Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

A Stable Organic Dye Catholyte for Long-life Aqueous Flow Battery

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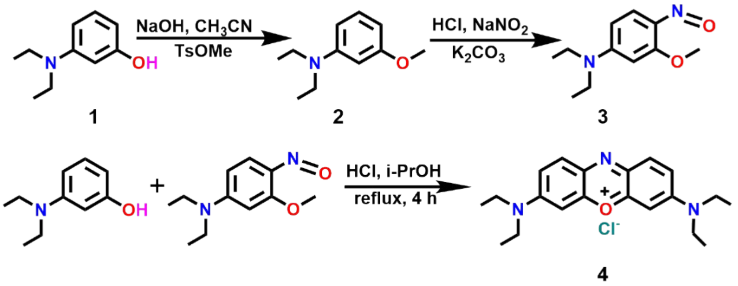
Materials

3-(dialkylamino)phenol (>98%), methyl p-toluenesulfonate (>98%), were purchased from DiBai Chemical Co., Ltd (Shanghai, China). Graphene oxide (GO) was supplied from Shaanxi Coal Chemical Industry Technology Research Institute Co., Ltd (Xi'an, China). Other chemicals and solvents were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Synthesis of Basic blue 3 (BB3)



Scheme S1. Synthesis procedures of Basic blue 3 (BB3).

The BB3 was synthesized through an asymmetric cyclization reaction.[1] 19.8 g **1** and 4.8 g NaOH were stirred in 180 mL MeCN for 1 h, followed by adding 22.32 g methyl p-toluenesulfonate. The mixture was stirred at 70 ℃ overnight and then vacuum filtrated and washed with MeCN. The filtrate was evaporated to get the oil residue, which was further dissolved in 300 mL 5% HCl and washed by diethyl ether for three times (3×200 mL). The pH of the solution was adjusted to 9.0 by addition of K_2CO_3. Then the solution was extracted by diethyl ether for three times (3×200 mL). The organic layer was washed by 1 M NaOH (2×200 mL) and NaCl (3×200 mL), and then dried with anhydrous Na_2SO_4. Subsequently, the solvent was removed by rotary evaporation, giving oil **2** (yield 91%).

7.8 g **2** and 15 mL HCl were dissolved in 300 mL water with an ice bath, followed by adding 4.2 g $NaNO_2$ in 1 h, giving a dark mixture. After continuous stirring for another 1 h with an ice bath, K_2CO_3 was added to adjust the solution at about pH=9. Then, the solvent was removed by filtering. Subsequently, the collected filter residue was washed with water and vacuum dried at 50 ℃ overnight, giving green powder **3** (yield 70%).

9.2 g **1** was dissolved in 100 mL i-PrOH in a 500 mL two-neck bottle with distilling apparatus and stirred at 70 ℃ under nitrogen atmosphere. Then, a suspended solution containing 10 g **3** and 4.6 mL HCl in 150 mL i-PrOH was slowly injected into the bottle with syringe in 2 h. Subsequently, the temperature rose to 100 ℃ and held at 100 ℃ for 10 h. During this process, 100 mL i-PrOH was added to the reaction mixture when about 100 mL of the solvent was distilled out. This procedure was repeated 8~10 times, obtaining a dark blue solution. After removing the solvent by evaporation, a dark blue power was gained, which was then purified by column chromatography with silica gel. The final green power **4** was washed by diethyl ether then dried in vacuum (yield 60%). The molecule structure was confirmed by ^{1}H NMR spectrum (AVANCE III HD 600 MHz) as shown in Figure S1.

Preparation of nitrogen doped graphene

20 mL of 4 mg/mL GO aqueous solution was mixed with 5 g urea and dried at 60 ℃ under stirring. Then the mixture was transferred to a furnace and thermally treated at 900 ℃ for 2 h in Ar atmosphere with a heating rate of 5 ℃/min. The black nitrogen doped graphene (NG) powder was obtained along with the furnace cooling.

Characterization

A spectrometer UV-3600 plus (Shimadzu Production Co., Ltd.) measured UV-vis spectrum from 600 to 800 nm. Fourier transform infrared spectrometry (FTIR) (Bruker Alpha spectrometer) was performed in the spectral area of 400-3600 cm^{-1}. SEM images were taken on a Zeiss Gemini SEM 500 field emission scanning electron microscope. XPS measurements were conducted with a Thermo Fisher ESCALABXi+ X-ray photoelectron spectroscopy.

