Supporting Information

Reduced graphene oxide-supported $NiCo_2O_4$ nanoparticles: An electrocatalyst for methanol oxidation

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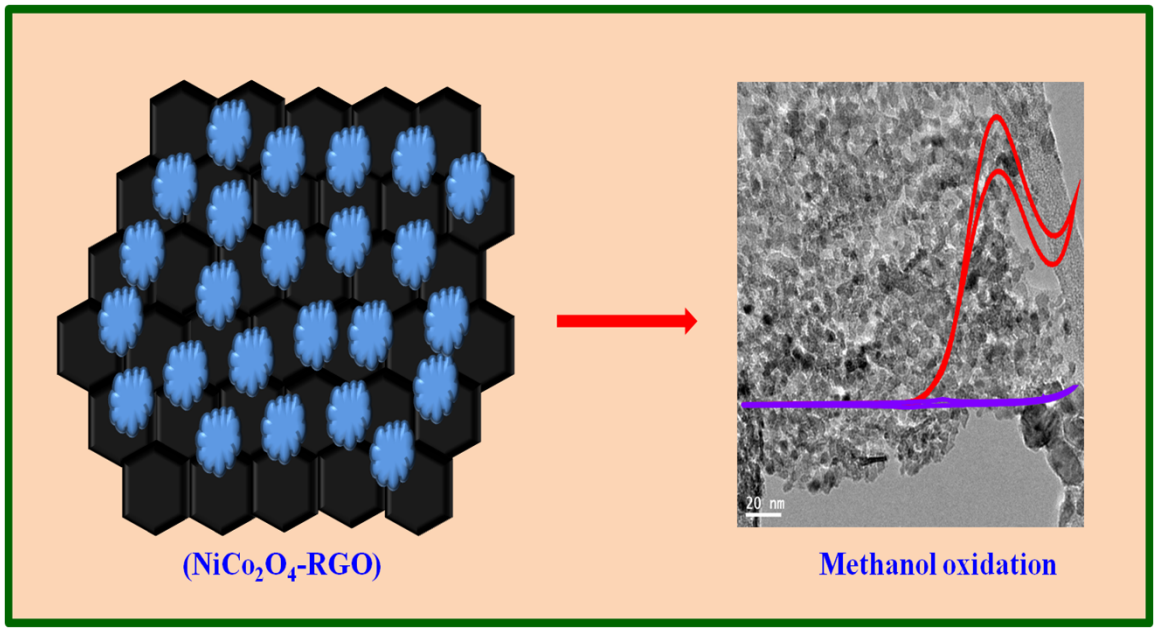


Experimental

1. Preparation of graphene oxide (GO)

Graphene oxide (GO) was synthesized by using a modified Hummers method.[1] Briefly, 2 g of natural graphite flakes were put in a round bottom flask containing 46 mL of concentrated H_2SO_4. This round-bottomed flask was transferred to an ice bath with a temperature of approximately 0-5 ºC, 6 g of solid $KMnO_4$ was then added slowly, and the mixture was stirred for 2 h. The round-bottomed flask was then transferred to an oil bath that had been pre-heated to 35 ºC and was stirred overnight. After that, 90 mL of de-ionized (DI) water was added to it, followed by stirring for another 2 h. Then, a 35% H_2O_2 was added slowly to achieve a bright yellow reaction mixture. The excess manganese salt that was present in the GO was removed using dilute hydrochloric acid (5% by volume). The GO was washed several times and dispersed in water for one month. After one month, the brown precipitate was collected and dried in a vacuum oven.

2. Preparation of the working electrodes

A glassy carbon (GC) electrode was polished with slurry of alumina powder and was subjected to ultrasonication for 5 min in deionized water. This electrode was washed carefully with water and dried in air before modification with the $NiCo_2O_4$-RGO hybrid. Typically, 10 mg of the $NiCo_2O_4$-RGO composite was dispersed ultrasonically in an ethanolic solution of 20% Nafion, and 20 μL was taken out of this dispersion and drop-casted on the electrode surface. The $NiCo_2O_4$-RGO hybrid modified electrode was dried at room temperature and was used in further electrochemical investigations. Similar method was followed for the preparation of the electrode based on $NiCo_2O_4$ and RGO using the same mass as in the case of $NiCo_2O_4$-RGO composite.

