Supporting Information

Facile Electrochemical Co-Deposition of a Graphene/Cobalt Nanocomposite for Highly Efficient Water Oxidation in Alkaline Media: Direct Detection of Underlying Electron Transfer Reactions Under Catalytic Turnover Conditions

Si-Xuan Guo,[a] Yuping Liu,[a] Alan M. Bond*[a] and Jie Zhang*[a]

Esakki Karthik,[b] Ilango Maheswaran,[b] Senthil Kumar[b] and Kanala L.N. Phani*[b]

[a] School of Chemistry, Monash University, Clayton, Vic 3800, Australia
E-mails: alan.bond@monash.edu, jie.zhang@monash.edu

[b] Nanoscale Electrocatalysis & Sensor Research Group, Electrodics and Electrocatalysis Division, CSIR-Central Electrochemical Research Institute, Karaikudi, Tamilnadu, India
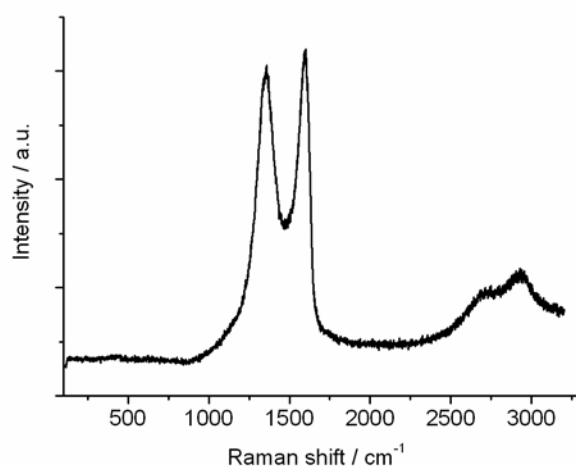E-mail: klnphani@cecri.res.in

Fig. S1 Raman spectrum derived from thick graphene layers present on a graphene/cobalt nanocomposite modified FTO electrode after deposition at -1.4 V for 1000 s.
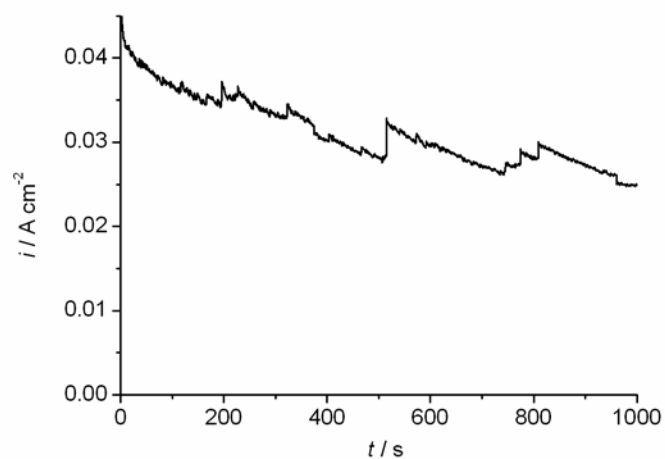

