Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary material

Exactly matched pore size for intercalation of electrolyte ions determined using tunable swelling of graphite oxide in supercapacitor electrodes

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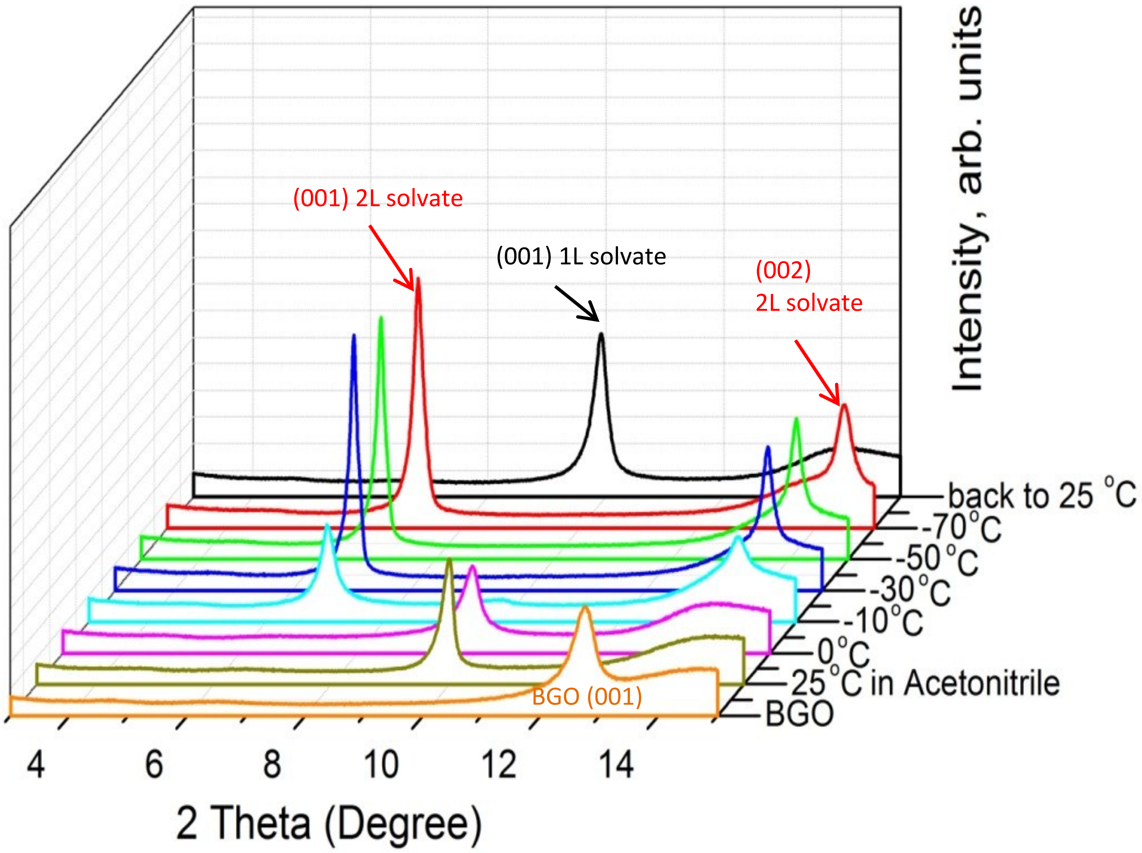

Fig. S1. XRD (λ=1.5418 Å) pattern recorded from BGO in acetonitrile upon cooling and heating back to 25 °C. BGO immersed in excess of acetonitrile shows phase transition between 1-layer solvate phase at ambient temperature to 2-layer solvate phase at low temperatures.

