Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Aqueous electrolyte mediated reversible K^+ ion insertion in graphite

Ritupurna Baishya[a], Devalina Sarmah[a], Debajyoti Mahanta[b], Shyamal K. Das[#a]

[a]Department of Physics, Tezpur University, Assam 784028, India
[b]Department of Chemistry, Gauhati University, Assam 781014, India

Experimental

Two types of graphite were used for the study. Pyrolytic graphite (0.017 mm) and natural graphite (0.5 mm) foils are respectively procured from MTI Corporation, USA and Nickunj Eximp Entp P Ltd, India. These foils were cleaned with ethanol prior to use and no other chemical treatment was performed unless specified. For another set of experiments, exfoliated natural graphite was utilized and the exfoliation was performed as reported by our group earlier and the surface of this exfoliated graphite consists of graphitic nanoflakes [20].

Cyclic voltammetry (CV) and galvanostatic discharge/charge experiments were performed in a conventional three-electrode electrochemical glass cell with graphite foil, Pt electrode and an aqueous Ag/AgCl electrode (in KCl solution) as working, counter and reference electrodes respectively. The utilized electrolyte was an aqueous solution of KOH (purity of 84%) of varying concentrations. The discharge/charge and CV experiments were performed in the voltage range of -0.9 V to 0.3 V. Electrochemical impedance spectroscopy was performed in the frequency range of 1 mHz -200 kHz with a signal amplitude of 10 mV.

Structural and morphological investigations were carried out using techniques such as XRD (BRUKER AXS D8 FOCUS; Cu-K_α radiation, $\lambda = 1.5406$ Å), Raman spectroscopy (RENISHAW BASIS SERIES having 514 laser excitation), atomic force microscopy and contact angle measurement. Raman experiments were performed in two types of natural graphite; one in pristine form another one with electrochemical experiments performed on it. The samples were washed and dried properly before performing Raman analysis. For ex-situ measurements, the graphite electrodes were cleaned with DI water after the electrochemical experiments and these electrodes were dried at 100°C for 12 h. The XPS measurements were performed in two sets of natural graphite electrodes. In the first set, electrochemical measurements were done in the graphite sheet after discharge. A reference XPS measurement was also performed. In this case, a piece of natural graphite electrode was submerged in 6 M KOH for 24 hour and, after it, it was washed with distilled water and dried at 100°C for 12 h. All experiments were carried out at room temperature and under ambient atmosphere.

[#] *Corresponding author; email: skdas@tezu.ernet.in; Tel: +91-3712275586; Fax: +91-3712267005*

Calculation of Diffusion coefficient

The Diffusion coefficient ($D_{K}{}^{+}$) can be estimated from the following Equation (ref 31,32 of main text):

$$D_{K}^{+} = 0.5\left(\frac{RT}{An^{2}F^{2}C\sigma_{w}}\right)^{2}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (298.15 K), A is the surface area of the electrode (1 cm^{2}), n is the number of electrons transferred, F is Faraday constant (96500 C mol^{-1}), C is the concentration of K^{+} ion in the solution (6 M), and σ_{w} is the Warburg coefficient, which is calculated by the following Equation (at low-frequency region).

$$Z' = R_{S} + R_{CT} + \sigma_{w}\,\omega^{-0.5}$$

where R_{S} is the electrolyte resistance, R_{CT} is the charge transfer resistance, σ_{w} can be obtained from the slope of linear fitting of the real part of impedance (Z′) vs. the reciprocal square root of angular frequency ($\omega^{-0.5}$). The linear fitting is shown in figure S15 (b) below. The calculated diffusion coefficient is in the range of 10^{-19} cm^{2} s^{-1}.

