Supporting Information

Tetrakis (4-carboxyphenyl) porphyrin and $Ru(bpy)_3^{2+}$ modified SiO_2 nanosphere for potential and wavelength resolved electrochemiluminescence

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S1. Preparation of $CRuSiO_2$ NPs

$CRuSiO_2$ NPs were synthesized through the W/O microemulsion system[1]. The W/O microemulsion system was prepared first by mixing 1.77 mL of TX-100, 7.5 mL of cyclohexane, 1.8 mL of 1-hexanol, and 100 μL 0.5% chitosan. Then 400 μL 2.5 mM $Ru(bpy)_3^{2+}$ aqueous solution was added into the mixture. In the presence of 90 μL of TEOS, a polymerization reaction was initiated by adding 60 μL of $NH_3 \cdot H_2O$ (25%−28%). The hydrolysis reaction was allowed to continue for 24 h. Acetone was then added to destroy the emulsion, followed by centrifuging and washing with ethanol and water. At last, the orange $CRuSiO_2$ NPs were obtained.

S2. XPS Ru spectra of TCPP@$CRuSiO_2$ NPs

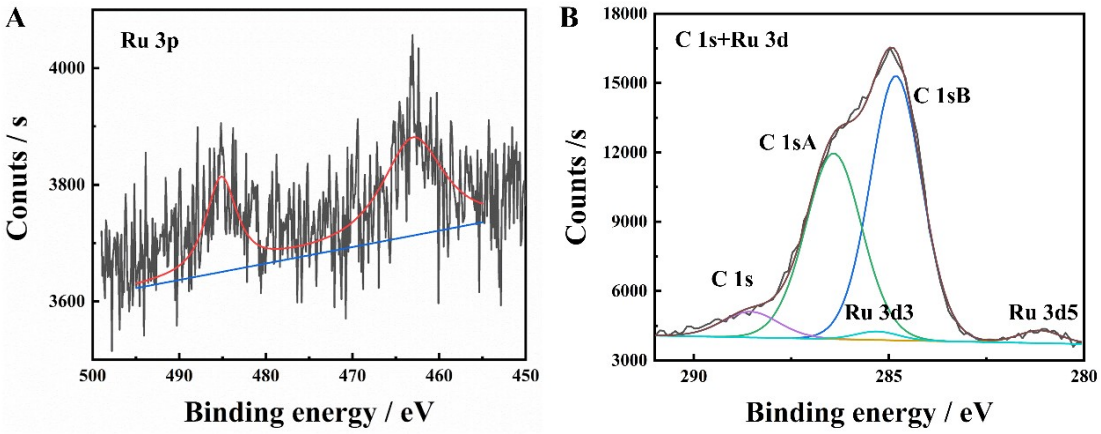

Figure S1. (A) Ru 3p spectra (B) C 1s and Ru 3d spectra of XPS of TCPP@$CRuSiO_2$.

S3. XRD patterns

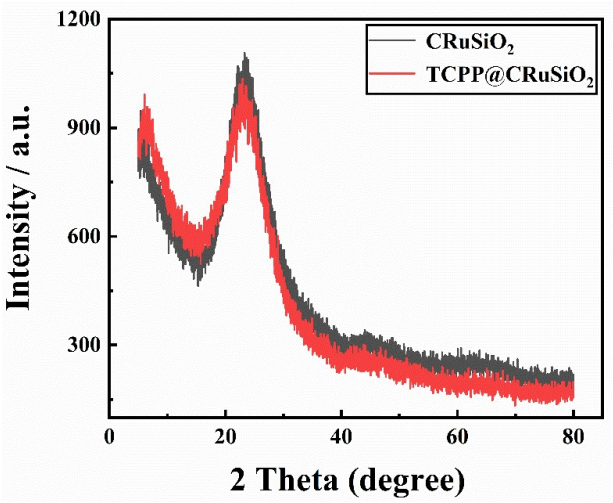

Figure S2. XRD patterns of $CRuSiO_2$ (black line) and TCPP@$CRuSiO_2$ (red line).