Fig. S2 Plot of catalytic current versus time during controlled potential electrolysis of a cobalt modified electrode in 1 M NaOH. Applied potential: + 0.8 V vs. Ag/AgCl. Cobalt deposition at -1.4 V for 1000 s in an aqueous solution containing 0.8 mM $Co(NO_3)_2$ and 0.1 M $NaNO_3$.
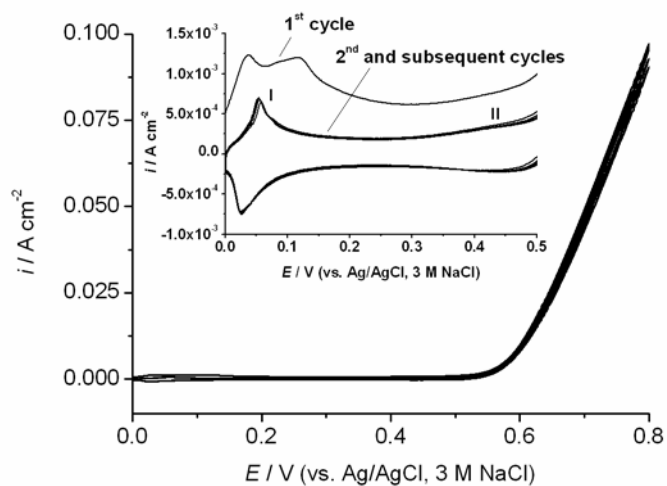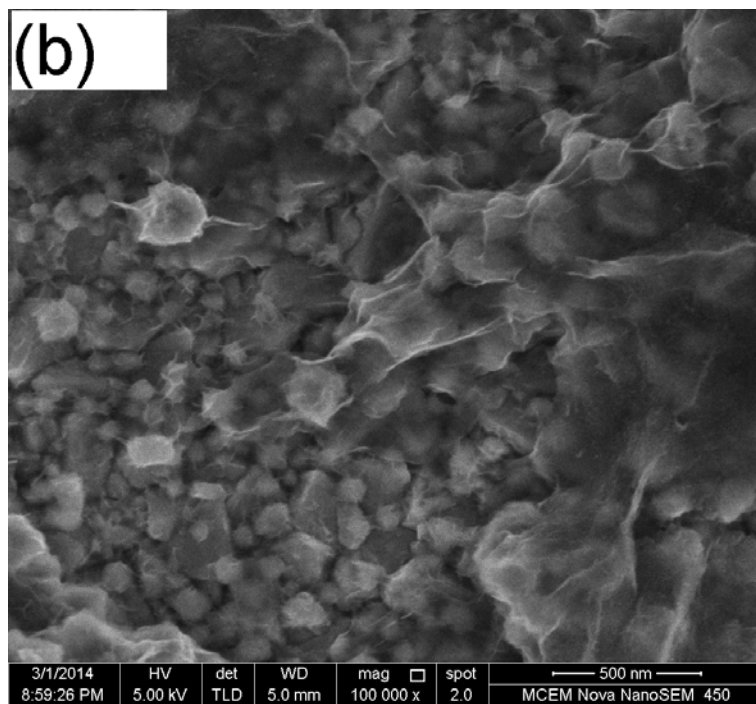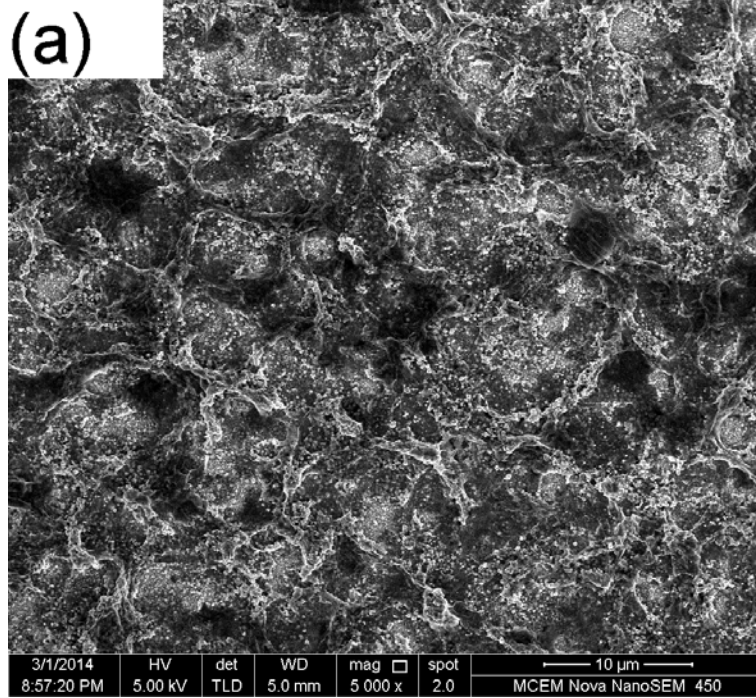
Fig. S3 Electrocatalytic water oxidation in aqueous 1 M NaOH electrolyte at a scan rate of 50 mV s^{-1} using a cobalt modified electrode, under conditions described in the main text. Inset shows the cobalt processes in the potential range of 0 – +0.5 V. Deposition of cobalt at -1.4 V for 1000 s in an aqueous 0.05 M phytic acid solution (pH 7) containing 0.8 mM Co(NO$_3$)$_2$.