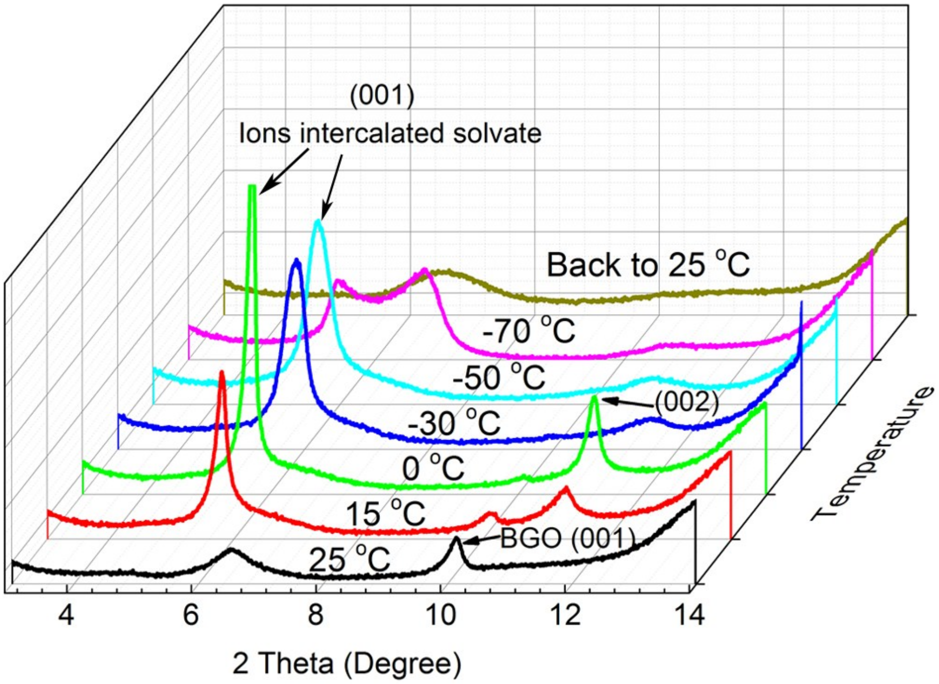

Fig. S2. XRD (λ=0.46794094 Å) patterns recorded from BGO in saturated TEA-BF_4 electrolyte upon cooling and heating back to 25 °C.