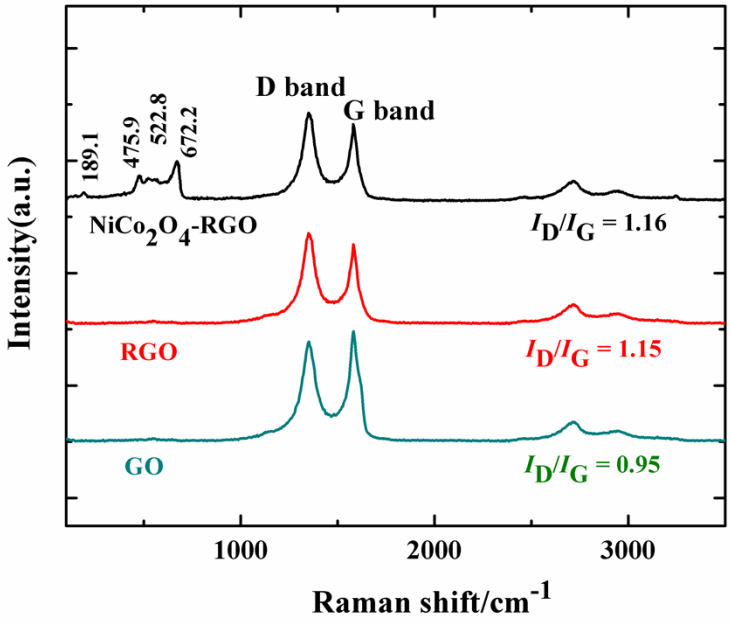
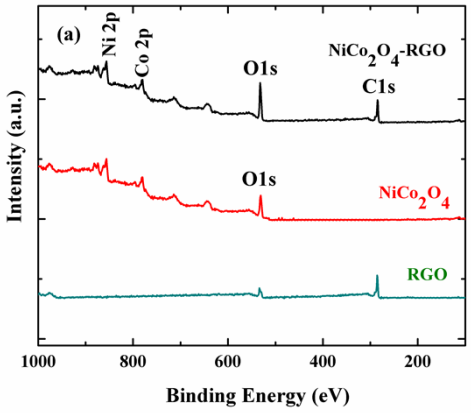
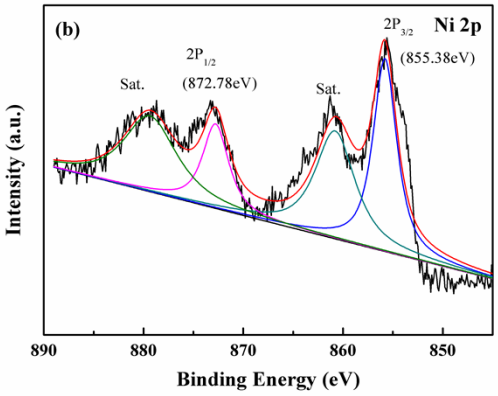
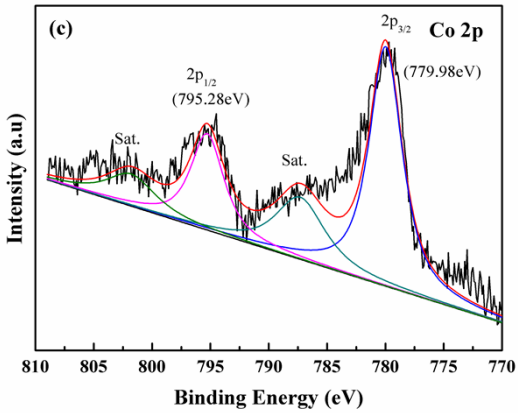


Fig. S1. Raman spectra obtained for GO, RGO and $NiCo_2O_4$-RGO hybrid.


(a)
Ni 2p
Co 2p
O1s
C1s
NiCo2O4-RGO
O1s
NiCo2O4
RGO
Intensity (a.u.)
1000
800
600
400
200
Binding Energy (eV)


(b)
2P3/2 Ni 2p
(855.38eV)
2P1/2
(872.78eV)
Sat.
Sat.
Intensity (a.u.)
890
880
870
860
850
Binding Energy (eV)


(c)
2p3/2 Co 2p
(779.98eV)
2p1/2
(795.28eV)
Sat.
Sat.
Intensity (a.u)
810
805
800
795
790
785
780
775
770
Binding Energy (eV)

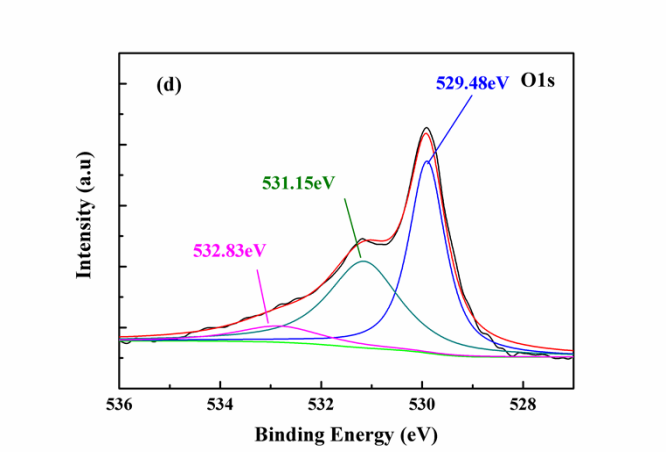


Fig. S2. XPS survey spectra of RGO, $NiCo_2O_4$ and $NiCo_2O_4$-RGO hybrid (a), and deconvoluted Ni 2p (b), Co 2p (c) and O 1s (d) XPS spectra of $NiCo_2O_4$-RGO hybrid