(a)

3/1/2014	HV	det	WD	mag □	spot	10 μm
8:57:20 PM	5.00 kV	TLD	5.0 mm	5 000 x	2.0	MCEM Nova NanoSEM 450

(b)

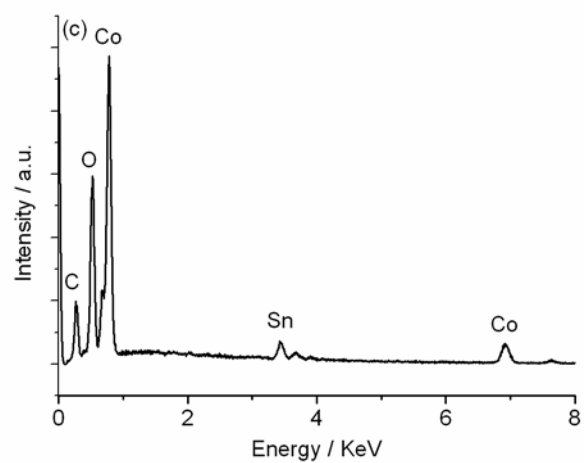| 3/1/2014	HV	det	WD	mag □	spot	500 nm
8:59:26 PM	5.00 kV	TLD	5.0 mm	100 000 x	2.0	MCEM Nova NanoSEM 450

