

Electronic Supporting Information

***In situ* Electrochemical Electron Paramagnetic Resonance Spectroscopy as a tool to probe Electrical Double Layer Capacitance**

Bin Wang[†], Alistair J. Fielding^{‡*}, Robert A.W. Dryfe^{†*}

[†]School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom.

[‡]School of Pharmacy and Biomolecular Science, Liverpool John Moores University, James Parsons Building, Byrom Street, Liverpool, L3 3AF, United Kingdom.

Experimental Section

Experimental Section

Activated Carbon The testing material was commercial activated carbon (AC, YEC-8B, surface area $\sim 2000 \text{ m}^2/\text{g}$, Fuzhou Yihuan Carbon), prepared at around $700\text{-}800^\circ\text{C}$. The C/O ratio was around 10 and the oxygen exists mainly as hydroxyl group and carboxyl groups. Different electrodes from the same batch of activated carbon (AC) gave similar results and are reflected in the error bars associated with the data. Different batches of AC (from our supplier: Fuzhou Yihuan Carbon) were also tested. The manufactures specifications are (Table S1):

- i) YEC-*B, specific surface area = $2000 \text{ m}^2/\text{g}$, capacitance = 150 F/g
- ii) YEC-*A, specific surface area = $2100 \text{ m}^2/\text{g}$, capacitance = 210 F/g

	YEC-8B	YEC-8A
Specific Surface Area (m^2/g)	2000	2100
Ash content (%)	0.21	0.26
Iron Salt (%)	0.003	0.005
Particle Size (μm)	10	10
Capacitance (F/g)	160	210

Table S1. Commercial specifications of AC.

The ash content of the two materials is also slightly different (0.05 %). The particle size is very similar for both grades and the impurity content (mostly Fe) is also the same, at around 0.1 %. Significantly, both these samples gave spectroscopic results that lay within the stated error.

Electrode Preparation Normally, the commercial AC was first suspended in IPA/Water (volume ratio 1:1) with sonication treatment (37 kHz, 350 W effective power, Fisherbrand FB11205 Ultrasonic Cleaner) for 1 h. The electrode was made by filtration of the AC suspensions using a PTFE film (25 mm hydrophilic PTFE membrane filter with a $0.1 \mu\text{m}$ pore size and the maximum thickness of $140 \mu\text{m}$, Merck Millipore

Company). After being dried at 80 °C, a layer of AC/PTFE film was rolled onto a platinum wire (0.5 mm diameter) with another Pt wire (99.99 %, 0.05 mm diameter, Advent, UK) intertwined around it. Before use, all Pt wires were flame cleaned. The final mass of AC was around 0.5 mg and the final surface area of AC electrode was around 5.5 mm². The thickness of the AC layer on PTFE membrane was around 10 µm as shown in Figure S1b. The conductivity of the AC membrane is around 4 S m⁻¹.

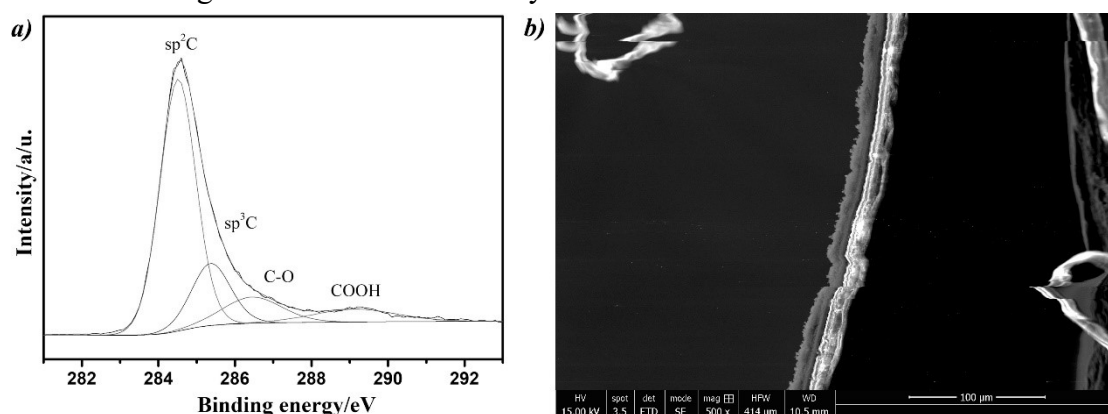


Figure S1. a) XPS of the AC powder and b) SEM image of prepared AC/PTFE membrane.