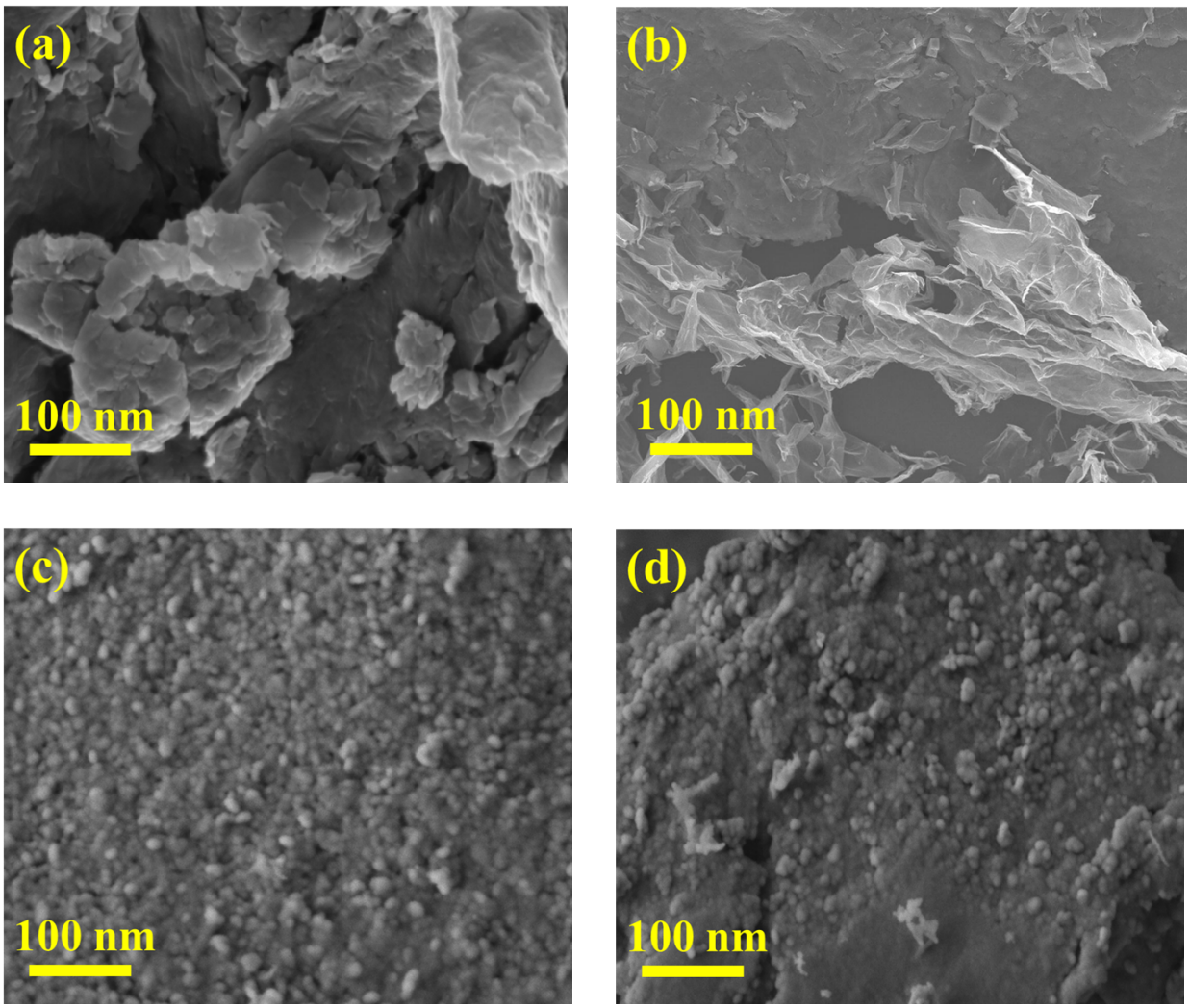


Fig. S3. FE-SEM images of (a) GO, (b) RGO, (c) $NiCo_2O_4$ and (d) $NiCo_2O_4$-RGO hybrid.

