

Supporting Information (A)

A Catalytic Nanostructured Cobalt Oxide Electrode Enables Positive Potential Operation for the Cathodic Electrogenerated Chemiluminescence of Ru(bpy)₃²⁺ with Dramatically Enhanced Intensity

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1. Experimental Details

The Co₃O₄ nanostructure covered ITO electrode was fabricated in a conventional three-electrode cell, consisting of ITO as the working electrode, a Pt foil as the counter electrode, and a Ag/AgCl as the reference electrode by controlled-potential electrolyzing 0.1 M Co(NO₃)₂ solution at -1.2 V (vs. Ag/AgCl), followed by drying and heating in air at 500 °C for 2 hours. Other Co₃O₄ nanostructure covered ITO electrodes were also fabricated by controlled-current electrolyzing in either 0.1 M Co(NO₃)₂ or 0.1 M CoCl₂ containing 0.05 M sodium citrate solution at -8 mA/cm² for 15 min, followed by drying and heating in air at 500 °C for 2 hours.

All electrochemical and ECL experiments were performed with an ECL & EC multi-functional detection system (MPI-E, Remex Electronic Instrument Lt. Co., Xi'an, China) in a three-electrode system consisting of Co₃O₄ nanostructure covered ITO as the working electrode, a Pt foil as the counter electrode, and a Ag/AgCl as the reference electrode. The photomultiplier tube (PMT) was biased at 500 V. The electrolyte was 0.1 M PBS (pH 7) with 0.3 mM Ru(bpy)₃²⁺ and 1.5 mM H₂C₂O₄. The ECL spectra were measured by using fluorescence spectroscopy (RF-5301 PC), where the working electrode of Co₃O₄ nanostructure covered ITO was biased at +0.6 V in 0.1 M PBS (pH 7) containing 0.3 mM Ru(bpy)₃²⁺ and 1.5 mM H₂C₂O₄.

A Hitachi S-4800 scanning electron microscopy (SEM) was used to investigate the morphology of the Co₃O₄ nanostructure. X-ray diffraction measurement (XRD) was carried out with a Rigaku D/max-2500 using filtered Cu K α radiation. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al K α radiation. The base pressure was about 3 \times 10⁻⁹ mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

2. Additional Data

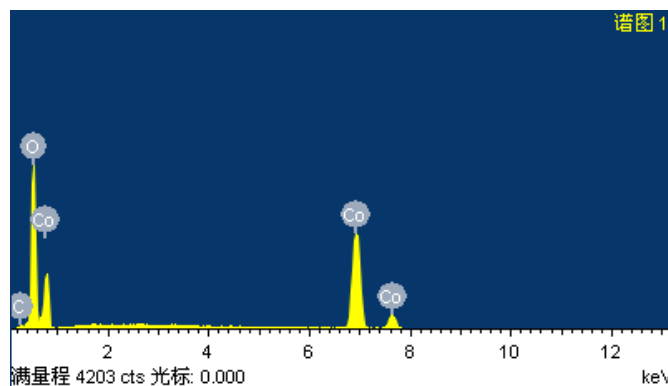


Figure S1. Representative EDX spectrum of Co_3O_4 nanostructures.