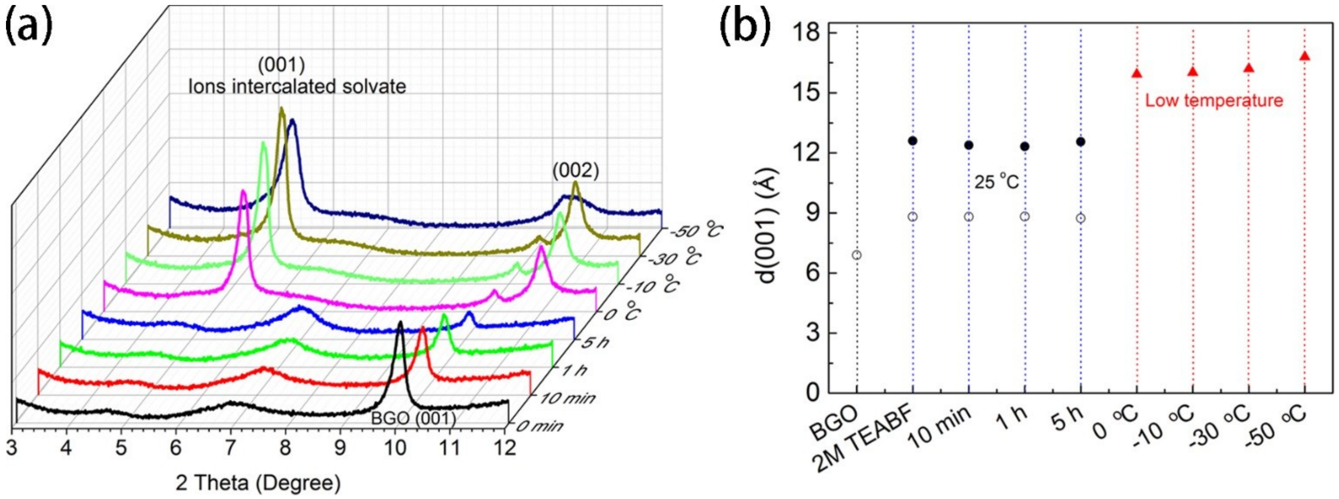

Fig. S3. (**A**) Selected XRD (λ=1.5418 Å) patterns recorded from BGO powder immersed in access 2 M TEA-BF_4/acetonitrile upon soaking up to 5h and then cooling to different temperatures with few minutes, and (**B**) the corresponding temperature dependence of d-spacings for 1-layer BGO/acetonitrile solvate phase (o), 2-layer BGO/acetonitrile phase (●) and TEA-BF_4 intercalated BGO/acetonitrile phase (□).