Fig. S4 SEM images (a, b) and EDX spectrum (c) obtained at a cobalt – graphene modified FTO electrode. Cobalt – graphene deposition at -1.4 V for 1000 s in an aqueous 0.05 M phosphate buffer solution (pH 7) containing 1 mg ml^{-1} graphene oxide and 0.8 mM Co(NO$_3$)$_2$.
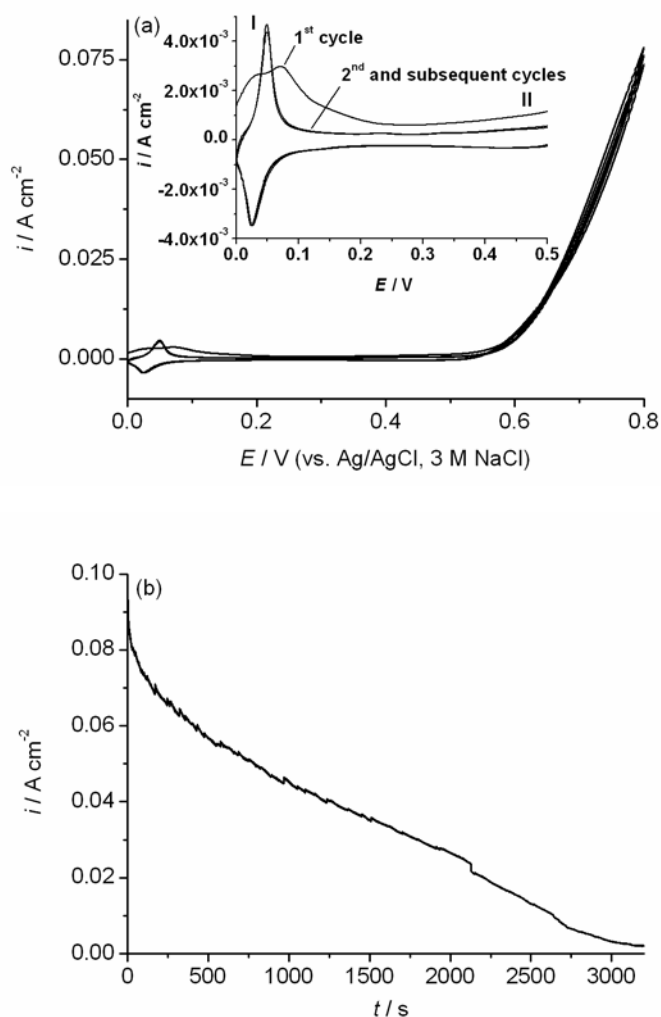
Fig. S5 (a) Cyclic voltammogram of electrocatalytic water oxidation by a cobalt – graphene modified GC electrode in aqueous 1 M NaOH electrolyte at a scan rate of 50 mV s^{-1}. Inset shows the cobalt processes in the potential range of 0 – +0.5 V. (b) Plot of catalytic current versus time during controlled potential electrolysis at the cobalt – graphene modified GC electrode in 1 M NaOH at a potential of +0.8 V. Cobalt – graphene deposition at -1.4 V for 1000 s in an aqueous 0.05 M phosphate buffer solution (pH 7) containing 1 mg ml^{-1} graphene oxide and 0.8 mM $Co(NO_3)_2$.
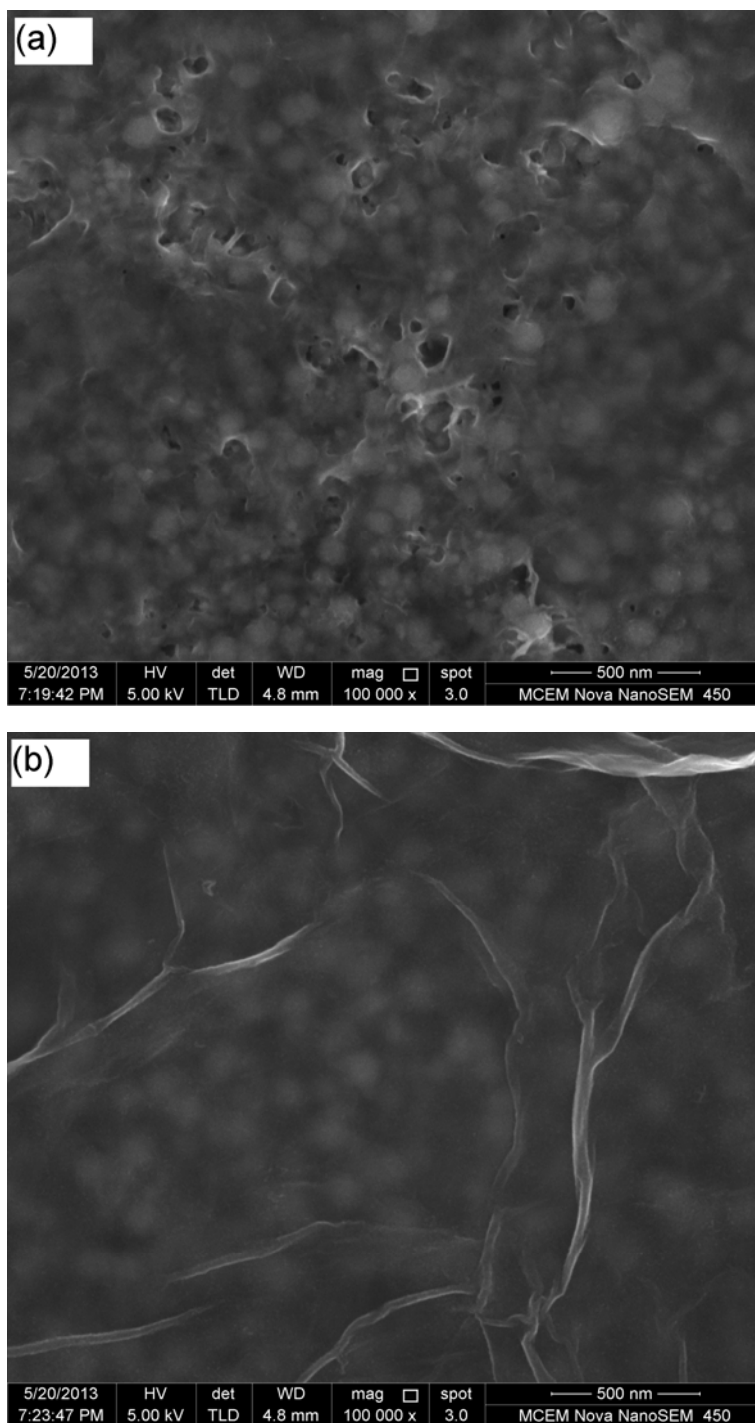
Fig. S6 SEM images of thin graphene layers showing holes (a) and intact thick layers (b) derived from a graphene/cobalt nanocomposite modified FTO electrode after controlled potential electrolysis at +0.8 V vs. Ag/AgCl for 1000 s in 1 M NaOH. Deposition of nanocomposite at -1.4 V for 1000 s.
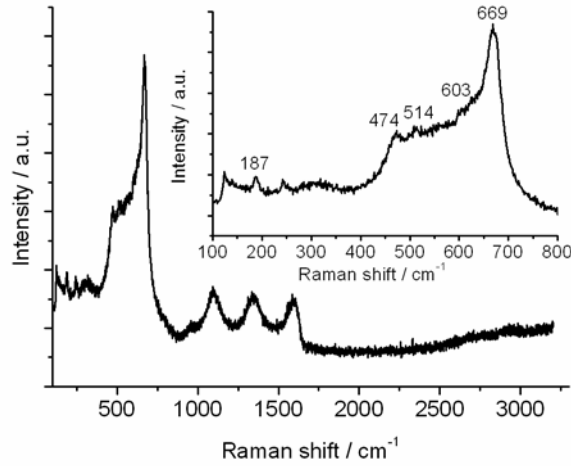
Fig. S7 Raman spectra obtained from a graphene/cobalt nanocomposite modified FTO electrode after controlled potential electrolysis in 1 M NaOH at +0.8 V for 1000s. Deposition of nanocomposite at -1.4 V for 1000 s.