Cell Design A photograph and a detailed schematic of the experimental setup are shown in Figure 1a. The Ag|AgCl reference electrode (RE) was made by oxidation of a partially exposed PTFE coated silver wire (0.2 mm diameter) in 0.1 M KCl solution. The counter electrode (CE) was made from platinum wire (0.125 mm diameter and the total area was around 1.5 mm²). The end of the prepared WE was linked with a partially exposed PTFE-coated silver wire (0.2 mm diameter) and worked as the current collector in order to reserve more space for other electrodes. The cell was assembled under anaerobic conditions in the glove box. Before assembly, the AC electrode was kept in vacuum (relative vacuum: -30 kPa) for 24 hours. After the electrodes were embedded into the quartz capillary (diameter 1 mm) used as the EPR cell, the opening was sealed by glue (Araldite 2-part epoxy). The electrolyte was bubbled with Ar for at least 1 h before use.

EPR Experiments The *in situ* electrochemistry was carried out with a small potentiostat (EmStat³⁺ Blue, PalmSens, the Netherlands). The signal was tested after the potential was applied for one minute, which produced a stable EPR signal. The EPR spectra were recorded at room temperature using a continuous-wave (CW) Bruker Micro

spectrometer. In all cases the microwave frequency was around 9.8 GHz and the modulation amplitude microwave power was 2 mW. The spectra were the average of 20 scans. The Q value of the microwave cavity was monitored during the course of the electrochemical experiment by using a Ruby placed inside the microwave cavity and was found to show a constant value over potential. The temperature dependence experiment was carried in the range between 200 K and 4.2 K under non-saturating conditions (Figure S2d). Temperature calibration was carried out using a temperature sensor probe (Cernox[®], Lake Shore Cryotronics, Inc.) inserted into the sample position. Normally, the electrode was frozen immediately with liquid nitrogen for low temperature measurement, after applying a potential for 5 mins.