Pretreatment of the Nafion membrane and carbon paper

According to previously published protocols[2], the fresh Nafion 212 membrane was firstly immersed in deionized water for 30 minutes at 80 ℃ and then soaked in 5% H_2O_2 for another 30 minutes. After that, the membrane was stored in 0.5 M H_2SO_4 at room temperature before use. The Toray 090 hydrophilic carbon paper (CP) was pretreated by heating in muffle furnace at 400 ℃ for 24 h.

Preparation of NG modified glass carbon (GC@NG) and NG modified carbon paper (CP@NG)

The NG ink was prepared by dispersing 300 mg NG in a mixed solution, consisting of 5% nafion, 7 mL deionized water and 3 mL of isopropyl alcohol by ultra-sonication for at least 30 minutes. The GC@NG was made by dropping 4 µL of the NG ink on the surface of GC with pipette and drying under the infrared lamp. The ~1 mg/cm^2 of NG ink was coated onto the CP and then dried at 50 ℃ for 1 h, giving CP@NG.

Electrochemical measurements

Cyclic voltammetry (CV) was measured on an electrochemical workstation CHI760e (CH Instruments, Shanghai) with three electrodes work system. The GC or GC@NG was used as working electrode, the platinum sheet (1 cm^2)

was used as counter electrode and the Ag/AgCl electrode was used as aqueous reference electrode (saturated KCl solution). The peak separation ΔE was calculated by $E_{oxidation}$-$E_{reduction}$ at the same sweep rate.

Linear sweep voltammetry (LSV) was measured on a rotating disk electrode device (Pine Instruments Co., USA) with various rotating rates of 400, 625, 900, 1225, 1600, 2025 and 2500 rpm with a seep rate of 10 mV/s. The diffusion coefficients (D, $cm^2\ s^{-1}$) of the reodx molecule was calculated by Levich equation:

$i_L=0.620nFACD^{2/3}\upsilon^{-1/6}\omega^{1/2}$,

where i_L is the limiting current, n is the number of electrons (n = 2 for the redox reaction of BB3), F is the Faraday constant (96485 C/mol), A is the area of the working electrode (0.125 cm^2), C is the concentration of compounds (0.05 M), D is the diffusion coefficient ($cm^2\ s^{-2}$), υ is the kinematic viscosity[3] at $1.55\times10^{-2}\ cm^2\ s^{-1}$, and ω is the rotating angular velocity (rad s^{-1}). The current measured at each potential was plotted versus the square root of the electrode rotation rate. The resulting fitted line was expressed by the Koutecký-Levich equation:

$1/i=1/i_K+1/i_L=1/i_K+1/0.620nFACD^{2/3}\upsilon^{-1/6}\omega^{1/2}$

where i_K is the mass-transfer-independent kinetic current, which was fitted by a Tafel plot. η was calculated from the difference between the measured potential. The fitted line was expressed by the Tafel equation:

$1n(i)= 1n(i_0)+\alpha nF\eta/RT$

where i_0 is the exchange current , α is the transfer coefficient, R is the universal gas constant (8.314 J $K^{-1}mol^{-1}$), and T is temperature (298 K). The exchange current i_0 was determined from the vertical-intercept, and the kinetic rate constant k_0 (cm s^{-1}) was calculated using the equation:

$k_0=i_0/nFCA$

Solubility measurement

The solubility of BB3 in the mixed solvent (H_2O/HoAc volume ratio of 1:1, containing 3.5 M H_2SO_4) was estimated by UV-vis spectrum. Firstly, add BB3 powder into the mixed solvent until no further solid could be dissolved. A saturated solution of BB3 was obtained. Then take a small amount of the saturated solution and diluted it with a known magnification. The concentration was measured by UV-vis spectrum from 600 to 800 nm. Finally, the concentration was calculated according to a pre-calibrated absorbance-concentration curve of known concentrations of BB3.