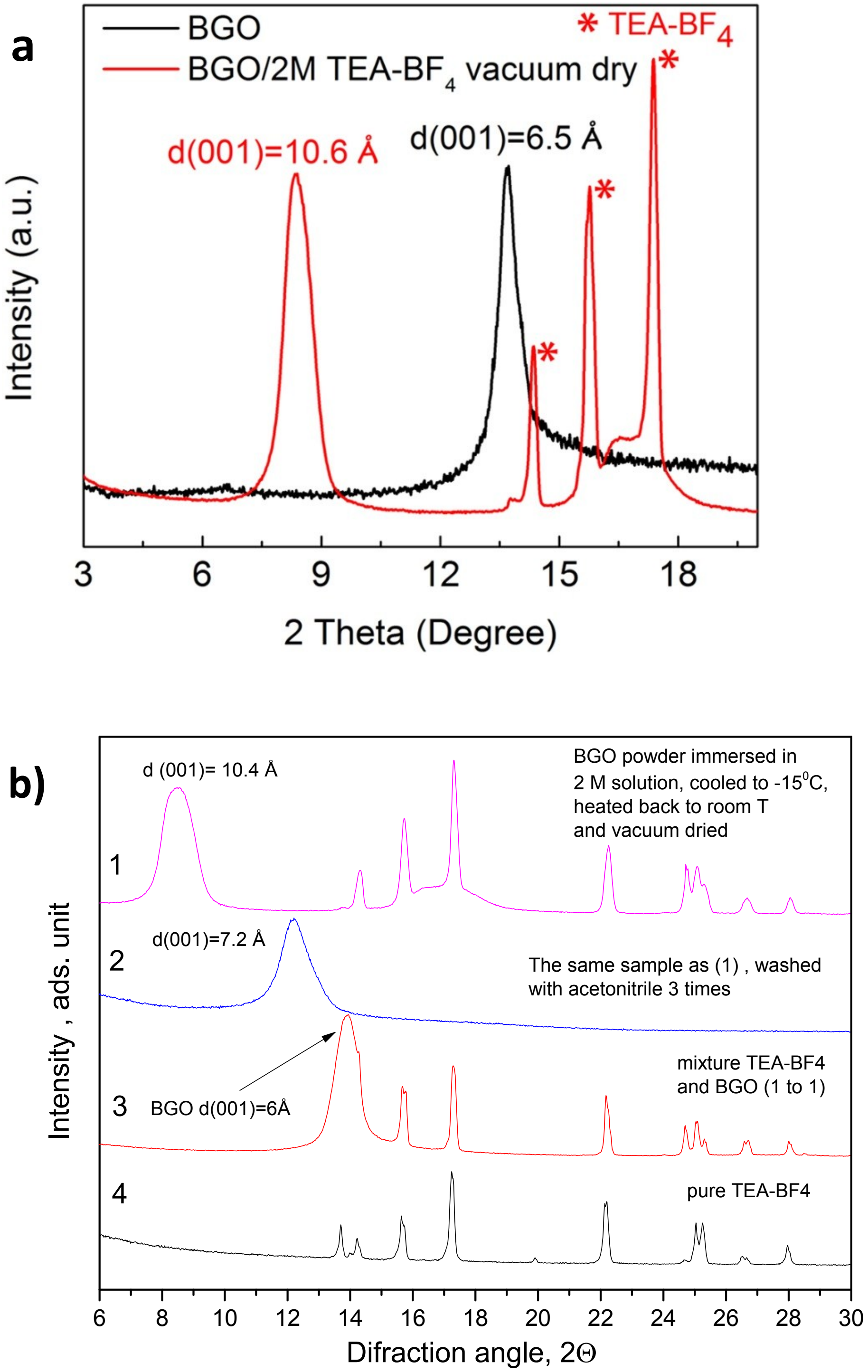

Fig. S4. XRD (λ=1.5418 Å) patterns recorded from: a) precursor BGO powder, BGO powder immersed in 2 M TEA-BF$_4$ electrolyte, cooled to -20 ^{0}C, heated back to ambient temperature and then vacuum dried overnight. Peaks marked by stars are from TEA-BF$_4$.

b) XRD patterns of TEA-BF_4 powder (4), mixture of BGO and TEA-BF_4 powders in 1:1 (by weight) proportion (3), sample immersed in 2M electrolyte, cooled to the temperature of solvate formation, heated back to ambient temperature and vacuum dried (1) and the same sample as (1) washed with acetonitrile three times (2). The sample (1) shows BGO lattice expanded to 10.6Å due to intercalation of TEA-$BF_{4.}$ The intercalation is non-covalent as it is evidences by easy removal of most of TEA-BF_4 by washing in acetonitrile.

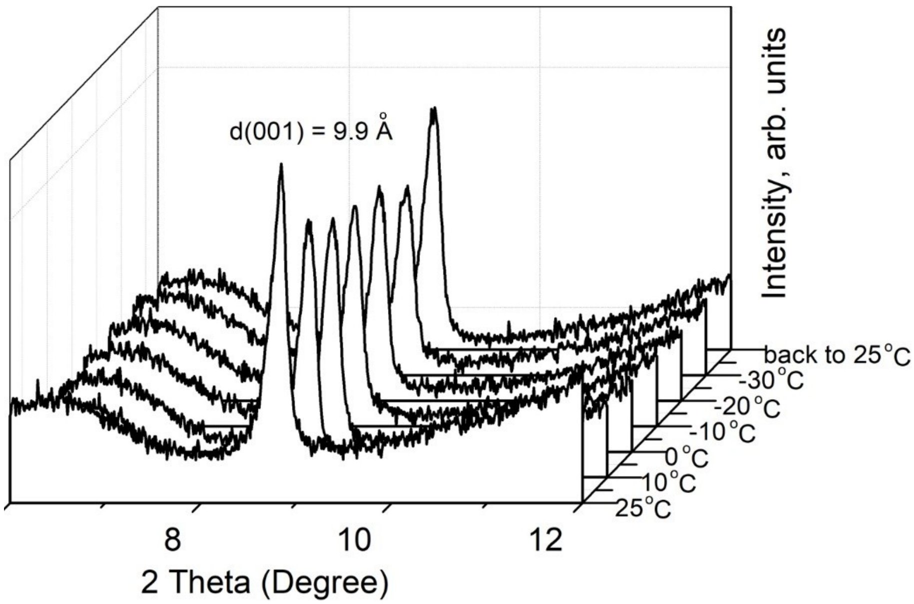

Fig. S5. XRD (λ=1.5418 Å) pattern recorded from BGO in 6 M KOH aqueous solution upon cooling and heating back to 25 °C.

KOH aqueous solution is commonly used aqueous electrolyte for supercapacitors. It was reported that both of the hydrated K^+ and OH^- ions are able to intercalate into GO after soaking in the corresponding solution for long time. However, the further expansion of GO interlayer distance was not observed upon cooling GO immersed in excess of 6 M KOH aqueous solution (Fig. S5). In agreement with our previous results, the d(001)= 9.9 Å found for BGO immersed in KOH solution is due to the intercalation of water into interlayers of GO. Note that BGO does not exhibit clear phase transitions when immersed in water. Moreover, it is impossible to detect intercalation of potassium ions into BGO structure using XRD methods.