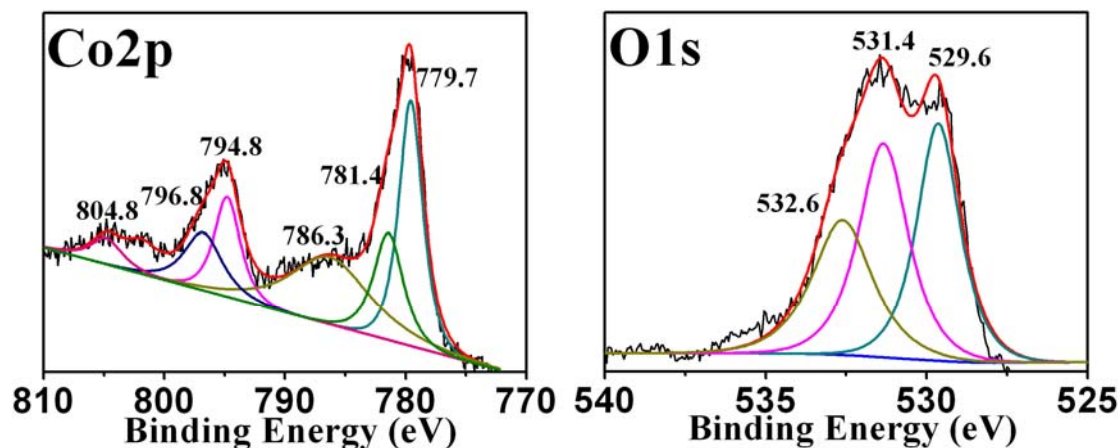


Figure S2. XPS spectra (Co 2p and O 1s) of the as prepared Co_3O_4 nanostructures. The prominent peak around 779.7 eV is attributed to a $\text{Co}^{3+} 2p_{3/2}$ configuration. The other small peak around 781.4 eV is ascribed to a $\text{Co}^{2+} 2p_{3/2}$ configuration. The other spin-orbit component, the $2p_{1/2}$, appears at 794.8 eV and 796.8 eV for $3+$ and $2+$, respectively. The two small peaks at 786.3 eV and 804.8 eV are Co^{2+} shake-up satellite peaks of Co_3O_4 . The energy difference between the peak of $\text{Co} 2p_{3/2}$ and the peak of $\text{Co} 2p_{1/2}$ is approximately 15 eV. The XPS O 1s spectra consist of at least three components. The peak at about 529.6 eV is due to oxygen in the Co_3O_4 crystal lattice, a value typical for cobalt oxide networks, while the peaks at about 531.4 eV and 532.6 eV are due to chemisorbed oxygen caused by surface hydroxyl. From XPS spectra, there is little CoO in Co_3O_4 nanostructures according to reference (Chen, H. M.; Liu, R. S.; Li, H. L.; Zeng, H. C. *Angew. Chem. Int. Ed.* 2006, 45, 2713-2717.), which is coincident with the result of XRD pattern.

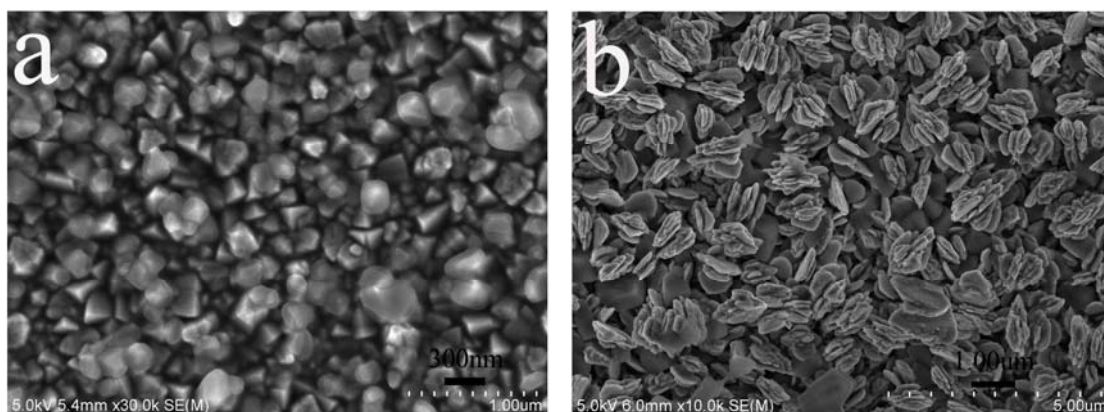


Figure S3. SEM images of Co_3O_4 nanostructures fabricated by constant-current electrolysis of 0.1 M CoCl_2 (a) and 0.1 M $\text{Co}(\text{NO}_3)_2$ (b) with 0.05 M sodium citrate mixed solution at 8 mA/cm^2 on ITO electrode for 15 min, followed by drying and heating in air at 500°C for 2 h. Then the similar cathodic ECL behavior as Figure 1b and 1c with smaller intensities could be also observed. The components of these two samples were determined to be Co_3O_4 . Therefore, it was the component (Co_3O_4) of the electrode that is responsible for the novel cathodic catalytic properties.

