Co<sub>3</sub>O<sub>4</sub> Nanofibers for Sensitive and Selective Glucose Detection. *Biosens. Bioelectron.* **2010**, *26* (2), 542-548.
7. Zhang, Y.; Xu, F. G.; Sun, Y. J.; Shi, Y.; Wen, Z. W.; Li, Z. Assembly of Ni(OH)<sub>2</sub> Nanoplates on Reduced Graphene Oxide: A Two Dimensional Nanocomposite for Enzyme-Free Glucose on Sensing. *J. Mater. Chem.* **2011**, *21* (42), 16949-16954.
8. Song, J.; Xu, L.; Xing, R. Q.; Qin, W. F.; Dai, Q. L.; Song, H. W. Ag Nanoparticles Coated NiO

Nanowires Hierarchical Nanocomposites Electrode for Nonenzymatic Glucose Biosensing. *Sens. Actuators, B* **2013**, *182*, 675-681.

9. Salimi, A.; Sharifi, E.; Noorbakhsh, A.; Soltanian, S. Direct Electrochemistry and Electrocatalytic Activity of Catalase Immobilized onto Electrodeposited Nano-Scale Islands of Nickel Oxide. *Biophys. Chem.* **2007**, *125* (2-3), 540-548.

10. Lad, U.; Kale, G. M.; Bryaskova, R. Glucose Oxidase Encapsulated Polyvinyl Alcohol-Silica Hybrid Films for an Electrochemical Glucose Sensing Electrode. *Anal. Chem.* **2013**, *85* (13), 6349-6355.

11. Mani, V.; Devadas, B.; Chen, S. M. Direct Electrochemistry of Glucose Oxidase at Electrochemically Reduced Graphene Oxide-Multiwalled Carbon Nanotubes Hybrid Material Modified Electrode for Glucose Biosensor. *Biosens. Bioelectron.* **2013**, *41*, 309-315.

12. Cui, H.-F.; Zhang, K.; Zhang, Y. F.; Sun, Y. L.; Wang, J.; Zhang, W.-D.; Luong, J. H. Immobilization of Glucose Oxidase into a Nanoporous TiO<sub>2</sub> Film Layered on Metallophthalocyanine Modified Vertically-Aligned Carbon Nanotubes for Efficient Direct Electron Transfer. *Biosens. Bioelectron.* **2013**, *46*, 113-118.

13. Pérez, J. H.; López-Ruiz, B.; López-Cabarcos, E. Synthesis and Characterization of Microparticles Based on Poly-Methacrylic Acid with Glucose Oxidase for Biosensor Applications. *Talanta* **2016**, *149*, 310-318.

14. Zhai, Y. L.; Zhai, S. Y.; Chen, G. F.; Zhang, K.; Yue, Q. L.; Wang, L.; Liu, J. F.; Jia, J. B. Effects of Morphology of Nanostructured ZnO on Direct Electrochemistry and Biosensing Properties of Glucose Oxidase. *J. Electroanal. Chem.* **2011**, *656* (1-2), 198-205.

15. Wang, K.; Liu, Q.; Guan, Q. M.; Wu, J.; Li, H. N.; Yan, J. J. Enhanced Direct Electrochemistry of Glucose Oxidase and Biosensing for Glucose via Synergy Effect of Graphene and CdS

Nanocrystals. *Biosens. Bioelectron.* **2011**, 26 (5), 2252-2257.

16. Palanisamy, S.; Karuppiah, C.; Chen, S. M. Direct Electrochemistry and Electrocatalysis of Glucose Oxidase Immobilized on Reduced Graphene Oxide and Silver Nanoparticles Nanocomposite Modified Electrode. *Colloids Surf. B* **2014**, 114, 164-169.

17. Tabrizi, M. A.; Varkani, J. N. Green Synthesis of Reduced Graphene Oxide Decorated with Gold Nanoparticles and Its Glucose Sensing Application. *Sens. Actuators B* **2014**, 202, 475-482.