Flow battery measurement

A home-made full battery was assembled with two Cu plate collectors, two graphite plates, and two electrodes, which was separated by Nafion 212 membrane. The electrode was composed with a stack of five sheets of Toray 090 hydrophilic CP with a 5 cm^2 geometric surface area. The rest of the space between the plates was sealed by silicone sheets. 7.5 mL of 0.05 M BB3 solution was used as catholyte and 10 mL of 0.1 M V^{2+} solution was used as anolyte. The supporting solution was 3.5 M H_2SO_4 in both sides. V^{2+} electrolyte was firstly prepared with the same method in all vanadium flow battery. The electrolytes were pumped into the cell at a flow rate of 80 mL/min through a peristaltic pump (BT300M, Baoding ChuangRui Precision Pump Co., Ltd.). The full cell test was conducted with Neware battery test system (Neware, Shenzhen, China) at room temperature. Galvanostatic charge-diacharge were performed between 0.2 and 1.4 V. The AC impedance spectroscopy (EIS) of cells was obtained by CHI 760e with a frequency range from 0.01 Hz to 10 kHz.

V^{2+} anolyte preparation

The V^{2+} anolyte was prepared according to the approach that used in the all-vanadium ARFB[4]. Typically, 25 mL 0.1 M $VOSO_4$ and 10 mL 0.1 M $VOSO_4$ in 3.5 M H_2SO_4 were used as the catholyte and anolyte, respectively. The electrolytes were pumped into the cell at a flow rate of 80 mL/min through a peristaltic pump. The battery is charged to 1.8 V at a constant current of 100 mA/cm^2 and then hold the potential at 1.8 V until the charging current density decreases to 5 mA/cm^2. During this process, the anolyte changed from sky blue to dark green firstly and purple finally, giving V^{2+} solution. The obtained V^{2+} anolyte was kept under nitrogen atmosphere before use.

Capacity calculation

The battery capacity is calculated by a formula as follow:

$$C = MnF/3600$$

Where C is the capacity (Ah/L), M is the redox active electrolyte concentration (M), n is the number of electrons transferred in the reaction for one mol, n=2 for BB3, F is the Faraday constant (F=96485 C/mol).

In order to reach a competitive capacity with all-vanadium ARFBs (~40 Ah/L), the M can be calculated as follow, where n=1 for V^{2+}/V^{3+} or V^{4+}/V^{5+},

$$M \geq \frac{3600C}{Fn} = \frac{3600 \times 40}{96485} = 1.5$$

considering n=1, so the equivalent electron concentration is 1.5 M.

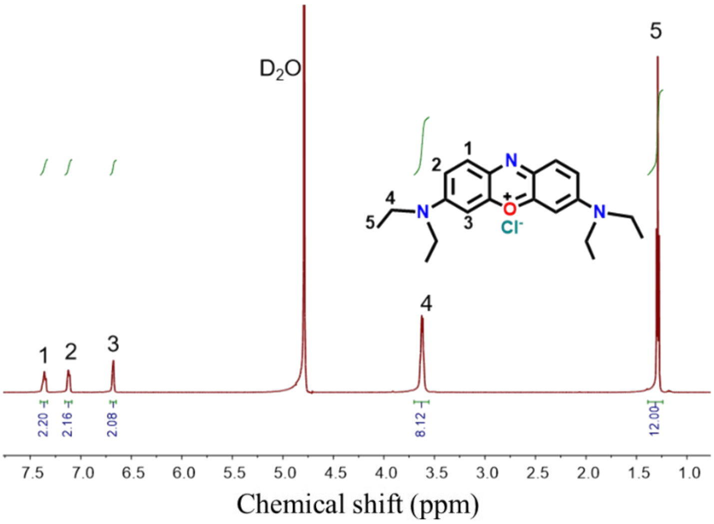


Figure S1. ^{1}H NMR spectrum of BB3 (400 MHz, D_2O). δ1.29 (t, 12H), 3.62 (q, 8H), 6.68 (d, 2H), 7.12 (d, 2H), 7.36 (d, 2H).