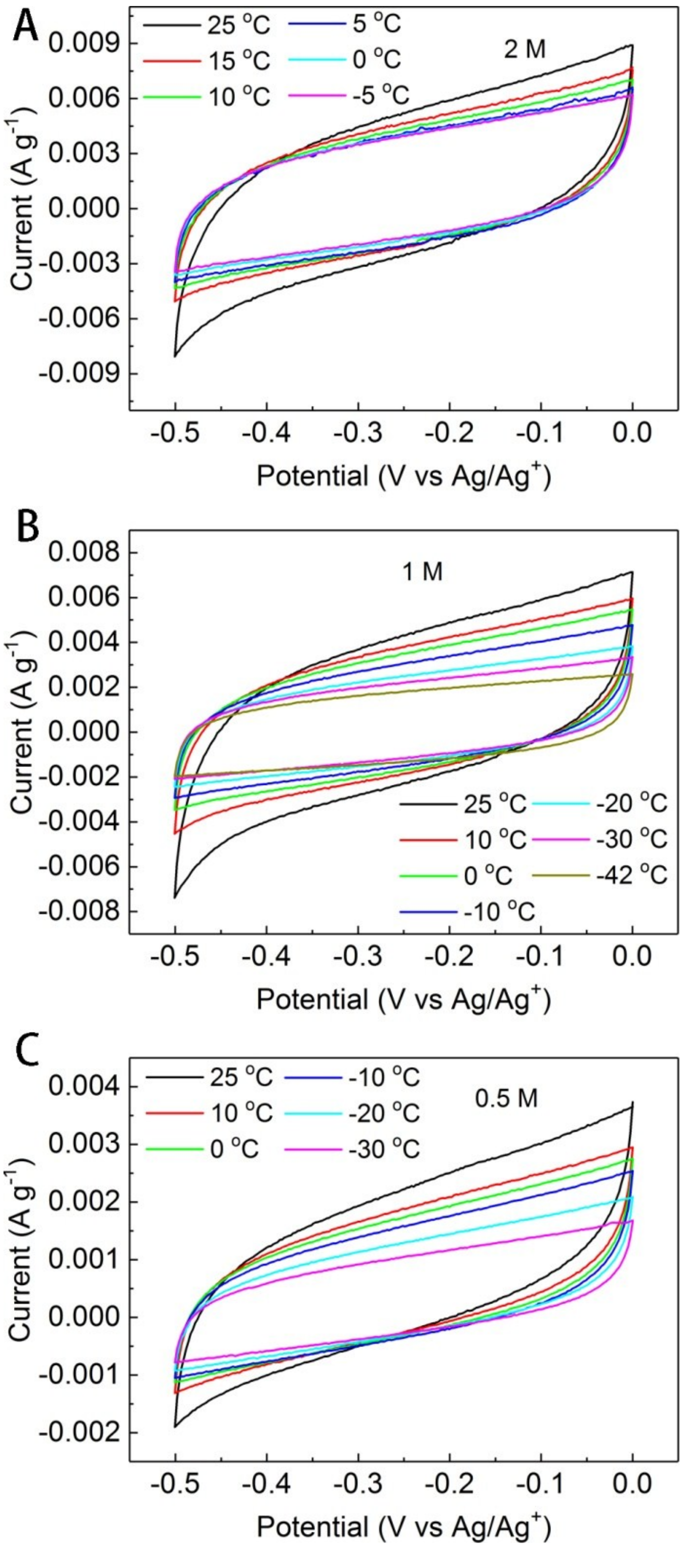

Fig. S6. CV curves of BGO electrodes in (**A**) 2 M, (**B**) 1M, and (**C**) 0.5M TEA-BF_4/acetonitrile upon cooling at scanning rate of 10 mV s^{-1}.