Estimation of the change of OH⁻ concentration during water electrolysis under stationary conditions.

Assuming the faradaic efficiency of electrolysis is 100%, the amount of OH⁻ consumed (N) during electrolysis ($4\ OH^- \rightarrow O_2 + 2\ H_2O + 4\ e^-$) can be calculated from Faraday's law,

$$Q = \int_0^t Idt = nNF \tag{1}$$

where n is the number of electron transferred per OH⁻ which is one, I is the time dependent electrolysis current, t is the electrolysis time and F is Faraday's constant. In our case, I is almost constant during electrolysis (Fig. 7), therefore eq 1 can be simplified to,

$$N = \frac{It}{F} \tag{2}$$

To calculate how the consumption of OH⁻ affects the OH⁻ concentration in the solution adjacent to the electrode surface under stationary condition, the volume of the solution (V), where the concentration of OH⁻ is affected, is estimated based on the diffusion layer thickness ($L = \sqrt{\pi Dt}$) and electrode area (A),

$$V = LA = A\sqrt{\pi Dt} \tag{3}$$

where D is the diffusion coefficient of OH⁻.

The change of the average molar concentration of OH⁻ ($\Delta[OH^-]$) in the diffusion layer can then be estimated using equation 4 which is derived from eqs 2 and 3,

$$\Delta[OH^-] = \frac{1000N}{V} = \frac{1000It}{FA\sqrt{\pi Dt}} = \frac{1000i\sqrt{t}}{F\sqrt{\pi D}} \tag{4}$$

where $i = I/A$ is the current density.

Based on eq 4, the amount of OH^- consumed chronoamperometricaly in 10 s is estimated to decrease the average OH^- concentration in the diffusion layer by $\sim$ 0.36 M, using a current density of 0.14 A cm^{-2} (Fig. 4) and a diffusion coefficient of 5.3×10^{-5} cm^2 s^{-1} for the OH^- ion (E. Samson, J. Marchand and K. A. Snyder, *Mater. Struct.*, 2003, **36**, 156-165.).