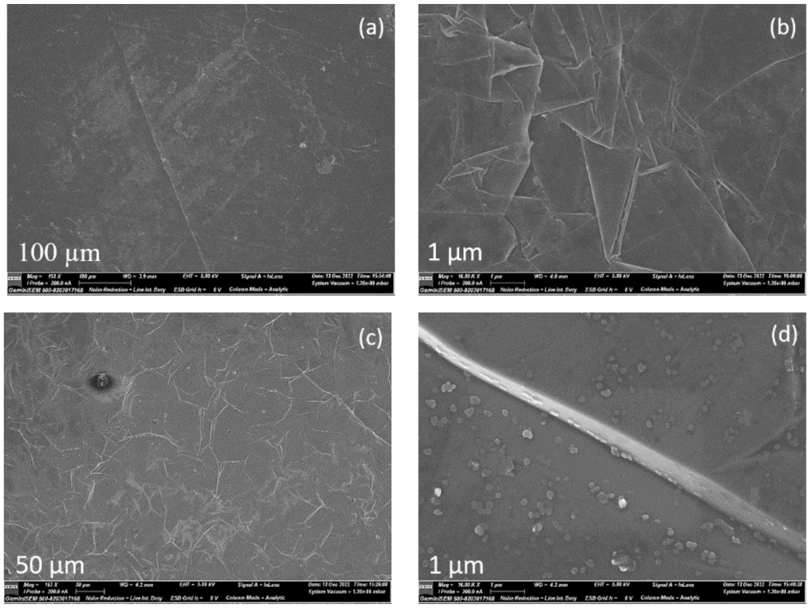

Figure S1. (a, b) FESEM images of natural graphite; (c, d) FESEM images of pyrolytic graphite

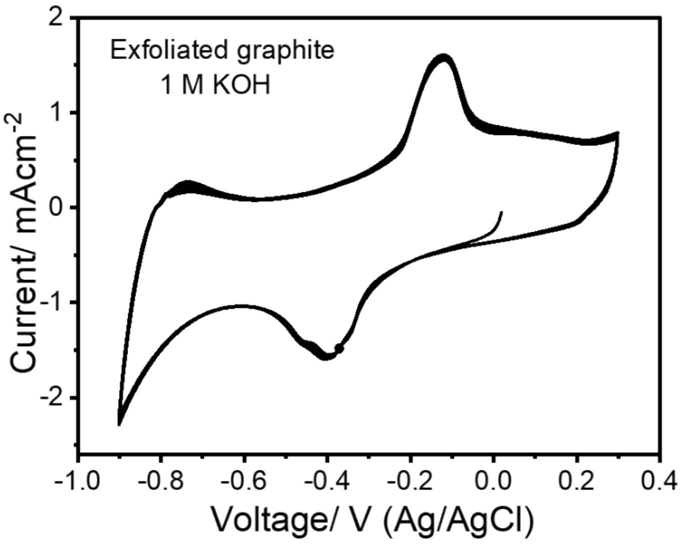

Figure S2. CV curve of exfoliated graphite in 1 M KOH electrolyte at a scan rate of 2.5 mVs^{-1} .

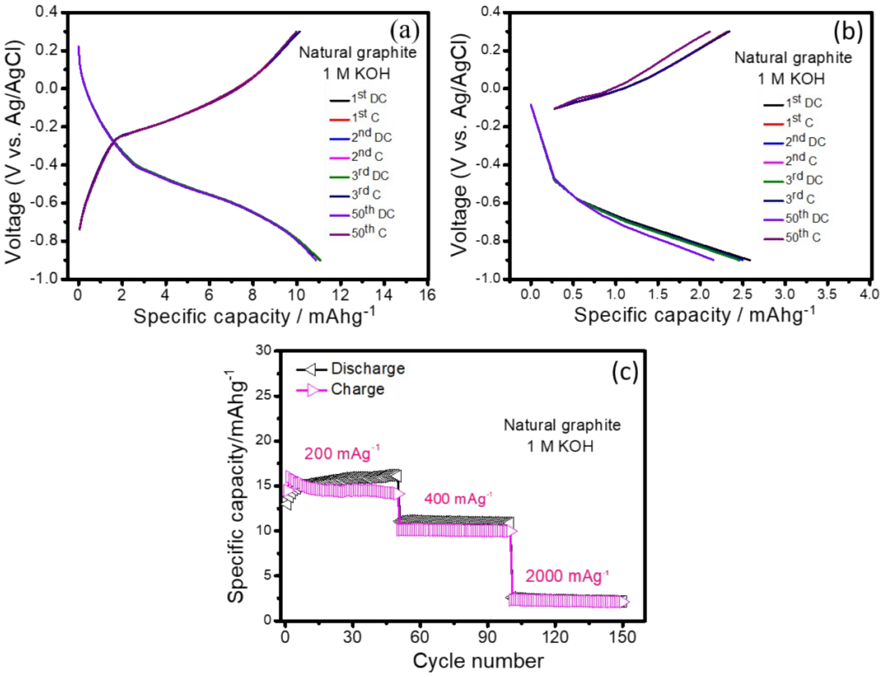

Figure S3. Charge/discharge curves of natural graphite in 1 M KOH electrolyte at (a) 400 mAg^{-1}, (b) 2 Ag^{-1}, (c) rate capability measurement.