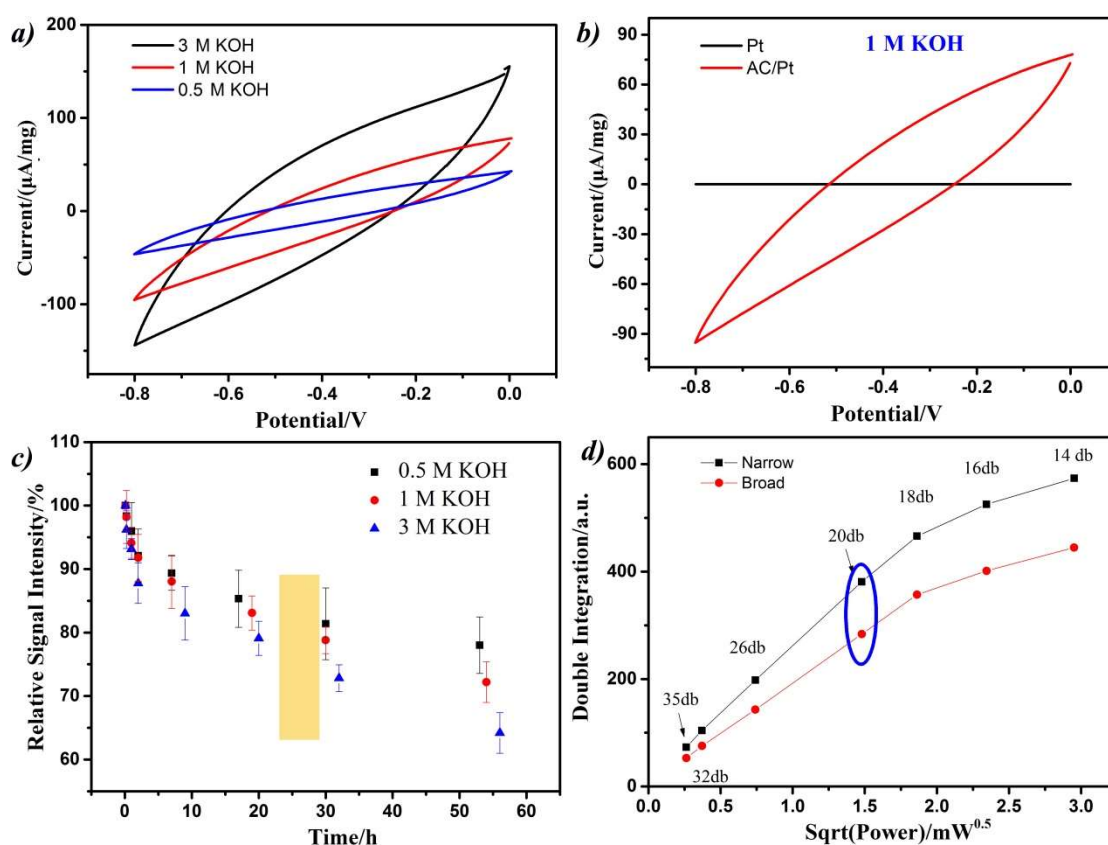


Figure S2. a) CV of the prepared AC electrode in KOH at different concentrations; b) CV of the pure Pt wire and AC electrode for comparative purposes; c) Time dependent EPR signal of AC in different electrolytes. d) EPR Power saturation curves of AC at 10 K.

The electrochemical performance of the assembled cells is shown in Figure S2 with the scan rate of 10 mV/s. The time dependent experiment shown in Figure S2c

was carried out by measuring the assembled cell. The benchmark was the intensity of the first EPR signal obtained (after ca. 10 mins exposure to the electrolyte). The prepared cell was left for 24 hours to reduce the influence from the chemical decay of the paramagnetic species in solution (see main text). The whole electrochemical process (for example, the potential excursion from -0.8 V to 0 V and back to -0.8 V) took ~ 2 h. Experiments were made after 24 hours (Figure S2c, yellow section) where in the 2 hour period of the electrochemistry the change due to the chemical decay was negligible in comparison (less than 3 %). As a result, we established that the change in Figure 1 was caused by the applied potential.

