

Supporting Information

Experimental Section

Reagents. Tris(4,7-diphenyl-1,10-phenanthroline)-ruthenium (II) (Rudpp) was kindly provided by Professor Kwok-Yin Wong of The Hong Kong Polytechnic University. Poly(vinylidene chloride-*co*-acrylonitrile) (PVDC-*co*-AN), 5 wt.% Nafion perfluorinated ion-exchange resin and Tripropylamine (99+%, TPA) were obtained from Sigma Aldrich. All chemicals were used without further purifications and all solutions were prepared with ultra-pure water obtained from a Millipore purification system.

Synthesis of Rudpp doped PVDC-*co*-PAN Nanobeads (RPN). The RPN were synthesized as reported^{18,19}. 40 mg PVDC-*co*-AN and 2 mg Rudpp were dissolved in 2 mL tetrahydrofuran (THF) and 18 mL acetone successively with stirring for 15 min. Then 60 mL ultra-pure water was added into the solution as fast as possible with stirring for 5 min. The THF and acetone were removed in a rotary evaporator under reduced pressure. Finally, an orange solution containing RPN resulted.

Preparation of Glassy Carbon Electrodes (GCE). The GCE were polished with 0.3 μm and 0.05 μm aluminum powder and sonicated in ultra-pure water for 5 min. Then they were dried with N_2 flow before each experiment.

RNP modified GCE (RPN-GCE) preparation. 3 mL RPN solution was centrifugated to obtain the solid RPN. The solid was suspended in 300 μL ultra pure water with sonication. Then 300 μL 0.5 %wt. Nafion solution was added under

sonication. The GCE were dipped into 20 μL of the mixture and allowed to dry at room temperature.

Rudpp modified GCE (TR-GCE) preparation. 1.0 mg Rudpp was dissolved in 1 mg THF under sonication. The solution was kept at 4 $^{\circ}\text{C}$ for 24 h. Then 2 μL of this solution was mixed with 80 μL 0.5% w.t. Nafion solution under sonication. The GCE were dipped into 20 μL of the mixture and then dried at room temperature.

Apparatus. Cyclic voltametric experiments were performed with a CH Instruments 660 voltametric analyzer (Shanghai Chenhua, China). All experiments were carried out under a three-electrode system using a modified GCE as the working electrode, silver wire as the reference electrode and stainless steel wire as the control electrode. The ECL signal was detected and recorded using an IFFM-D flow injection chemiluminescence analyzer (Xi'an Remax Electronic Science Tech. Co. Ltd., China); fluorescence data was obtained with an F-4500 Spectrofluorimeter (HITACHI, Japan); and UV-Vis data with a DU-7400 Spectrophotometer (Beckman, USA). The control of gas flow was achieved using two sets of CMOSens SFC 4000 mass flow controllers (Sensirion AG, Switzerland). O_2 and N_2 were precisely mixed using the controller and injected into a sealed electrochemical cell with only one outlet. Scanning electron microscope (SEM) images were taken using an S-4800 (HITACHI, Japan).

Fig. S1

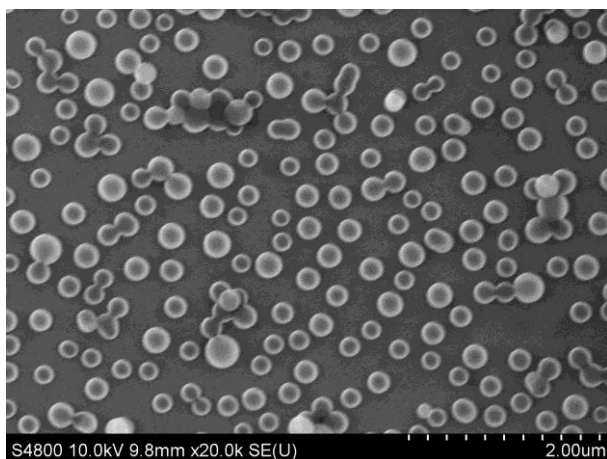


Fig. S1 SEM image of RPN.

Fig. S2

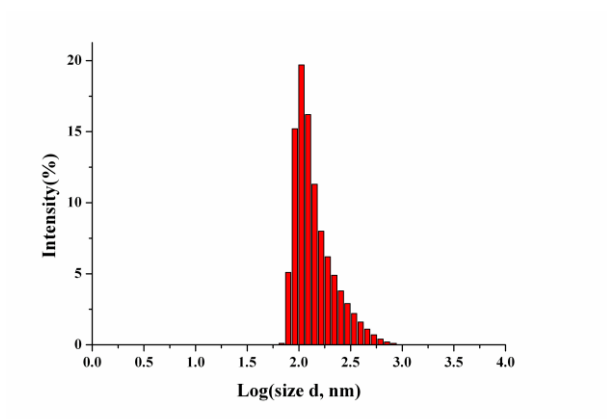


Fig. S2 Size distribution of an RPN sample.

Fig. S3

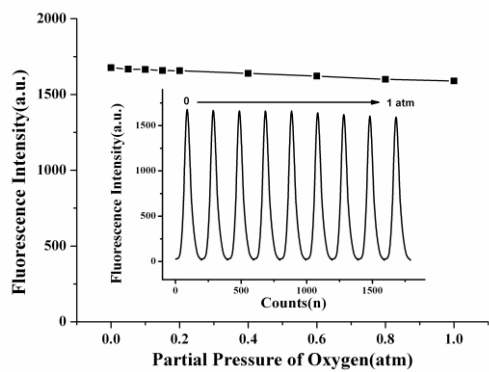


Fig. S3 Fluorescence intensity of RPN under different oxygen partial pressures.