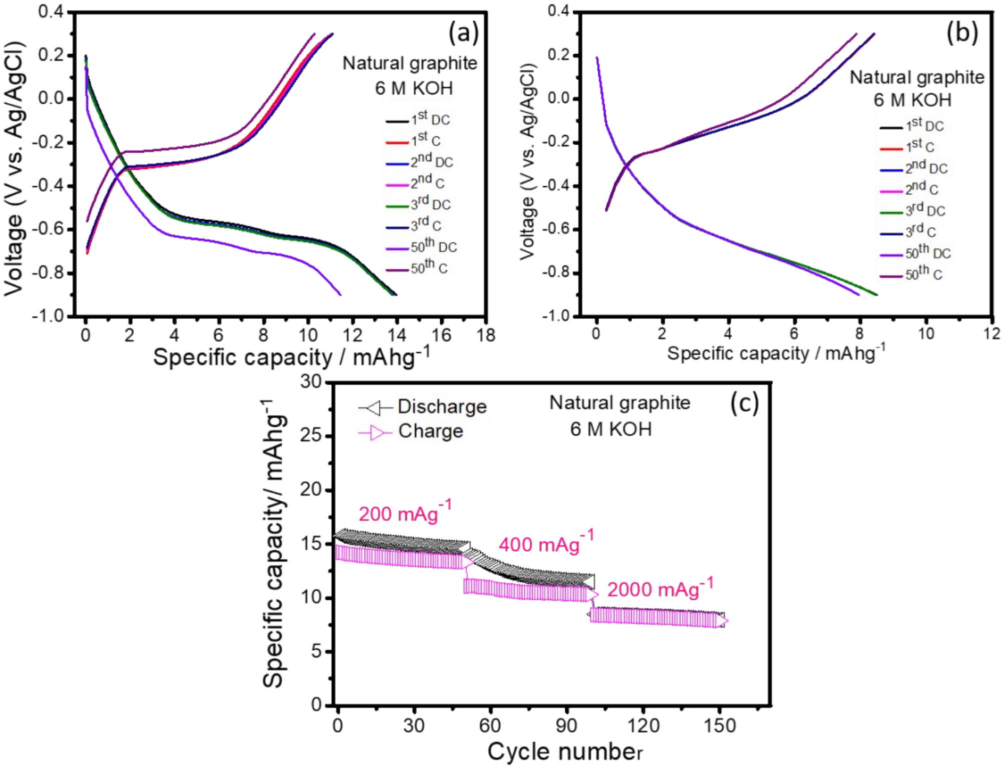

Figure S4. Charge/discharge curves of natural graphite in 6 M KOH electrolyte at (a) 400 mAg^{-1}, (b) 2 Ag^{-1}, (c) rate capability measurement.

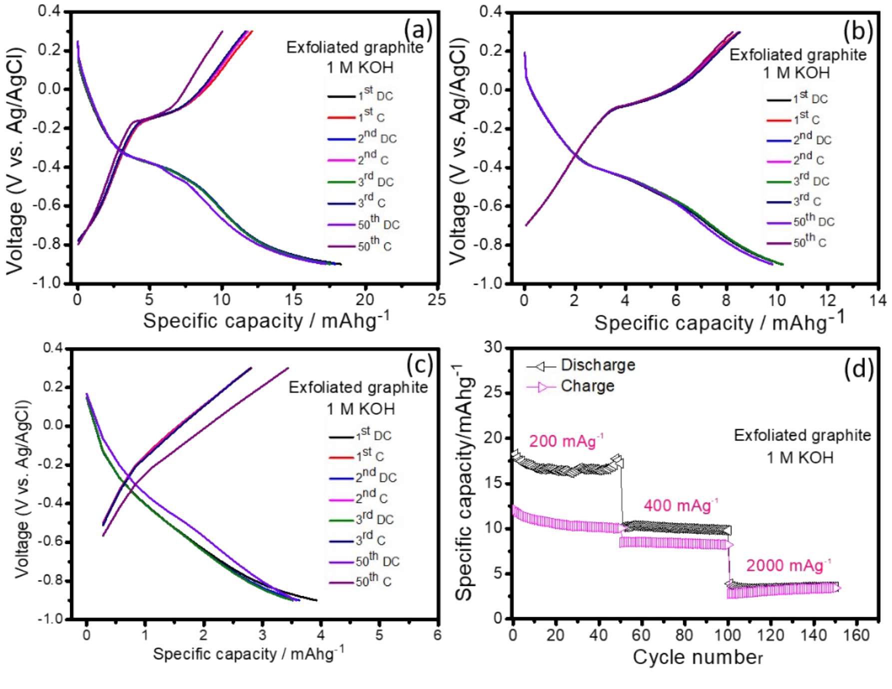

Figure S5. Charge/discharge curves of exfoliated graphite in 1 M KOH electrolyte at (a) 200 mAg^{-1}, (b) 400 mAg^{-1}, (c) 2 Ag^{-1}, (d) rate capability measurement.