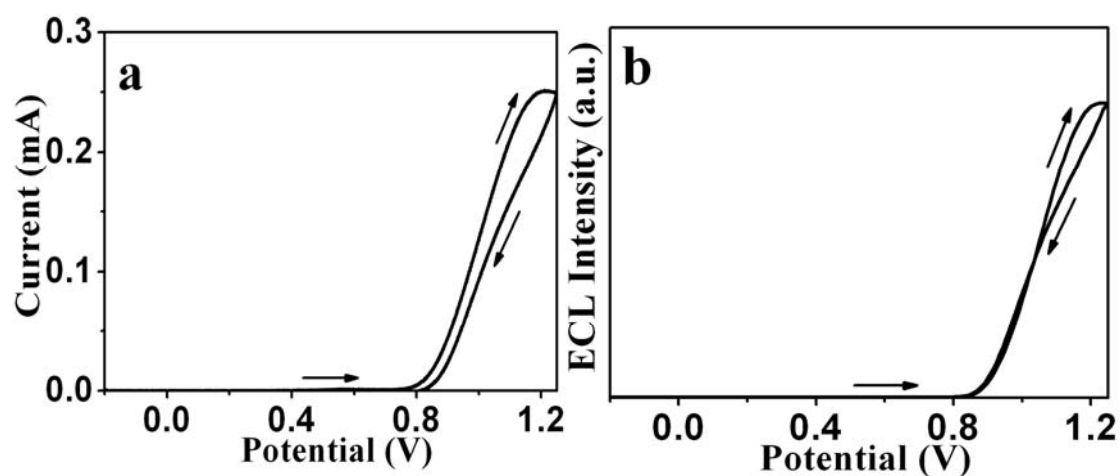


Figure S4. The cyclic voltammogram (a) and the corresponding ECL intensity profile (b) of $0.3 \text{ mM Ru}(\text{bpy})_3^{2+}$ at bare ITO electrode in air-saturated 0.1 M PBS (pH 7.0) containing 1.5 mM $\text{H}_2\text{C}_2\text{O}_4$. Scan rate: 0.1 V/s. As shown in (b), an anodic ECL is generated at +1.2 V, but no cathodic ECL is observed.

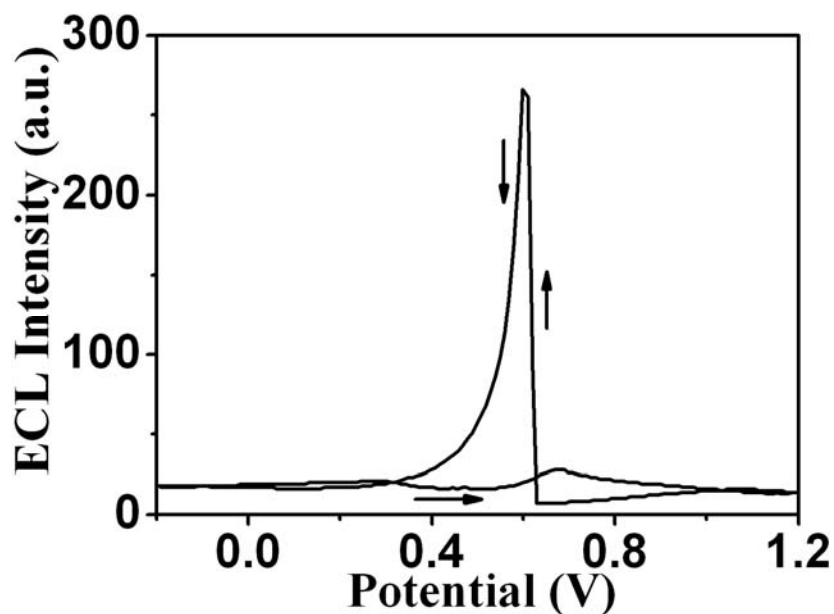


Figure S5. ECL intensity of 0.3 mM $\text{Ru}(\text{bpy})_3^{2+}$ at Co_3O_4 nanostructure covered ITO electrode in air-saturated 0.1 M PBS (pH 7.0) without $\text{H}_2\text{C}_2\text{O}_4$. Scan rate: 0.1 V/s. The light emission observed is still at +0.6 V and the CV is the same as that in Figure 1b. $\text{H}_2\text{C}_2\text{O}_4$ plays the role of the coreactant to heighten the intensity of ECL.