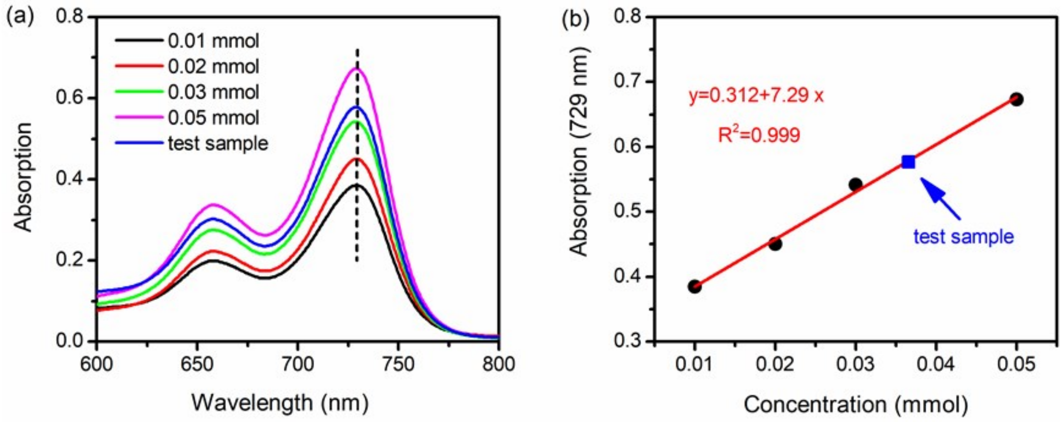


Figure S2. UV-vis calibration lines for determination of the solubility of BB3. (a) UV-vis spectrum of BB3 of different concentration in the mixed solution (BB3 in H_2O/HoAc mixture with a volume ratio of 1:1, containing 3.5 M H_2SO_4). (b) The absorbance at 730 nm of BB3 versus the concentration of BB3 aqueous solution. The dilution ratio of the tested sample is 65000 times.

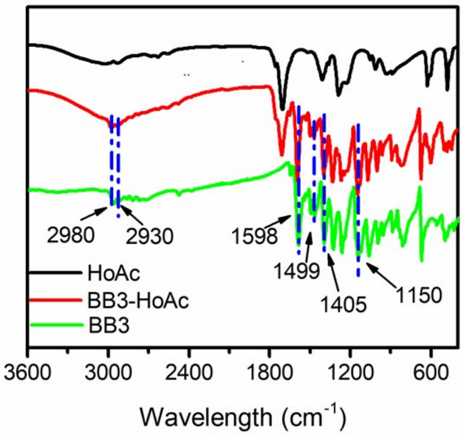


Figure S3. FTIR spectra of HoAc, BB3 and BB3-HoAc samples. The characteristic peaks (neat, cm^{-1}) of BB3 are at 2980, 2930 (alkyl-CH), 1598, 1499, 1405 (phenoxazinium skeleton), 1150 (C-N), respectively.[1] In the mixture of BB3 and HoAc, the characteristic peaks of BB3 remain intact, indicating negligible structure change of BB3.

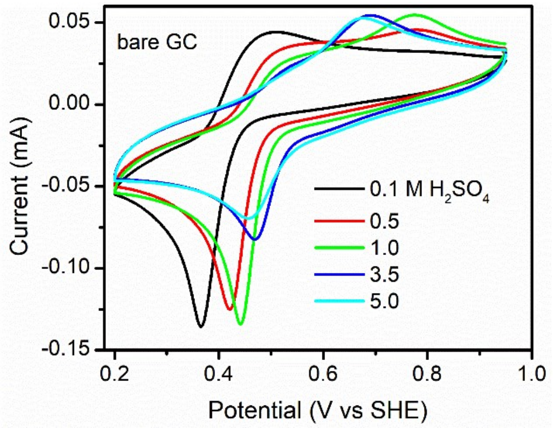


Figure S4. CV curves of 1 mM BB3 molecules at different H_2SO_4 concentrations. With the increasing of H_2SO_4 concentration ranging from 0.1 to 5 M, the redox potential gradually increased from 0.41 V vs SHE in 0.1 M to 0.54 V in 3.5 M.

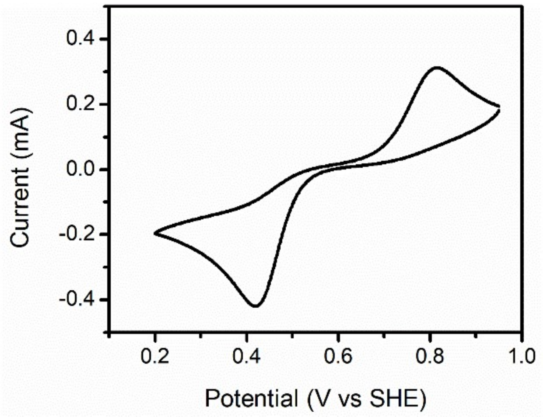


Figure S5. CV curve of 0.05 M BB3 on pure graphene modified glass carbon electrode under 0.1 V/s.