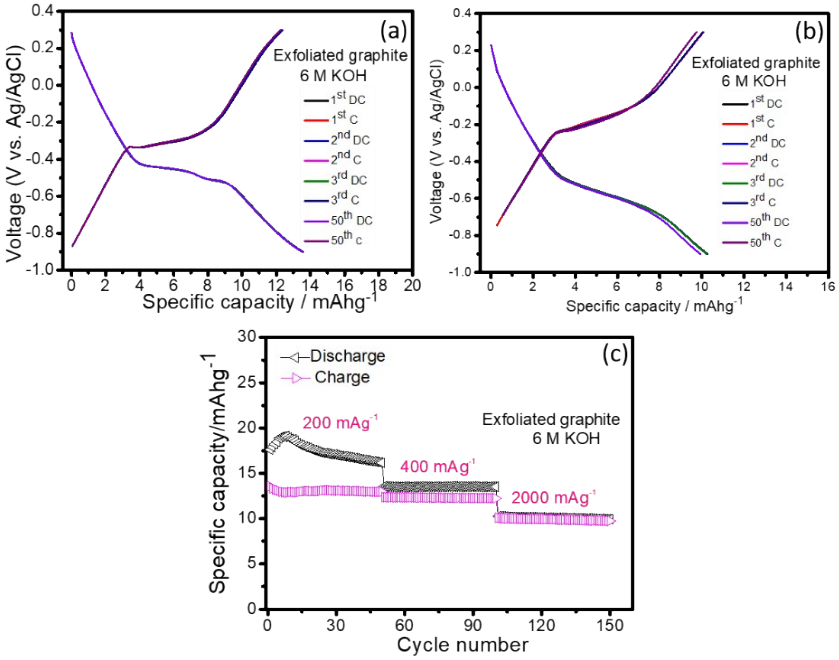

Figure S6. Charge/discharge curves of exfoliated graphite in 6 M KOH electrolyte at (a) 400 mAg^{-1}, (b) 2 Ag^{-1}, (c) rate capability measurement.

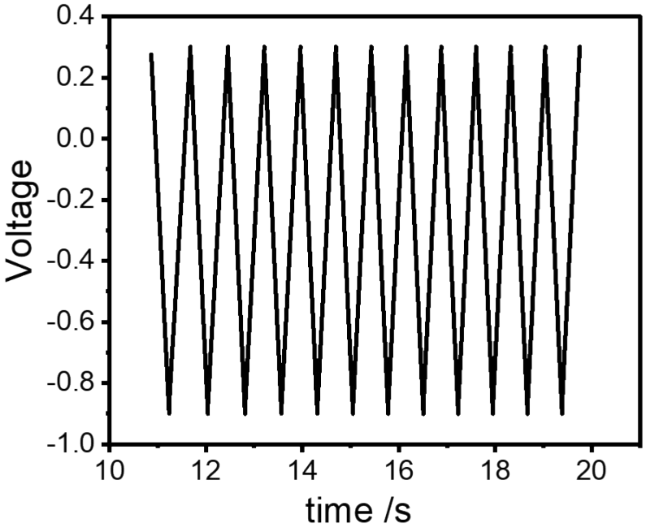

Figure S7. Charge/discharge curve of pyrolytic graphite in 6 M KOH electrolyte at 200 mAg^{-1}.