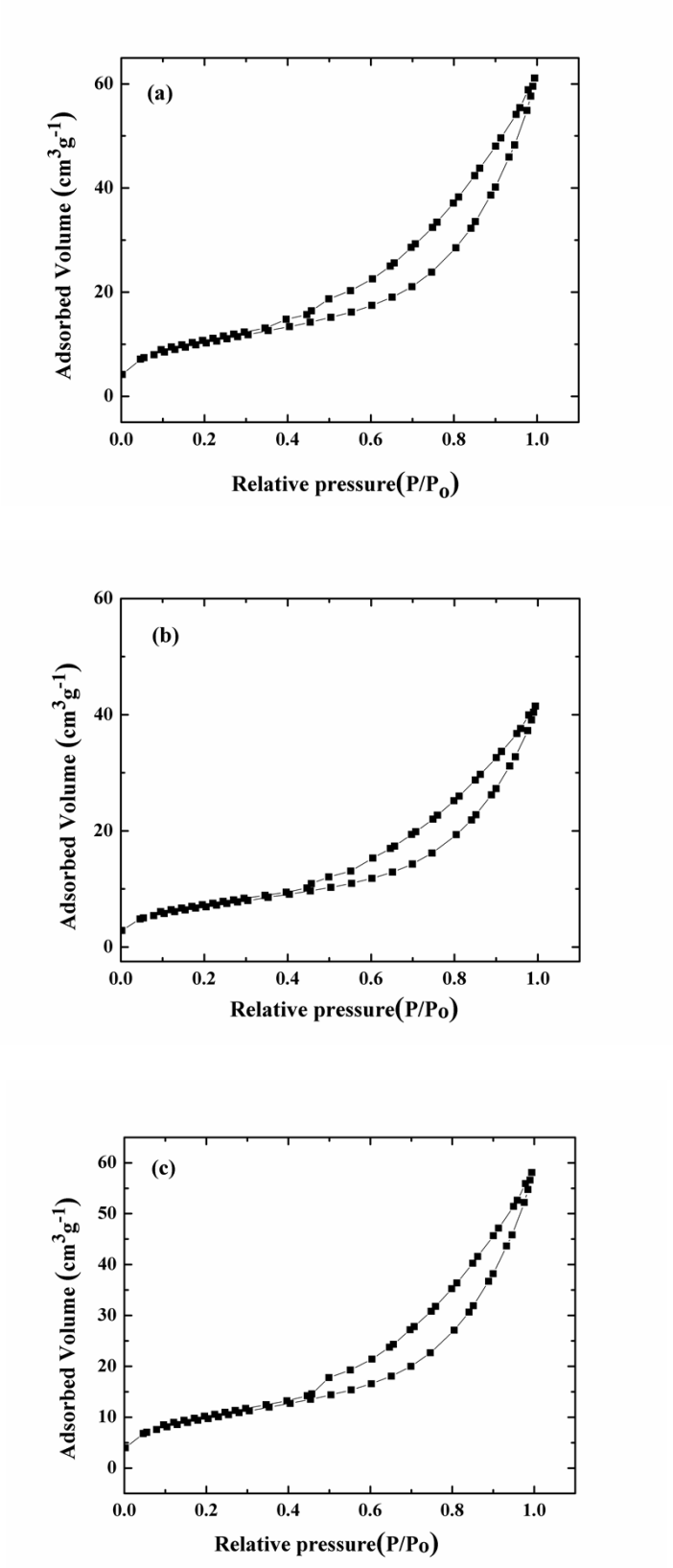


Fig. S4. BET surface area of (a) RGO, (b) $NiCo_2O_4$ and (c) $NiCo_2O_4$-RGO hybrid