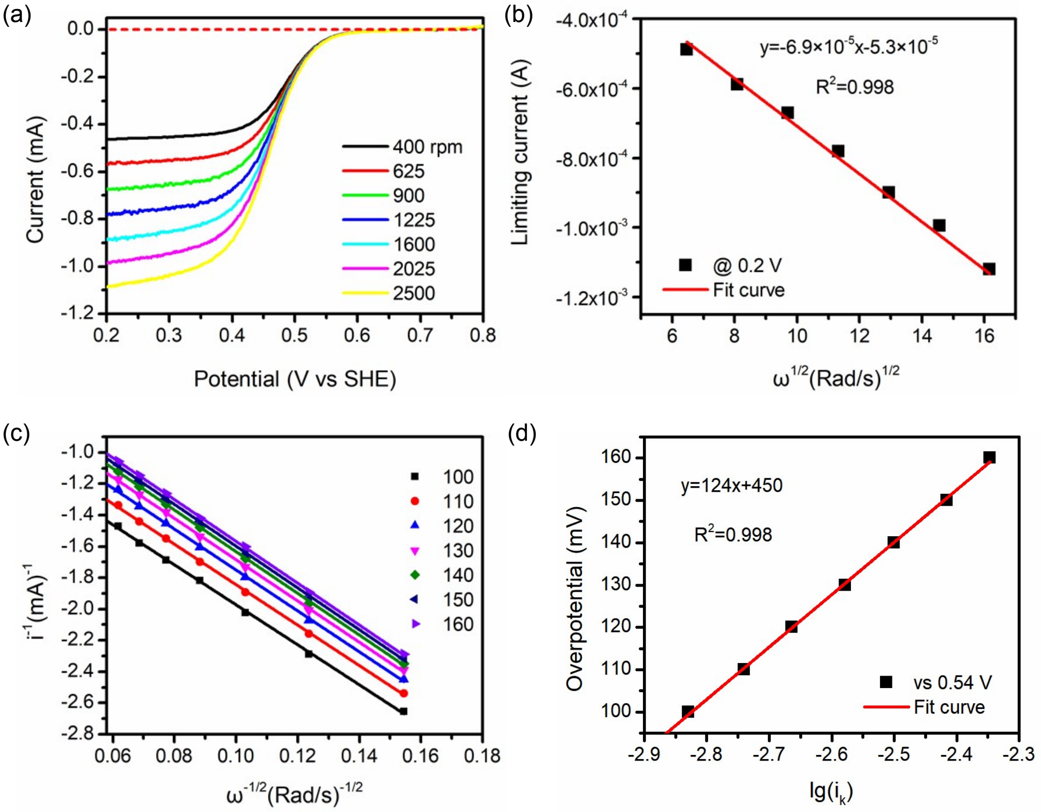


Figure S6. Rotating-disk-electrode (RDE) experiment of BB3 (0.05 M in 3.5 M H_2SO_4) on bare GC. (a) LSV curves at 0.01 V/s from positive to negative potential with rotating rates from 400 to 2500 rpm. (b) Levich plot of limiting current (at 0.2 V vs SHE) versus square root of rotation rate. (c) Koutecky-Levich plot at different overpotentials. (d) Tafel plot, the logarithm of kinetically limited current versus overpotential.