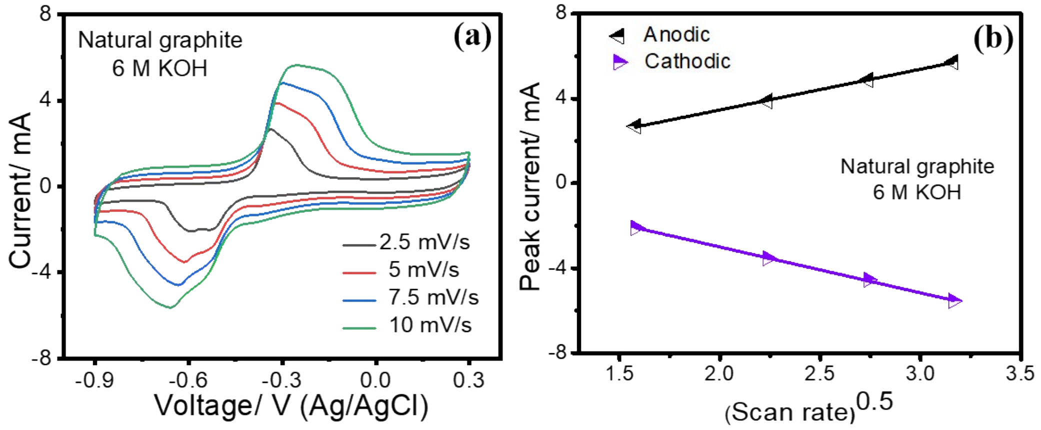

Figure S8. (a) CV curves of natural graphite at different scan rates and (b) plot of peak current vs scan rate. The electrolyte is 6 M KOH**.**

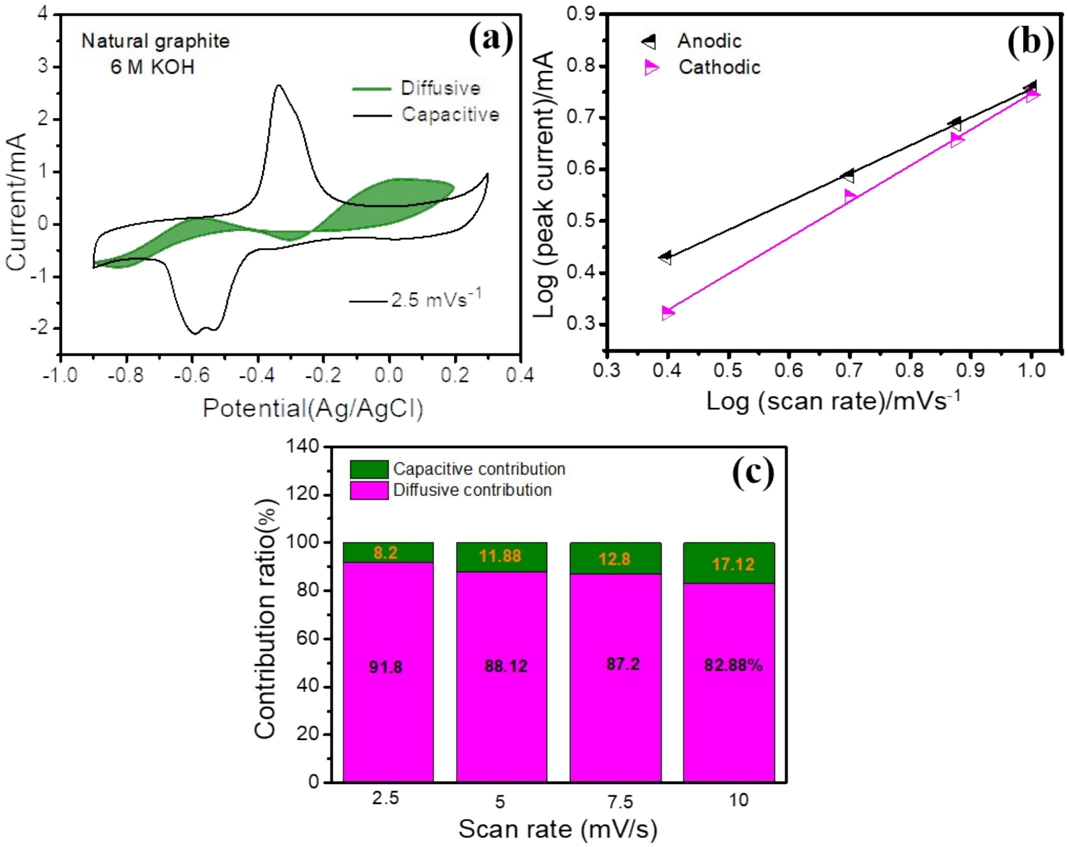

Figure S9. (a) Capacitive and diffusive contributions for 6 M KOH in natural graphite at 2.5 mVs^{-1}, **(b)** Log (peak current) vs Log (Scan rate), **(c)** Diffusive and capacitive contributions in percentage.