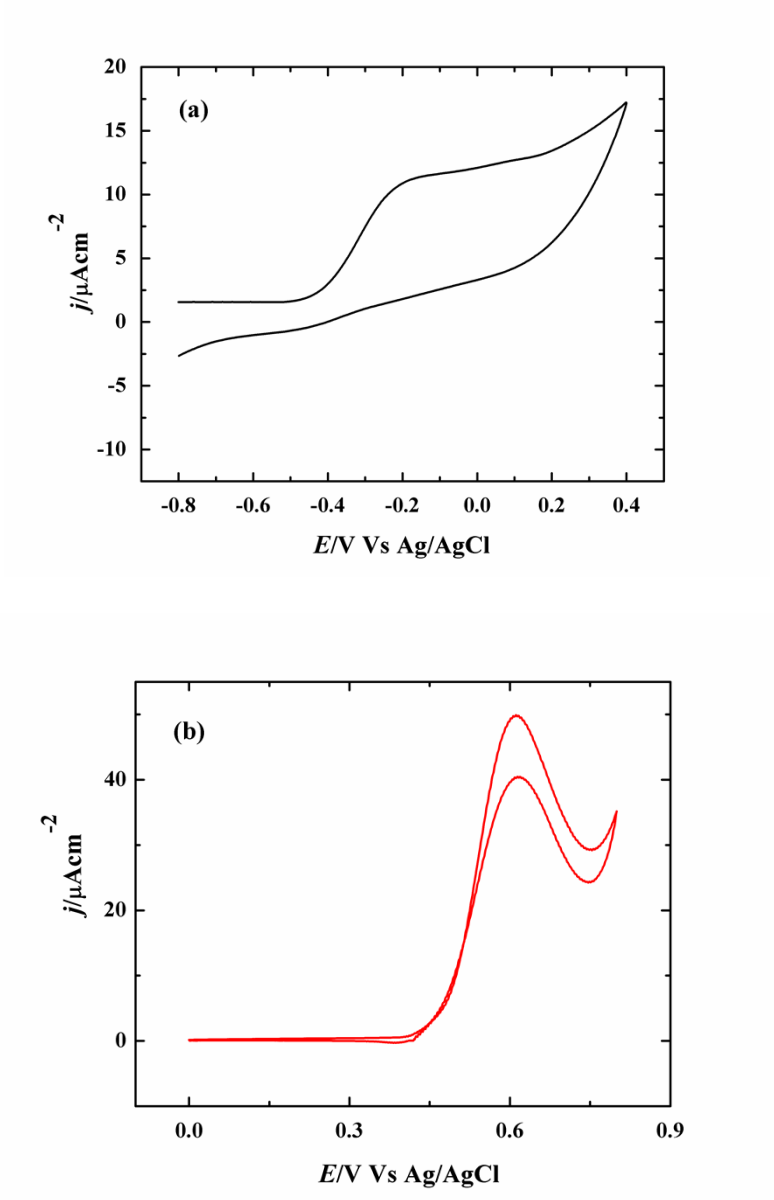


Fig. S5. Cyclic voltammetric response of the electrodes modified with (a) Pt/C and (b) $NiCo_2O_4$-RGO in 0.1 M KOH containing 0.5M methanol. Scan rate: 50 mV/s.

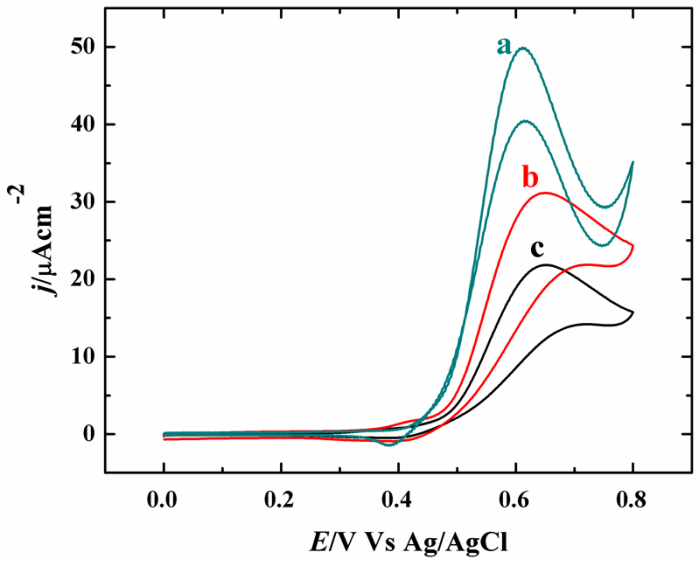
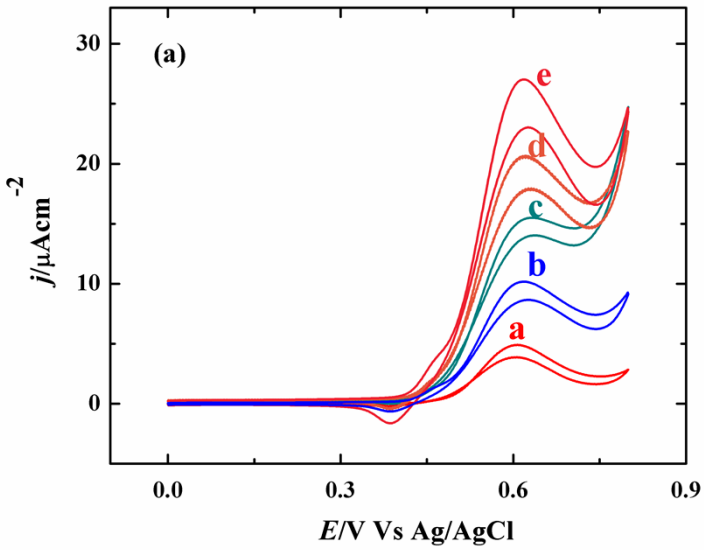


Fig. S6. Cyclic voltammetric response of the electrodes modified with $NiCo_2O_4$-RGO hybrid of (a) 2:1, (b) 1:1 and (c) 0.5:1 molar ratio in 0.1 M KOH containing 0.5M methanol at scan rate: 50 mV/s.