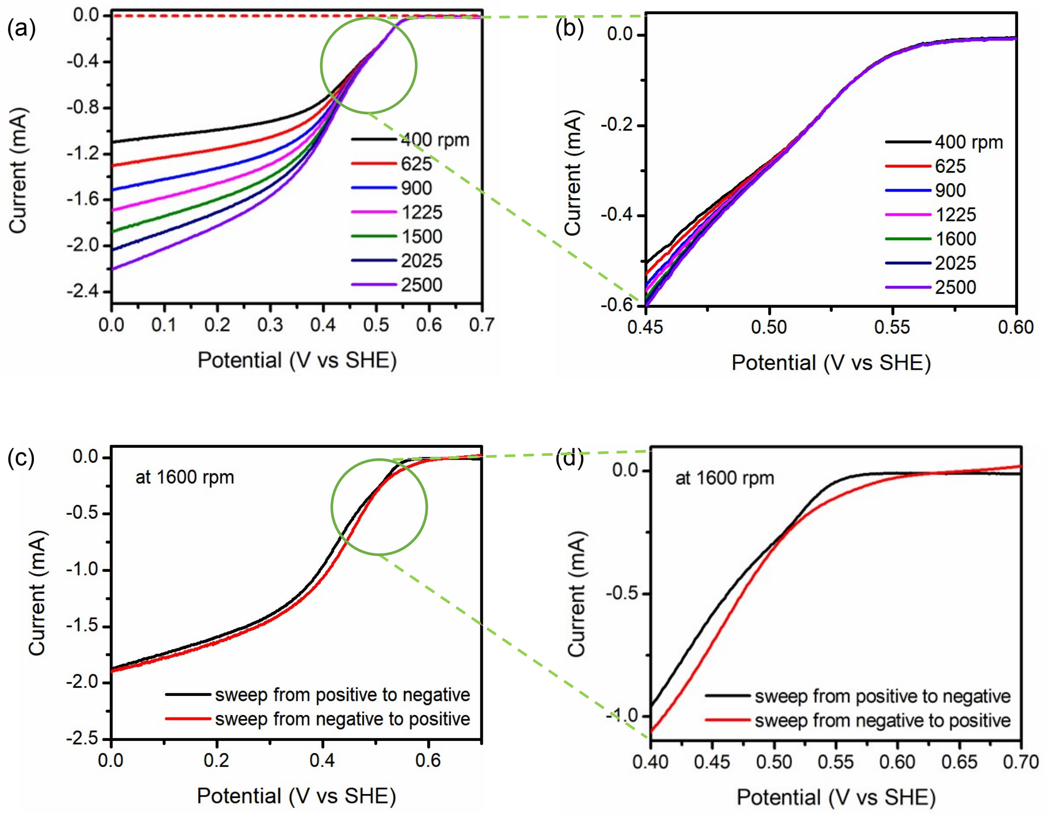


Figure S7. (a) LSV curves of BB3 (0.05 M in 3.5 M H_2SO_4) on GC@NG in the RDE experiment. The curves were swept at 0.01 V/s from positive to negative potential with rotating rates from 400 to 2500 rpm. (b) The enlarged LSV curves from (a). (c) Comparison of LSV curves of BB3 (0.05 M in 3.5 M H_2SO_4) on GC@NG at 1600 rpm with sweeping from positive to negative potential (black line) and negative to positive potential (red line), respectively. (d) The enlarged LSV curves from (c).