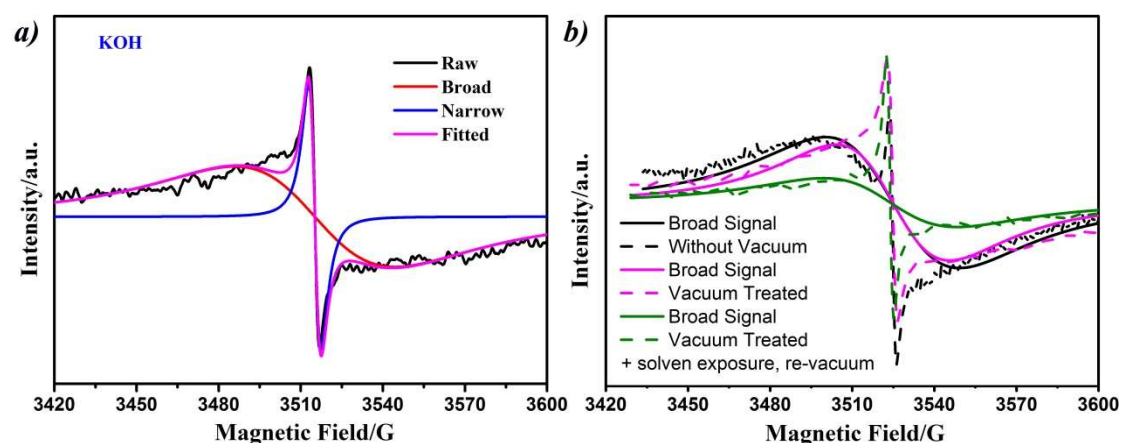


Figure S3. (a) CW EPR spectra of AC in KOH with different simulation components. (b) EPR signal of AC in KOH with different oxygen removal methods. The EPR signal intensity was normalized among different treatment methods so that the intensity of the narrow component was same. Solid lines represent the simulation of the broad component for ease of presentation.

EPR simulations were carried out using MatlabTM software. The lineshape of both components was assumed to be Lorentzian. The EPR signal of AC was found to have two components (Figure S3): a narrow curve with a width around 3 G and a broad component of (~ 40 G wide). A simple contrast experiment was used to test the influence of oxygen (Figure S3b). We did not find any change of the narrow curve with oxygen exposure. The AC gave a strong, broad component if AC was not vacuum treated. When the sample was vacuum treated, a far weaker broad signal was observed. If the sample was briefly exposed to electrolyte and re-exposed to the vacuum, the broad component

was the weakest, and attributed to greater removal efficiency of O₂. After the exposure, water molecules are more effective in displacing the oxygen molecules from the pores of the AC; resulting in the broad component becoming much weaker.