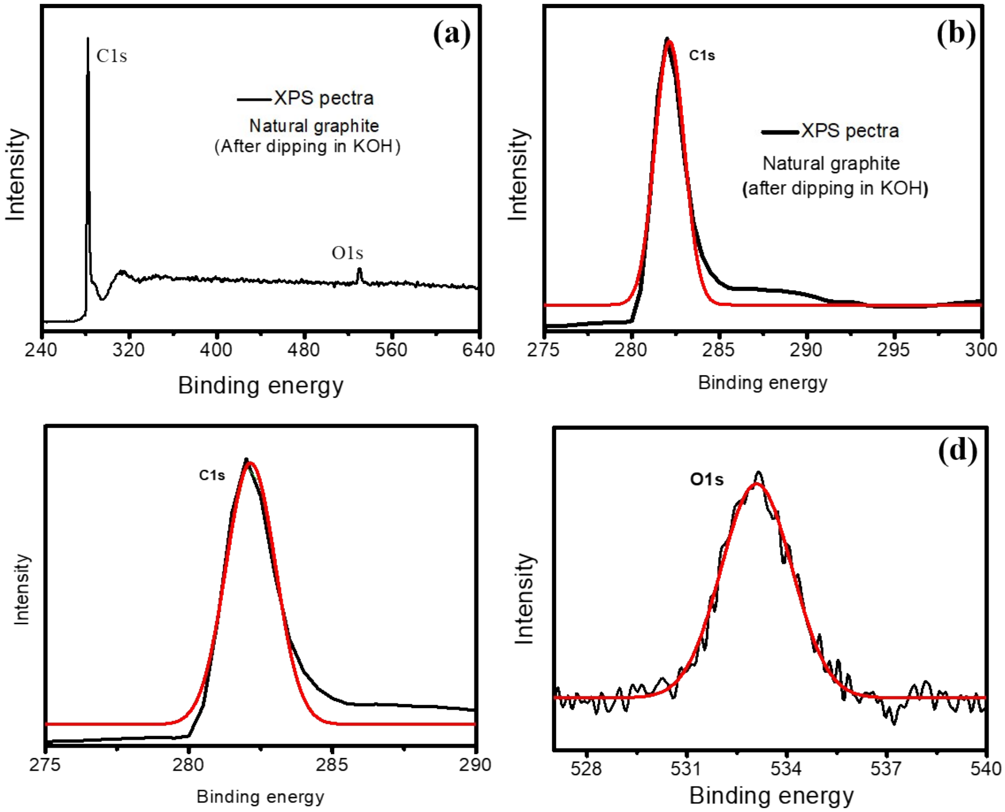

Figure S10. High resolution XPS spectra for the natural graphite electrode submerged in 6 M KOH. (a) Full XPS spectrum, (b) C 1s peak (no noticeable K2p peaks), (c) Enlarged C 1s, (d) O 1s.

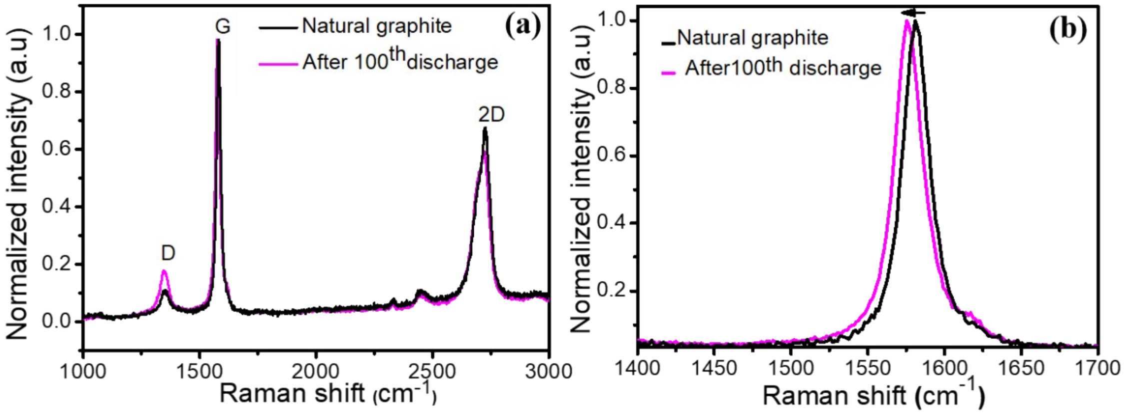

Figure S11. (a) Full raman spectra of natural graphite and natural graphite after discharge, (b) enlarged view of G band showing shift in the band position.