S4. Measurement of TCPP and $Ru(bpy)_3^{2+}$ content

As shown in Figure S3A, the UV-vis spectrum of TCPP@$CRuSiO_2$ showed two characteristic absorption peaks at 288 and 405 nm, which were attributed to $Ru(bpy)_3^{2+}$ and TCPP, respectively. Based on this, the concentrations of $Ru(bpy)_3^{2+}$ and TCPP were determined by the UV-vis spectrophotometry. First, the standard curves between the concentration and absorbance intensity of $Ru(bpy)_3^{2+}$ and TCPP were established as shown in Figure S3B and S3C, respectively. Then, the molar concentrations of TCPP and $Ru(bpy)_3^{2+}$ in TCPP@$CRuSiO_2$ were calculated to be 0.070 and 0.099 mmol/L, respectively. Thus, the molar ratio of TCPP to $Ru(bpy)_3^{2+}$ in TCPP@$CRuSiO_2$ was 1:1.41 (Figure S3D).

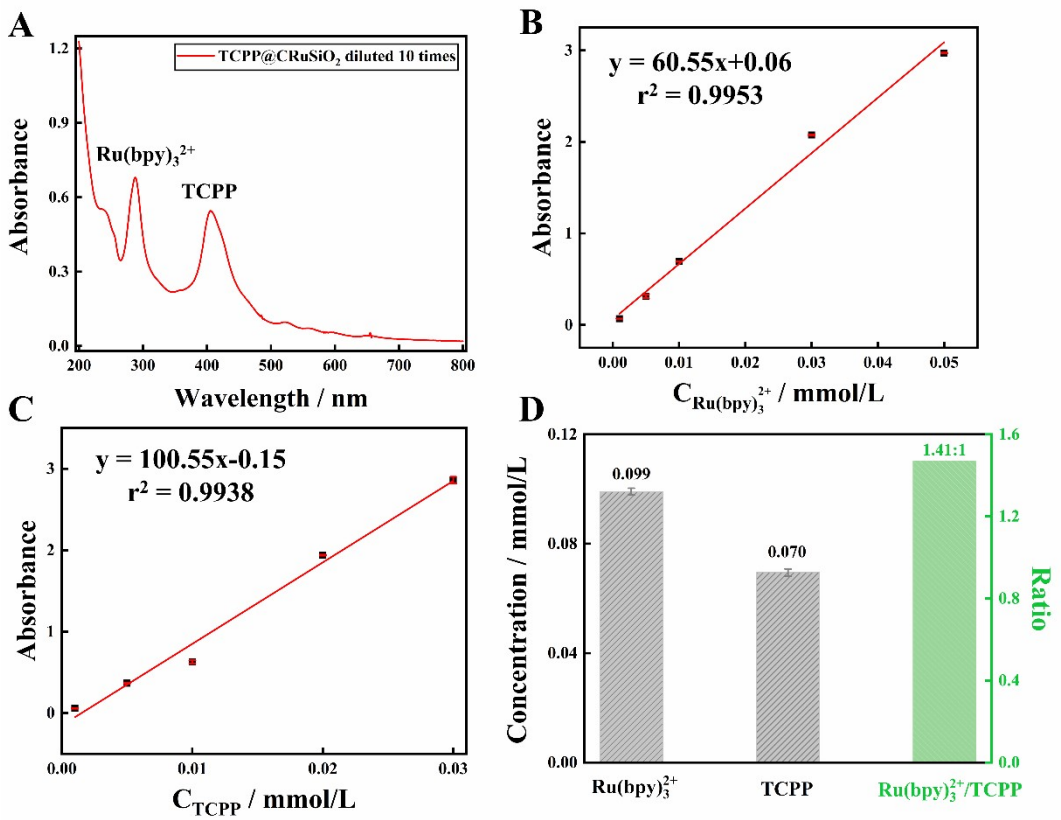

Figure S3. (A) UV-vis spectrum of TCPP@$CRuSiO_2$ diluted 10 times. Absorbance-concentration fitted curve of (B) $Ru(bpy)_3^{2+}$ and (C) TCPP. (D) Concentrations and molar ratio of $Ru(bpy)_3^{2+}$ and TCPP.