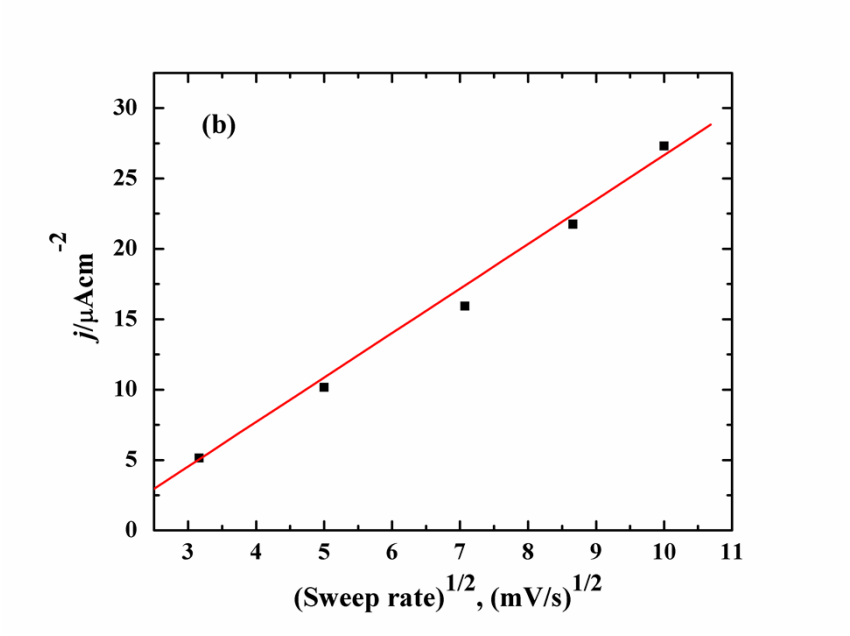


Fig. S7. (a) Cyclic voltammetric response of $NiCo_2O_4$-RGO hybrid based electrode in 0.1 M KOH containing 0.5 M methanol at different scan rates; a:10, b: 25, c: 50, d: 75 and e: 100 mV/ s, and (b) the plot of catalytic current Vs square root of scan rate.

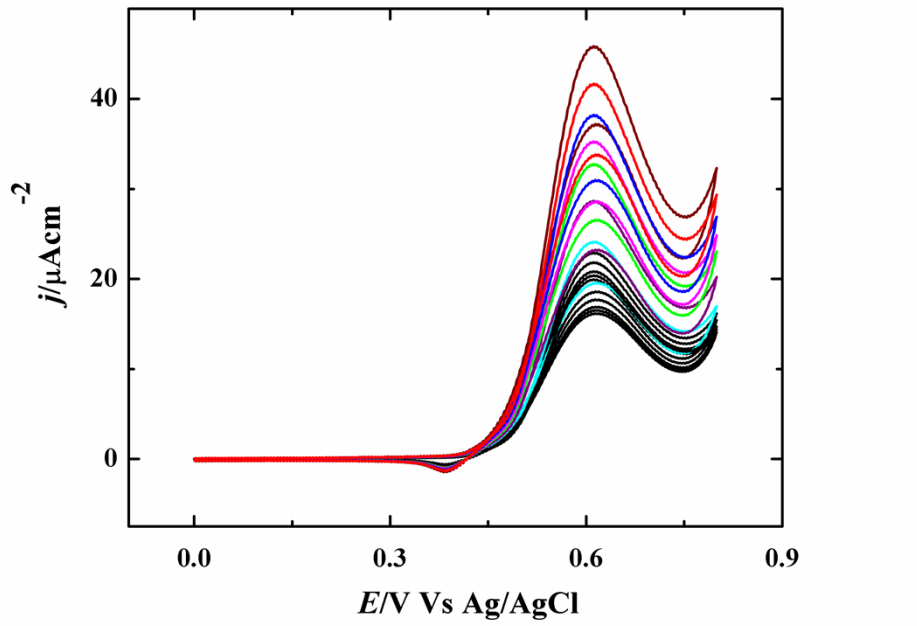


Fig. S8. Cyclic voltammetric response of $NiCo_2O_4$-RGO hybrid in 0.1 M KOH containing different concentrations of methanol at scan rate: 50 mV/s.