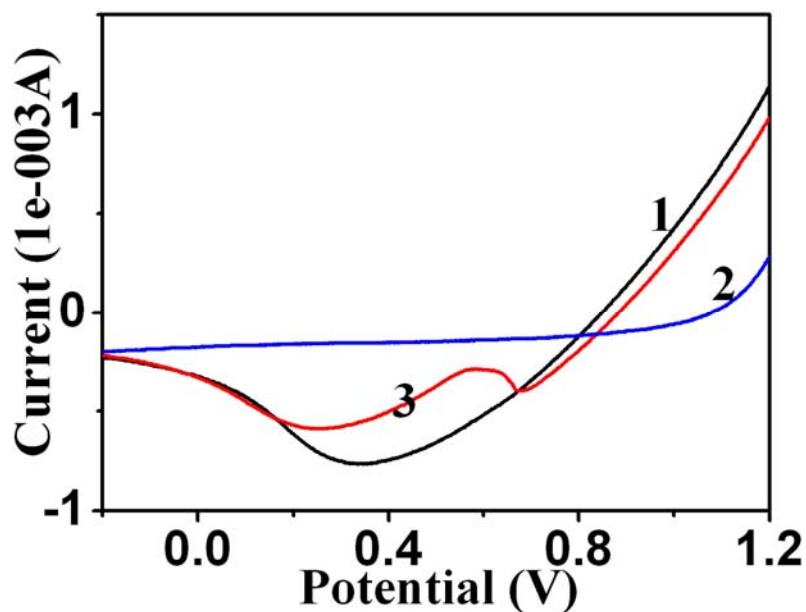


Figure S6. The voltammograms of single potential scan from 1.2 V to -0.2 V at Co_3O_4 nanostructure covered ITO electrode in 0.1 M PBS (pH 7.0) with saturated air (curve 1), nitrogen (curve 2) and oxygen (curve 3). Scan rate: 0.1 V/s. The similar reduction shapes to that of Figure 2d further confirm that the reduction at +0.6 V is associated with the reduction of the dissolved oxygen.

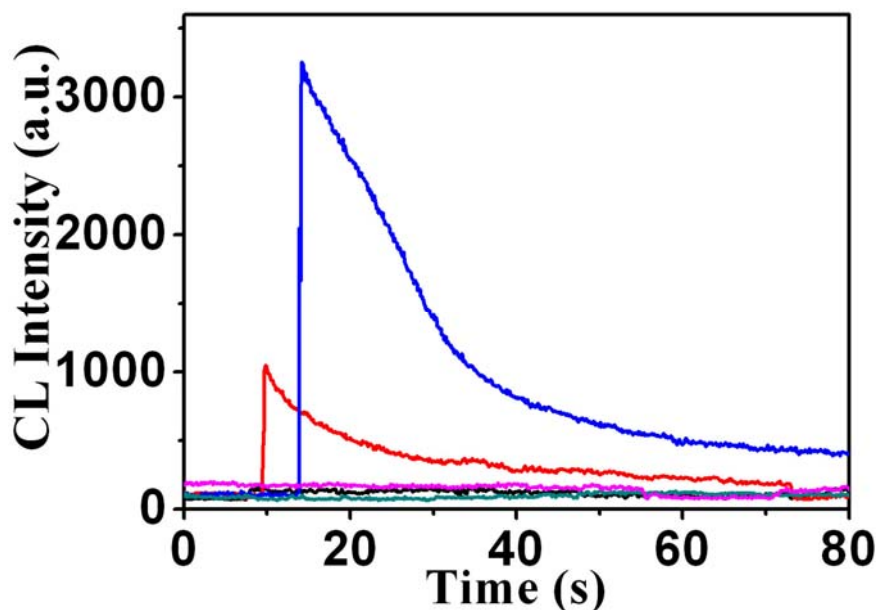


Figure S7. In a typical reaction, KIO_4 reacts with H_2O_2 to produce $\text{O}_2^{\bullet-}$ in an alkaline solution. In the absence of $\text{Ru}(\text{bpy})_3^{2+}$, the reaction of 0.01 M KIO_4 with 0.03% H_2O_2 did not generate light (green curve). However, when $\text{Ru}(\text{bpy})_3^{2+}$ (and $\text{H}_2\text{C}_2\text{O}_4$) was added, a strong light emission was observed immediately (red and blue curve, respectively). No light emission occurred when $\text{Ru}(\text{bpy})_3^{2+}$ was added into 0.01 M KIO_4 or H_2O_2 alone (pink and black curve, respectively).