S5. SEM of TCPP@$CRuSiO_2$ modified GCE electrode

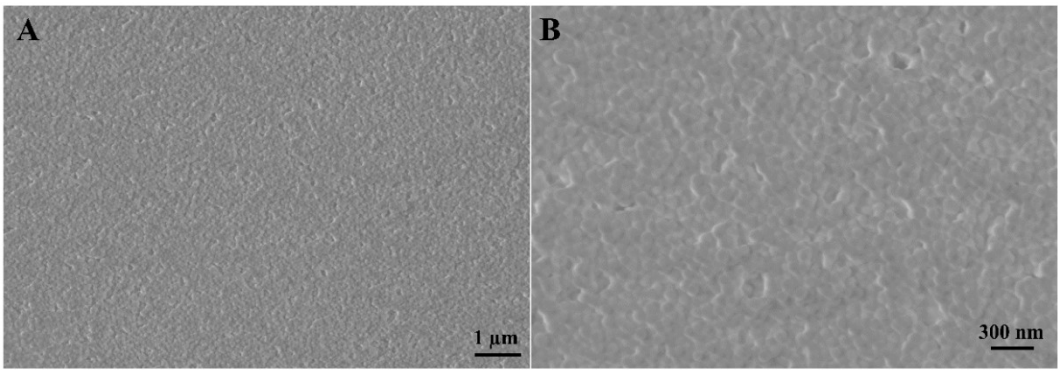

Figure S4. SEM images of TCPP@CRuSiO$_2$ modified GCE electrode in different scales: (A) 1 μm and (B) 300 nm.

