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

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**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(NO₃)₂.
**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.
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 \((4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^-)\) can be calculated from Faraday’s law,

\[
Q = \int_0^t I(t) dt = nNF
\]  

(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,

\[
N = \frac{It}{F}
\]  

(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 \((L = \sqrt{\pi D t})\) and electrode area \((A)\),

\[
V = LA = A\sqrt{\pi D t}
\]  

(3)

where \(D\) is the diffusion coefficient of OH⁻.

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

\[
\Delta[\text{OH}^-] = \frac{N}{V}
\]  

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.
\[
\Delta[\text{OH}^-] = \frac{1000 N}{V} = \frac{1000It}{FA\sqrt{\pi Dt}} = \frac{1000\sqrt{t}}{F\sqrt{\pi D}}
\] (4)

where \( i = I/A \) is the current density.

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