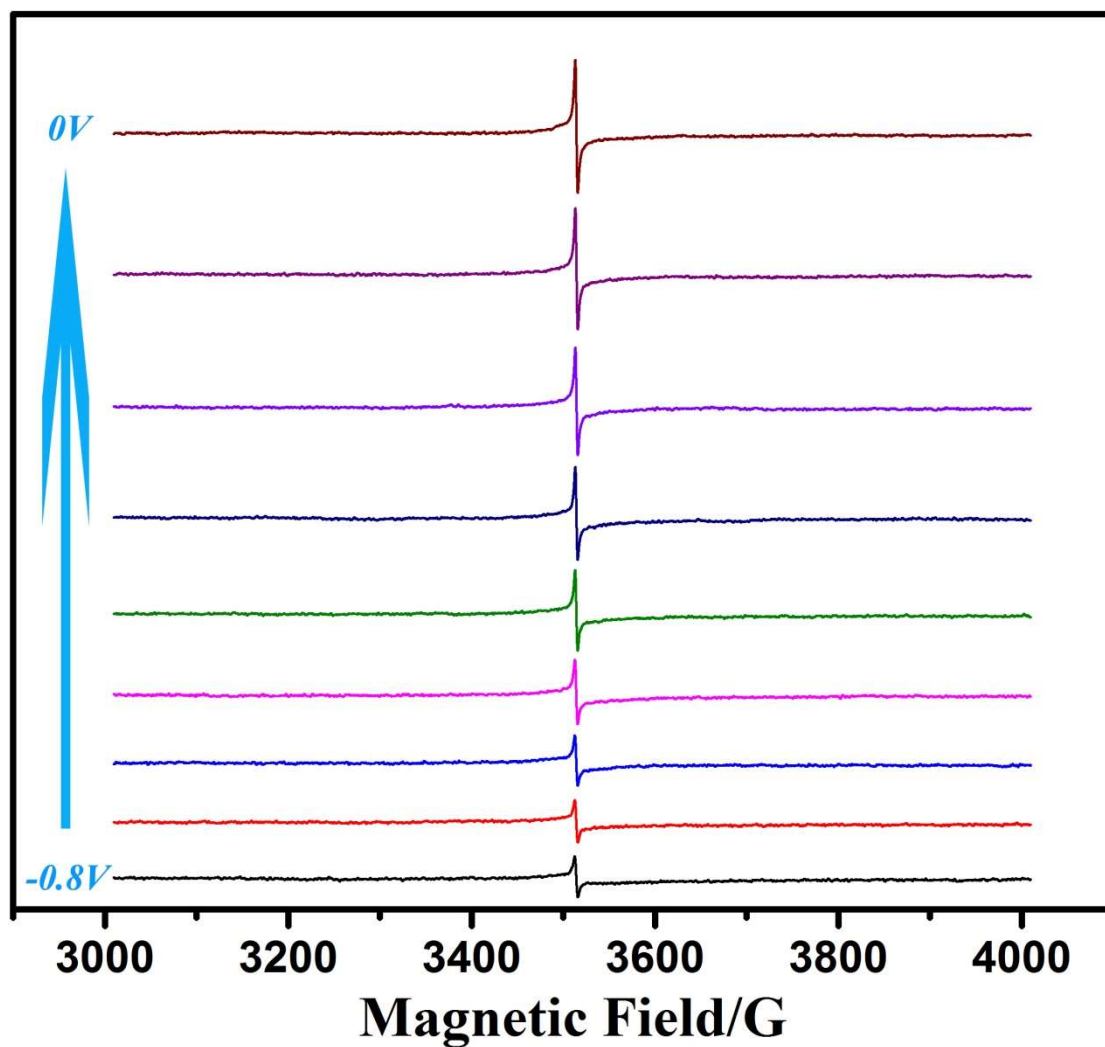


Figure S4. CW EPR spectra using a wide magnetic field range during the *in situ* process

EPR spectra using a wider field range (1000 G) were obtained using the same EPR parameters with 5 scans. No other peaks were found during the *in situ* electrochemical process.