S6. Stacked spectra of ECL-1 and ECL-2

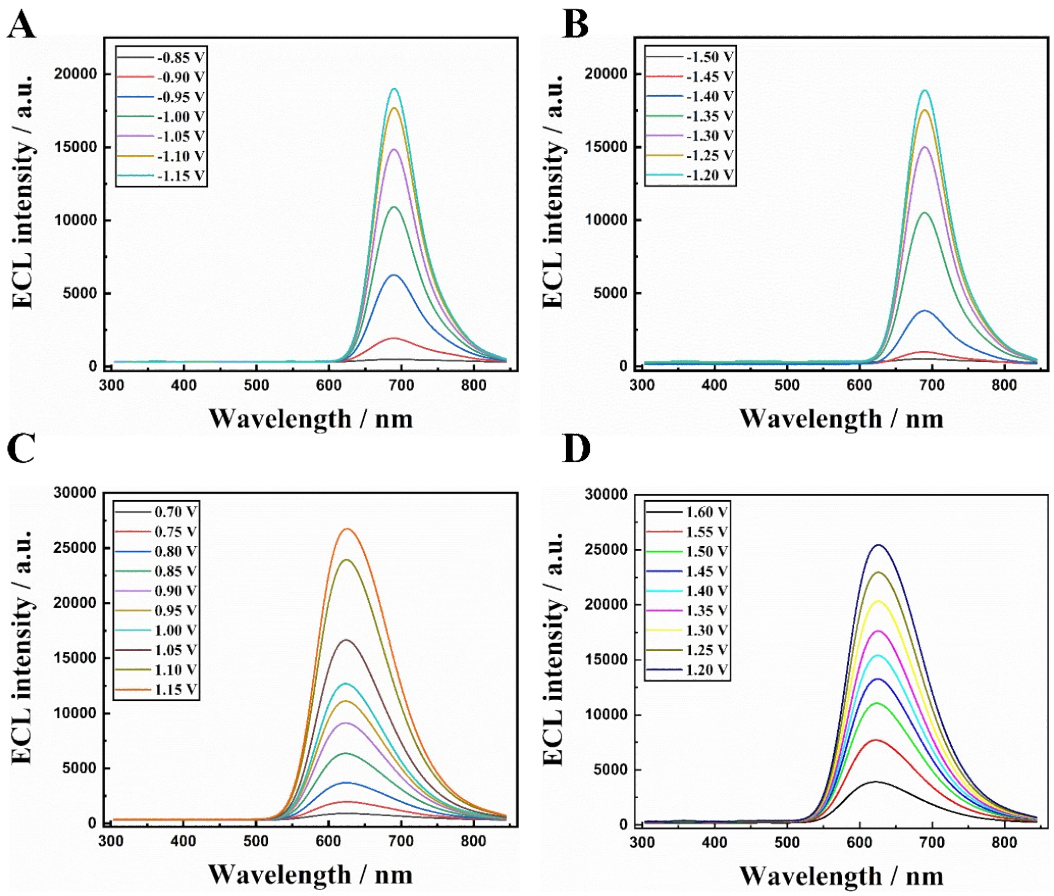

Figure S5. Spectra of ECL-1 (A and B) and ECL-2 (C and D) at different potentials. Reaction conditions: 0.01 M $K_2S_2O_8$ and 0.01 M TprA in 10 mM PBS buffer. Test conditions: sweep speed, 0.05 V/s.

S7. Measurement of relative ECL efficiency

The relative ECL efficiency was calculated using the following equation with 1 mM $Ru(bpy)_3^{2+}$ as a reference[2,3].

$$\Phi_{ECL} = \Phi_{ECL}^{\theta} \times \frac{I \times Q^{\theta}}{I^{\theta} \times Q} \qquad (S1)$$

where I and I^{θ} are the integrated ECL intensities (integrating ECL spectrum vs wavelength), Q and Q^{θ} are the consumed charges (integrating current vs time), Φ_{ECL} and Φ_{ECL}^{θ} are the ECL efficiency value of the sample and standard, respectively.

As a result, the relative ECL efficiency of ECL-1 was calculated to be 201.9 % relative to the $Ru(bpy)_3^{2+}/K_2S_2O_8$ standard and the relative ECL efficiency of ECL-1 was calculated to be 95.3 % relative to the $Ru(bpy)_3^{2+}$/TPrA standard.

S8. Influence of molar ratio of TCPP and $Ru(bpy)_3^{2+}$ for ECL emissions

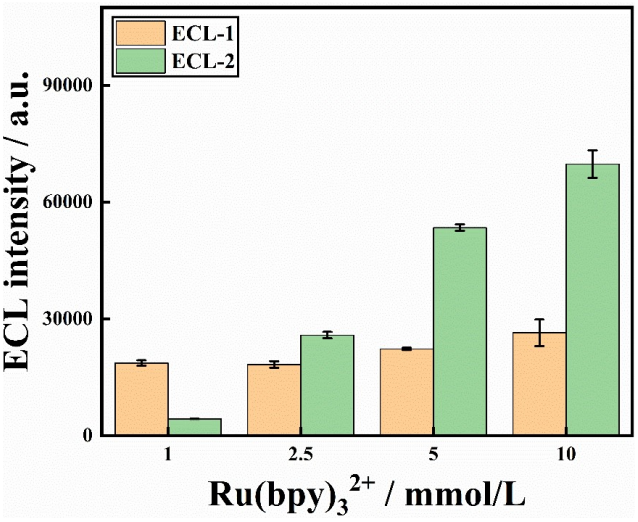

Figure S6. Influence of molar ratio of $Ru(bpy)_3^{2+}$ and TCPP in the process of synthesis for ECL emissions.