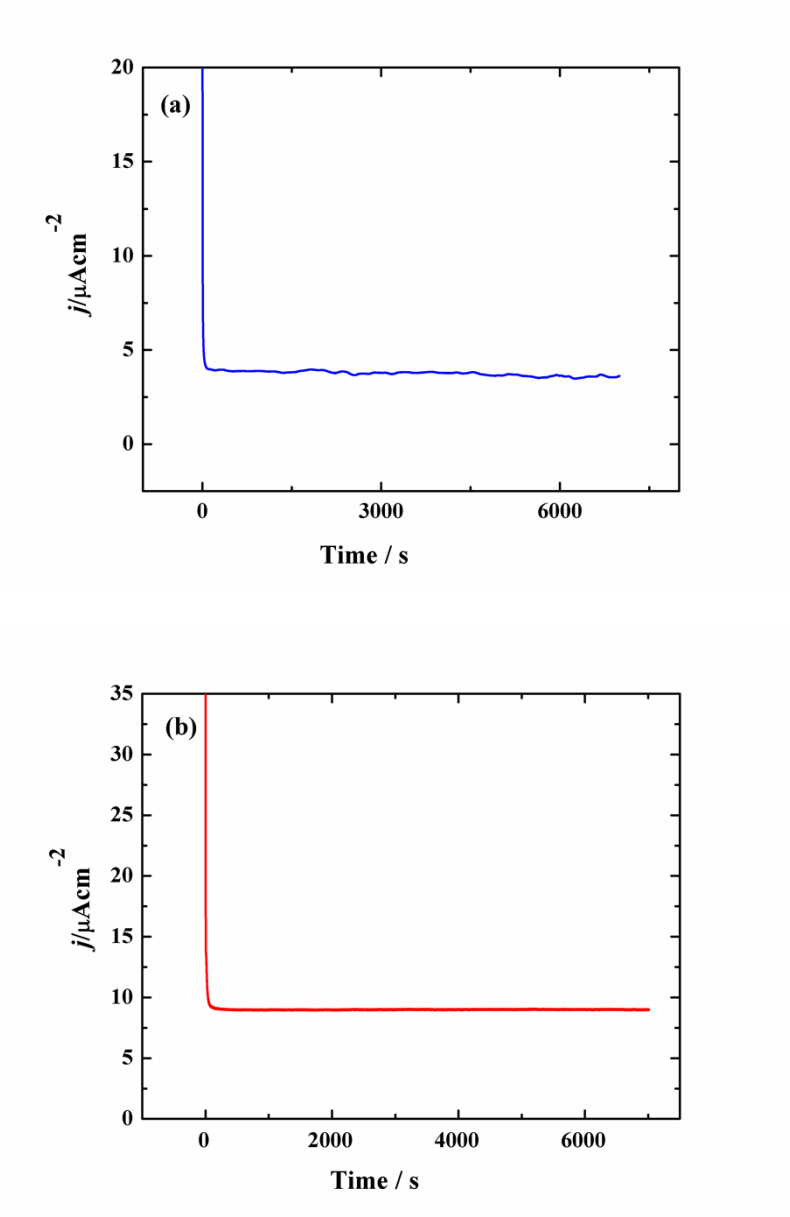


Fig. S9. Chronoamperometry curves obtained on (a) Pt/C and (b) $NiCo_2O_4$-RGO-based electrode in 0.1 M KOH containing 0.1M methanol.