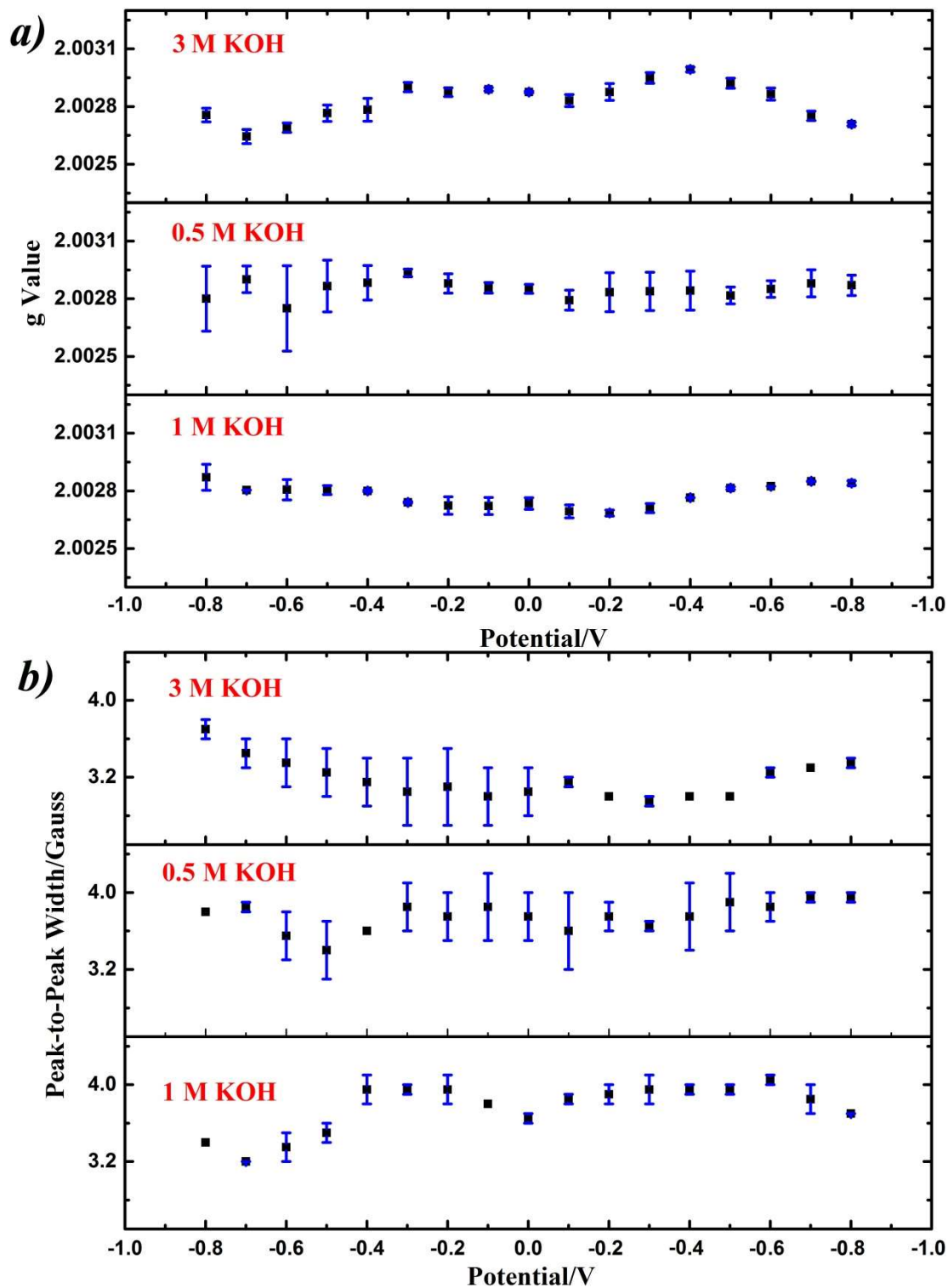


Figure S5. (a) *g* Value and peak-to-peak linewidth. Corrections were made for any drift of microwave frequency. (b) Change with potential in different concentrations of KOH electrolyte.

The fluctuation range of the *g* value in each electrolyte was 0.0002 (3 M), 0.0003

(0.5 M) and 0.0004 (1 M), which was very small. This indicated that only carbon-centred/carbon-oxygen centered radicals were generated during the experiments. Also, little change was observed in the peak-to-peak width, which fluctuated around ~ 3.8 G.