S9. Effects of coreactant concentration on ECL

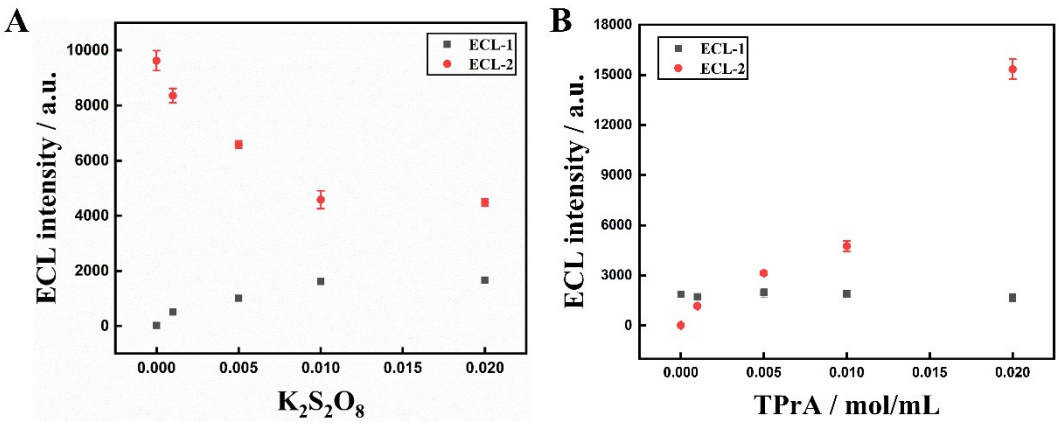

Figure S7. Effect of the concentration of coreactants on the intensities of ECL-1 and ECL-2: (A) $K_2S_2O_8$ (TPrA, 0.01 mol/L) (B) TPrA ($K_2S_2O_8$, 0.01 mol/L).

S10. Effects of various atmospheres on ECL

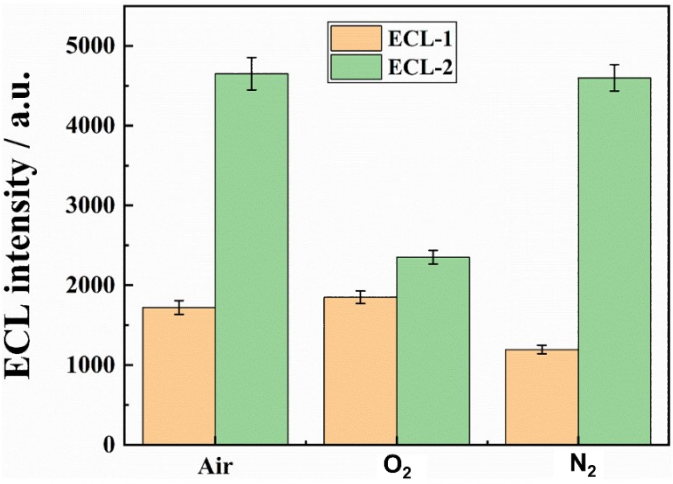

Figure S8. ECL intensities of TCPP@CRuSiO$_2$ nanoluminophores in O_2, N_2 and air-saturated atmospheres. Test conditions: 0.01 M $K_2S_2O_8$ and 0.01 M TPrA in 10 mM PBS buffer; scan rate: 0.05 V/s; PMT: -500 V.

Reference

1. H. Ma, X. Li, T. Yan, Y. Li, H. Liu, Y. Zhang, D. Wu, B. Du and Q. Wei, *ACS applied materials & interfaces*, 2016, **8**, 10121-10127.

2. A. Kondyurin, K. Tsoutas, Q. X. Latour, M. J. Higgins, S. E. Moulton, D. R. McKenzie, and M. M. M Bilek, *ACS Biomater. Sci. Eng.* 2017, **3**, 2247-2258.

3. D. Luo, B. Huang, L. Wang, A. M. Idris, S. Wang, and X. Lu, *Electrochim. Acta*. 2015, 151, 42-49.