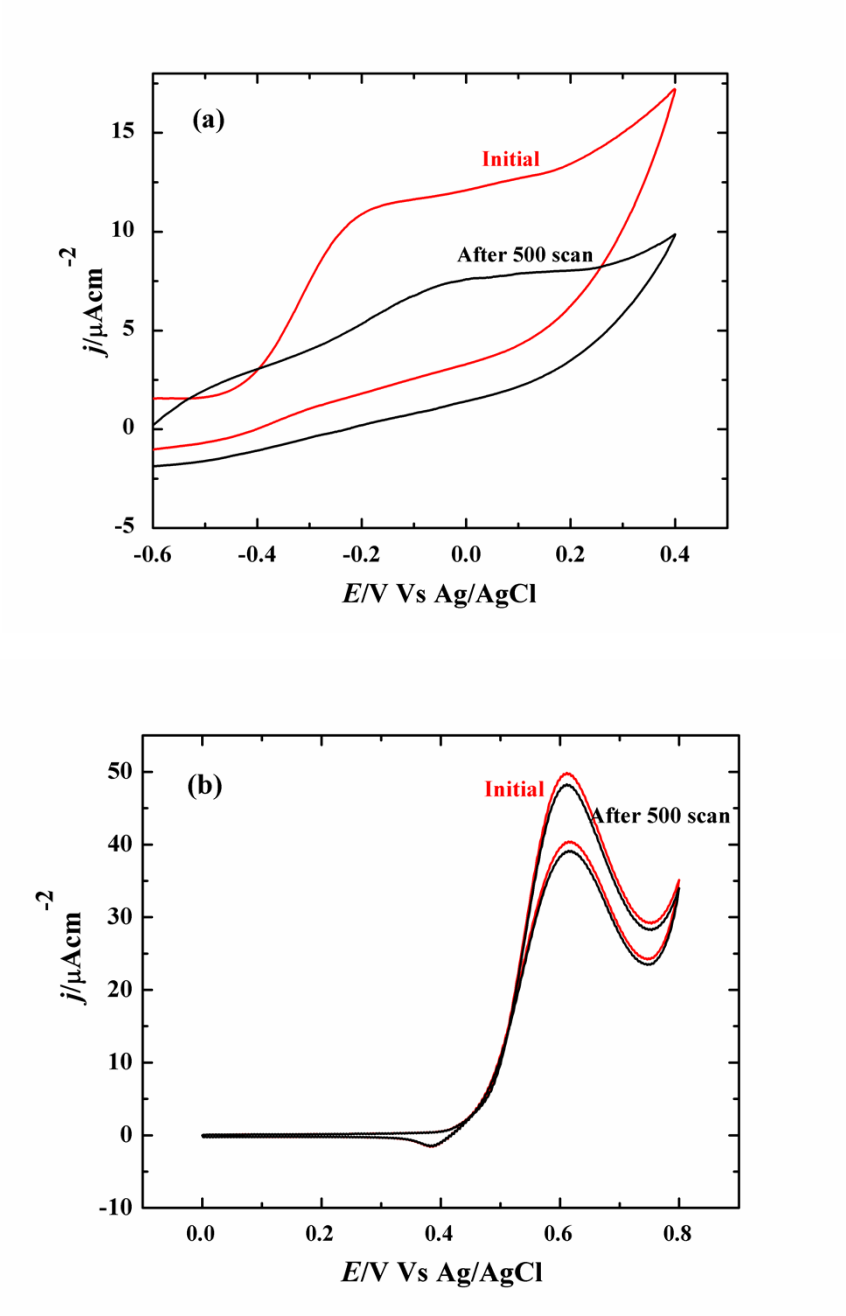


Fig. S10. Cyclic voltammetric response of (a) Pt/C and $NiCo_2O_4$-RGO-based electrode in 0.1 M KOH containing 0.5 M methanol at initial and after 500 scans. Scan rate: 50 mV/s.

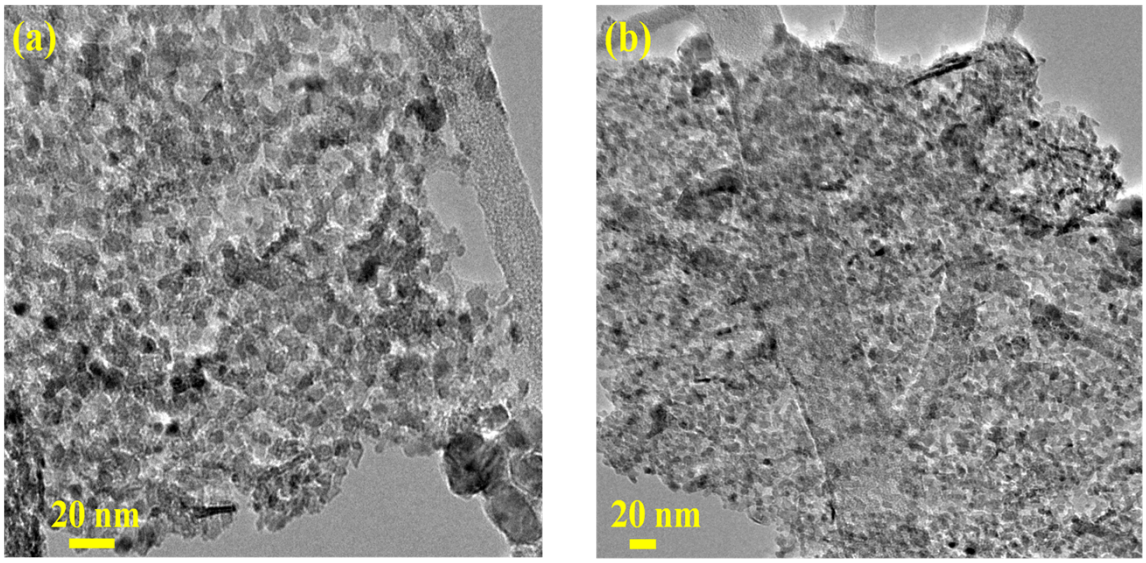


Fig. S11. TEM image of $NiCo_2O_4$-RGO hybrid (a) before and (b) after 500 cycles

Table S1 Comparison of the oxidation peak potentials reported for electrochemical oxidation of methanol on the different electrodes.

Samples	Oxidation potential (V)	References
$NiCo_2O_4$-RGO	0.6	Present work
Mesoporous nickel phosphate	0.65	2
Si- nickel phosphates	0.65	3
Nickel oxide	0.75	4
Ni–Co alloy	0.62	5
Ni-Salophen	0.65	6
Ni/NiODMG	0.65	7
$NiCo_2O_4$	0.65	8

References

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