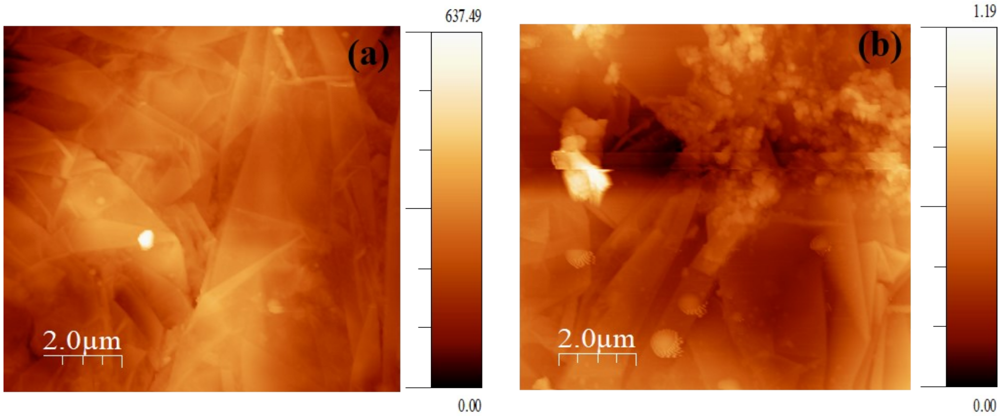

Figure S12. AFM analysis of natural graphite. (a) 2D AFM image of natural graphite, (b) 3D image of natural graphite after discharge.

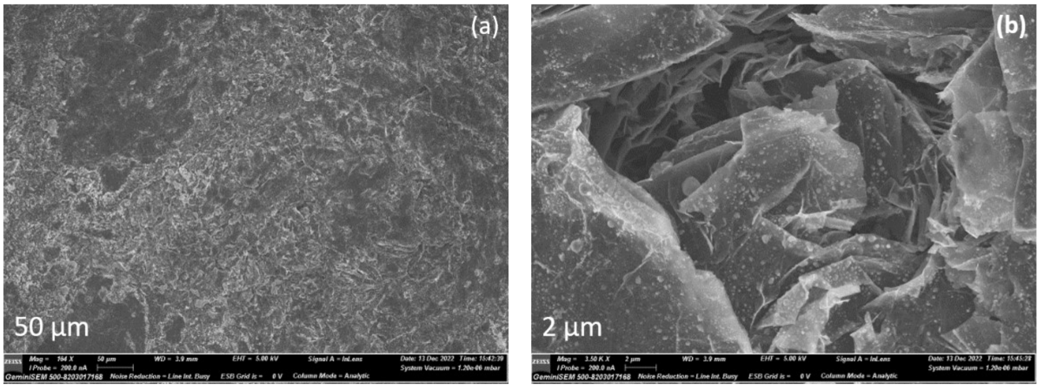

Figure S13. (a, b) FESEM images of natural graphite after discharge.

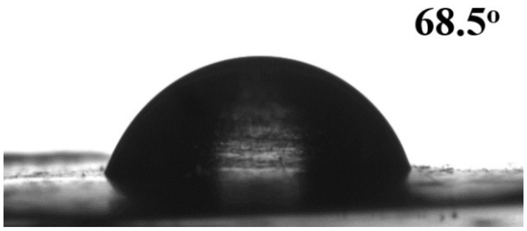

Figure S14. Contact angle measurement for natural graphite dipped in 6 M KOH electrolyte for 12 h.

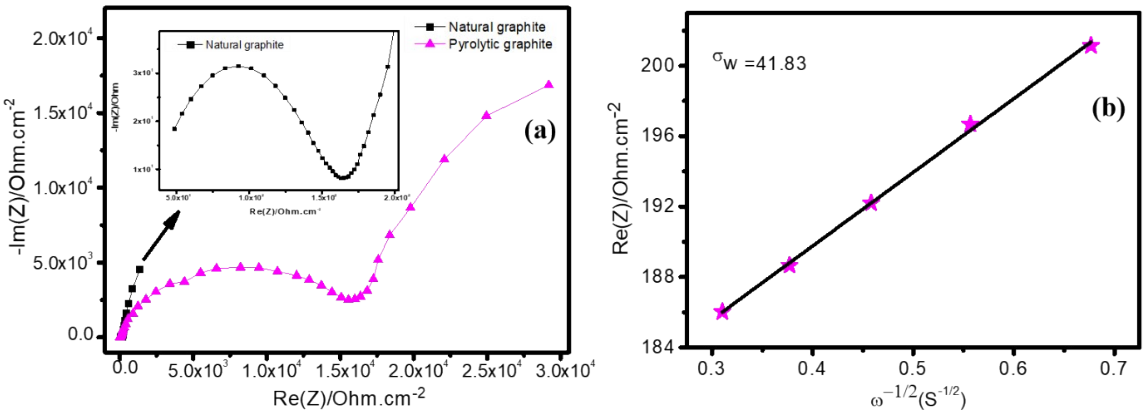

Figure S15. EIS spectra for (a) natural graphite and pyrolytic graphite, (b) The relationship curve between Z′ and $\omega^{-1/2}$ in the low-frequency range for natural graphite in 6 M KOH.