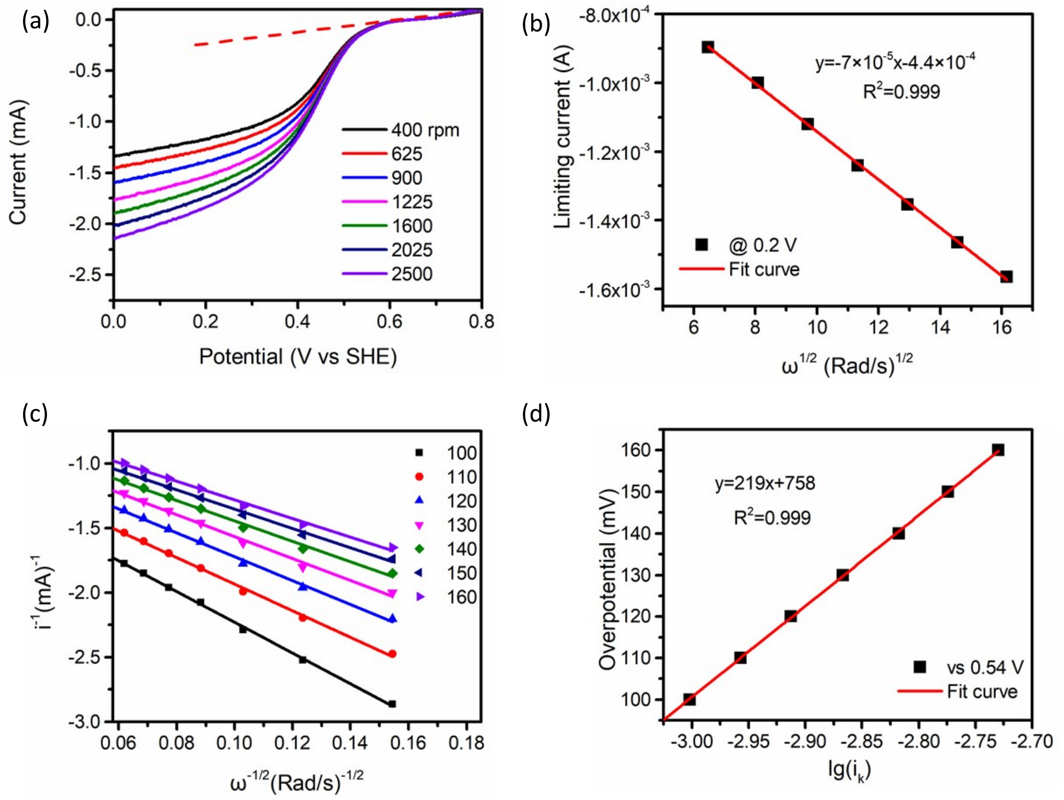


Figure S8. RDE experiment of BB3 (0.05 M in 3.5 M H_2SO_4) on GC@NG. (a) LSV curves at 0.01 V/s from negative to positive potential with rotating rates from 400 to 2500 rpm. (b) Levich plot of limiting current (at 0.2 V vs SHE) versus square root of rotation rate. (c) Koutecky-Levich plot at different overpotentials. (d) Tafel plot, the logarithm of kinetically limited current versus overpotential.

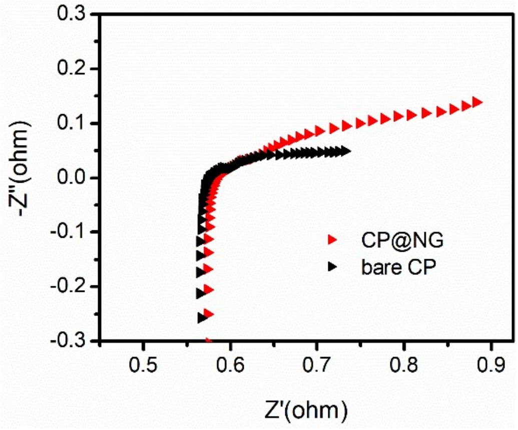


Figure S9. Electrochemical impedance spectroscopy (EIS) of bare CP based battery and CP@NG based battery.

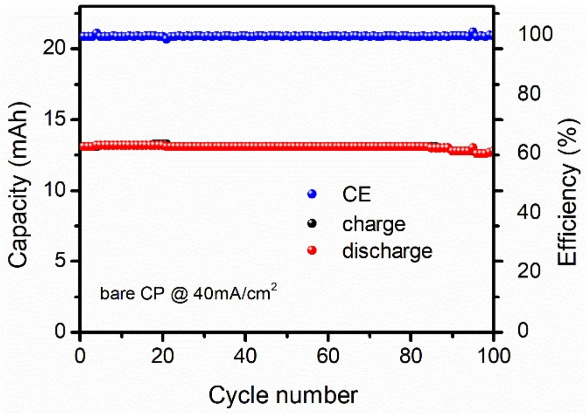


Figure S10. Charge/discharge capacity and CE of the ARFB with 0.05 M BB3 catholyte using bare CP as electrode at 40 mA/cm^2 for 100 cycles.

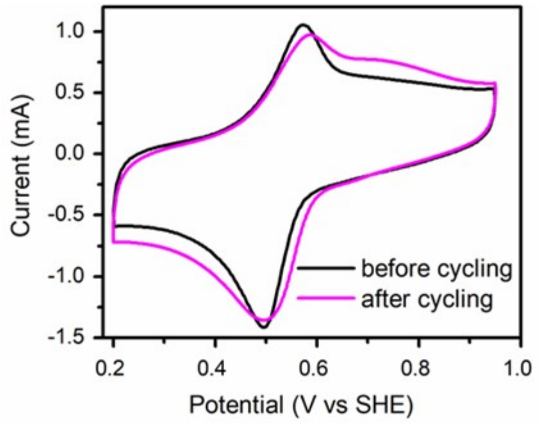


Figure S11. CV curves of 0.05 M BB3 catholyte before and after 1500 cycles in full battery on GC@NG.