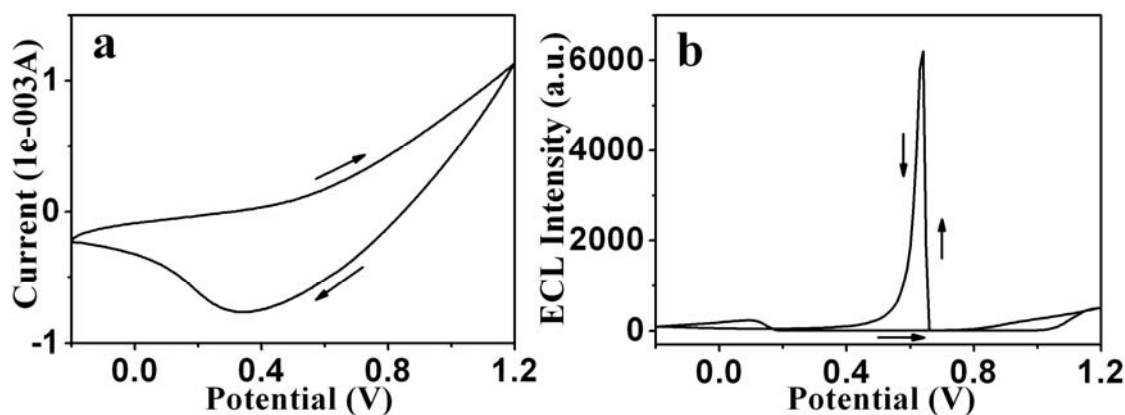


Figure S8. Cyclic voltammogram (a) and corresponding ECL intensity (b) of 0.3 mM $\text{Ru}(\text{bpy})_3^{2+}$ at Co_3O_4 nanostructure covered ITO electrode in air-saturated 0.1 M phosphate buffer solution (pH 7.0) containing 1.5 mM $\text{H}_2\text{C}_2\text{O}_4$. Scan rate: 0.1 V/s. As shown in the cyclic voltammogram (a), even if the first reduction wave does not appear, the strong cathodic ECL (b) is still generated at +0.6 V, indicating that the catalysis of O_2 reduction takes place by electron transfer to O_2 from Co^{2+} in Co_3O_4 .

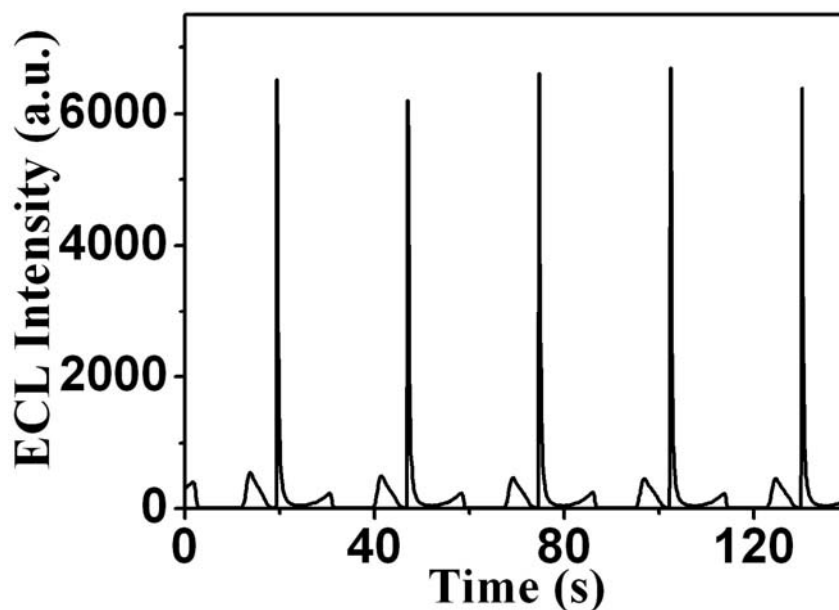


Fig. S9. ECL intensity-time curve of 0.3 mM $\text{Ru}(\text{bpy})_3^{2+}$ at Co_3O_4 nanostructure covered ITO electrode in air-saturated 0.1 M phosphate buffer solution (pH 7.0) containing 1.5 mM $\text{H}_2\text{C}_2\text{O}_4$ under continuous potential scanning from the 51st to 55th cycling scans. Scan rate: 0.1 V/s. As shown, a stable ECL signal ($\sim 6690\text{au}$) is observed after continuous potential scanning 50 cycling scans, and is 72% of the initial ECL signal ($\sim 9270\text{ au}$, shown in Fig.1).