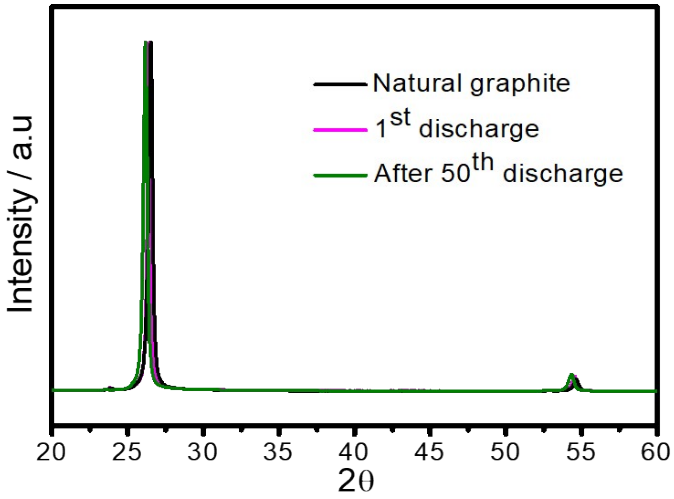

Figure S16. XRD patterns of natural graphite, after 1st and 50th discharge.

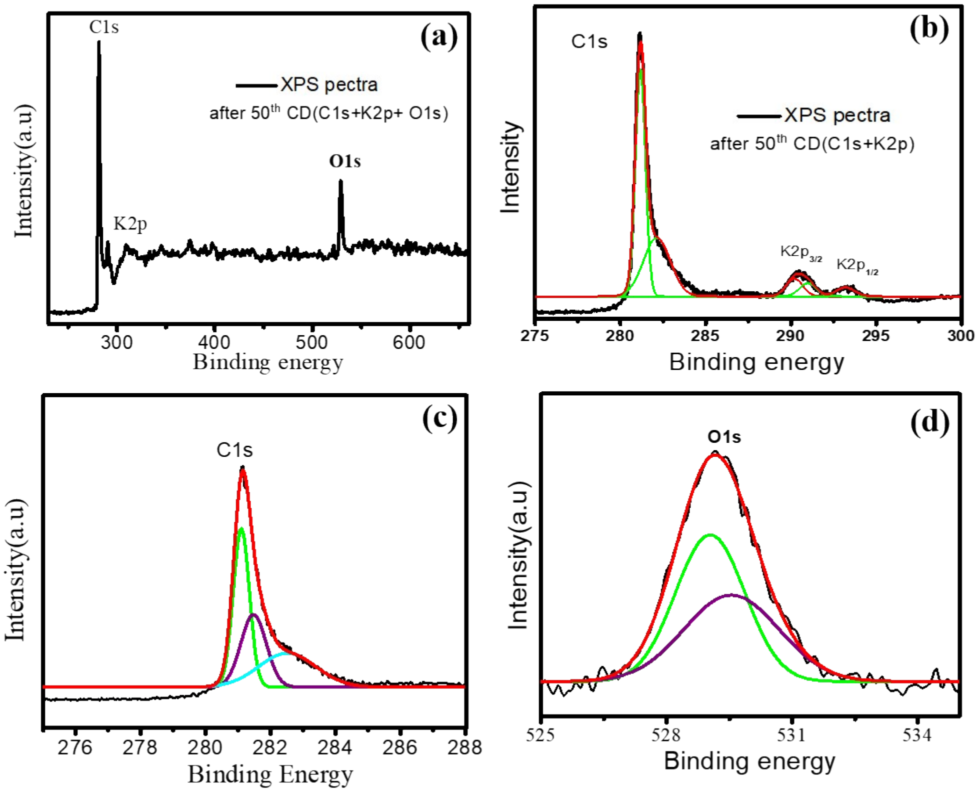

Figure S17. High resolution XPS spectra for discharged natural graphite electrode (a) Full XPS spectra, (b) C 1s and K2p peaks, (c) C 1s, (d) O 1s.