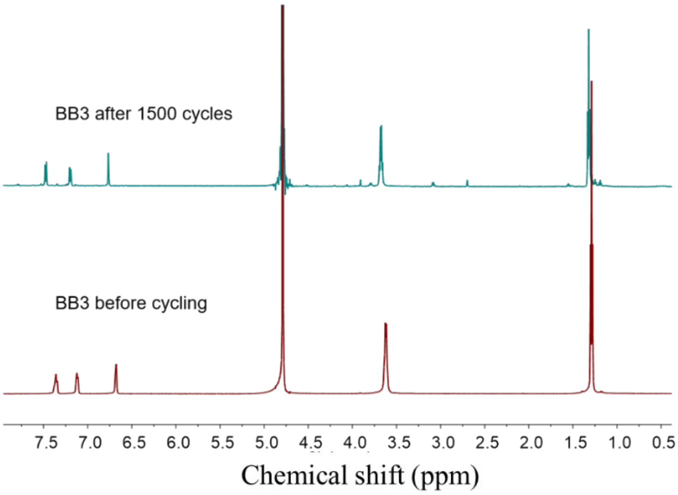


Figure S12. Typical ^{1}H NMR spectra of BB3 before and after 1500 cycles in full battery.

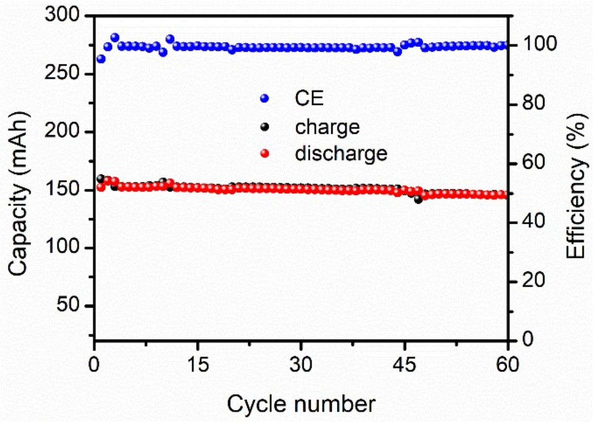


Figure S13. Charge/discharge capacity and CE of the ARFB with 0.5 M BB3 catholyte using CP@NG as the working electrode at 60 mA/cm^2 for 60 cycles.

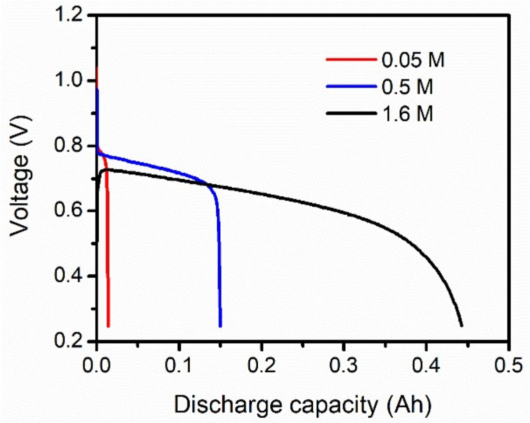
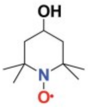
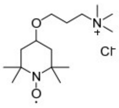
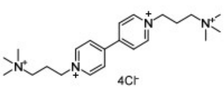
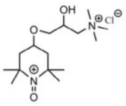
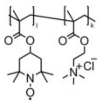
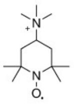
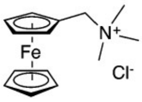
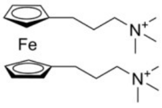
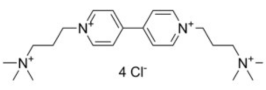
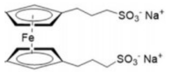
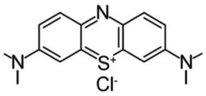
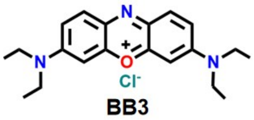


Figure S14. Discharge curves of 0.05 M, 0.5 M and 1.6 M BB3 catholyte used in CP@NG based full batteries, respectively.

Table S1. Comparison of technical characters of the reported catholytes in ARFBs

catholyte	anolyte	Supporting solution	C (M)	Cycles (n)	Capacity retention (per cycle)	Ref
		1 M NaCl	0.1	100	>99%	5
		2 M NaCl	0.1	1000	99.995%	6
	Zn	1 M NaCl	0.2	140	99.954%	7
	Zn	1 M NaCl	0.01	1000	99.979%	8
		0.1 M NaCl	2	100	99.92%	9
		2 M NaCl	0.5	700	99.99%	10
		2 M NaCl	0.75~1	500	99.9989%	11

	Zn	0.5 M Na_2SO_4	1.5	60	No fade	12
	V^{2+}	3.5 M H_2SO_4	0.1	900	No fade	13
 **BB3**	**V^{2+}**	**3.5 M H_2SO_4**	**0.05**	**1500**	**>99.991%**	**This work**

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