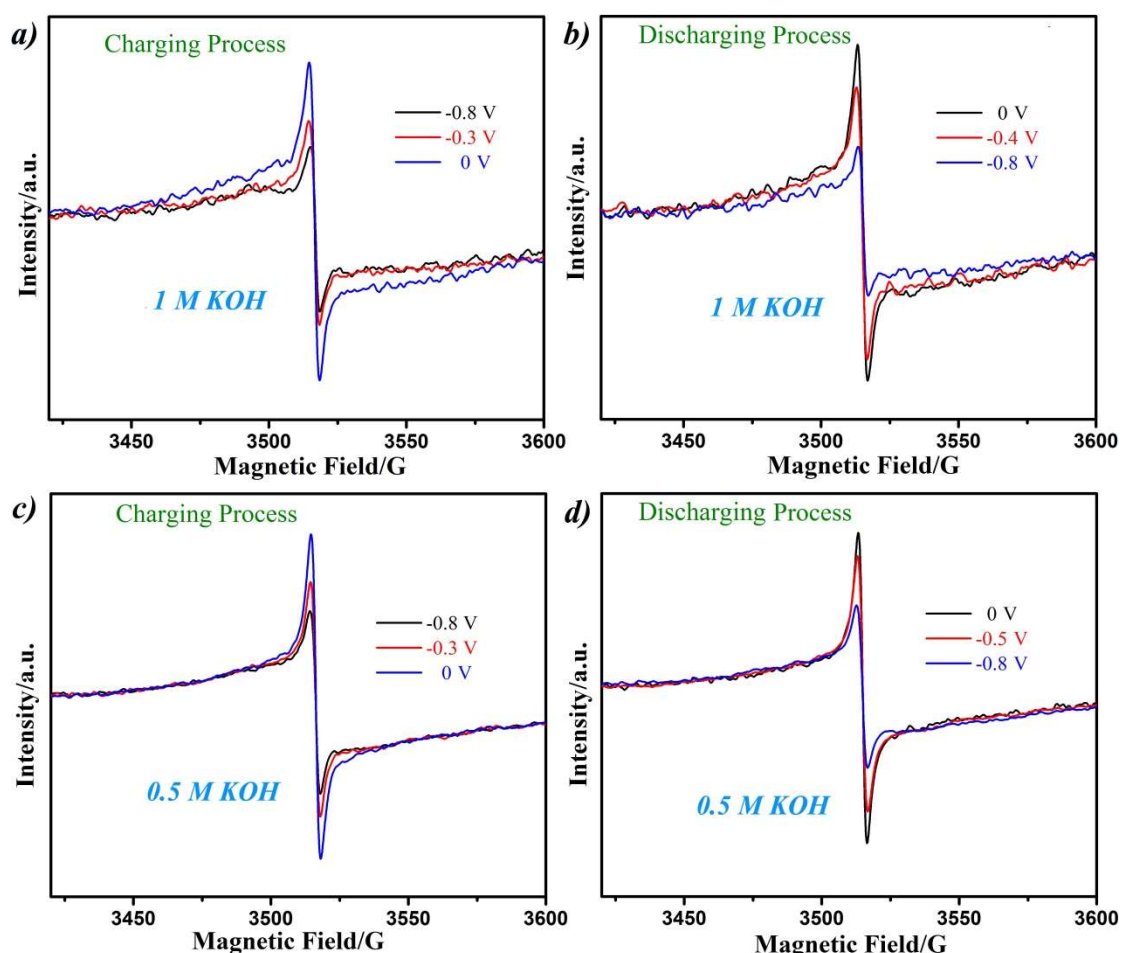


Figure S6. EPR signal change during charging (a) and discharging (b) in 1 M KOH; EPR signal change during charging (c) and discharging (d) in 0.5 M KOH.

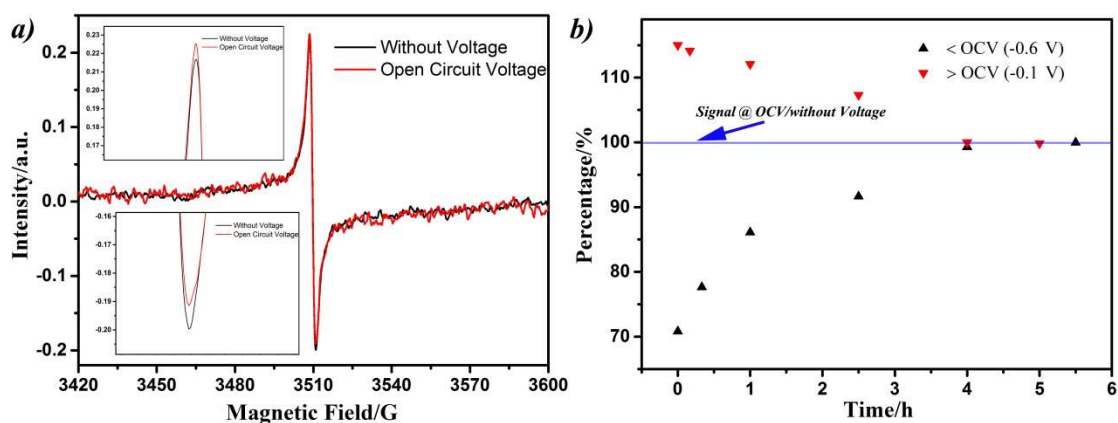


Figure S7. (a) EPR signal under OCV and (b) the stability of signal after an applied voltage

The experiment was carried out in 1 M KOH solution and the open circuit voltage (OCV) was around -0.3 V. The stability experiment shown in Figure S7b was carried out as following: Initially, the electrode was set to a potential for 10 mins and, then, the first signal was collected. Afterwards, the applied potential was removed and the signal change was monitored.