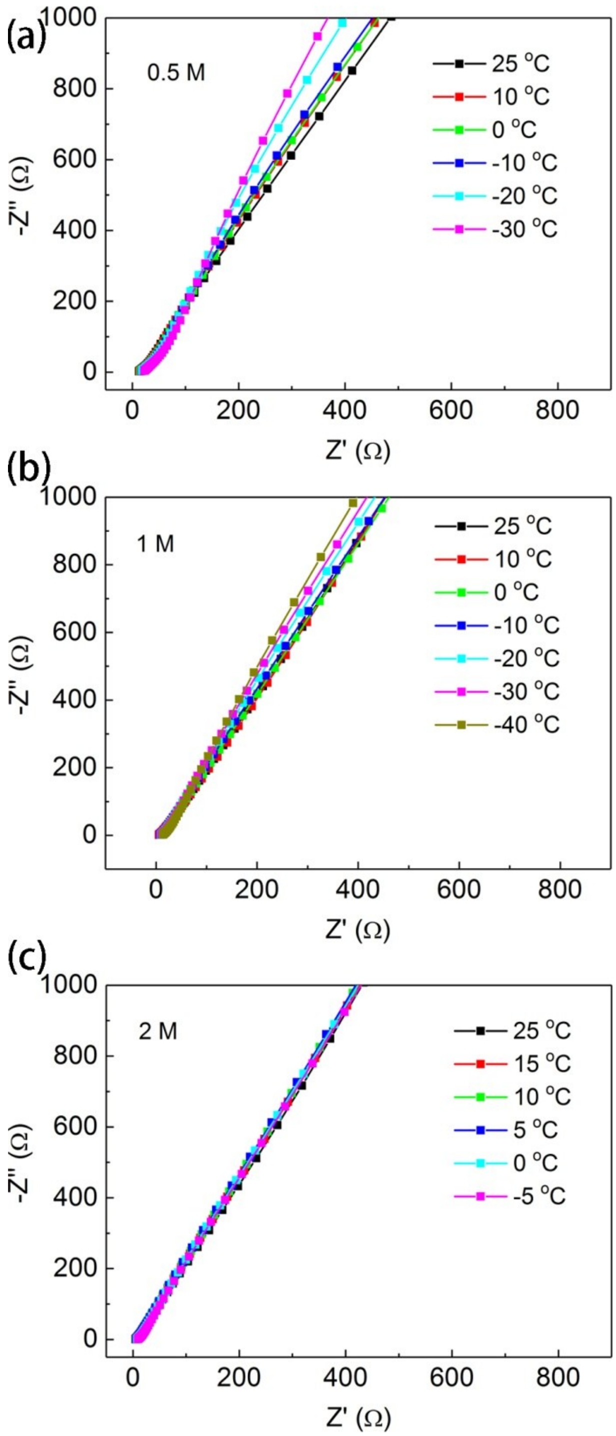

Fig. S7. Nyquist plots of BGO electrodes in (**A**) 0.5 M, (**B**) 1 M, and (**C**) 2 M TEA-BF$_4$/acetonitrile at different temperatures.

Nyquist plots for BGO electrodes immersed in 0.5 M, 1 M and 2 M electrolyte solutions were recorded at different temperature points starting from ambient and down to -40 ^{0}C (Fig. S7). The series resistance of BGO electrode obtained by intercept of Nyquist plots at the Z_{re} axis increased gradually upon cooling for all of three electrolytes. That is due to decrease in ionic conductivity of the bulk electrolyte. However, the ions diffusion within the BGO electrode improved upon cooling as evidenced by the steeper inclined line of Nyquist plots at low frequency region. This result is in agreement with expansion of interlayer distance of BGO upon cooling which result in the faster diffusion of ions in the enlarged interlayer space of BGO.

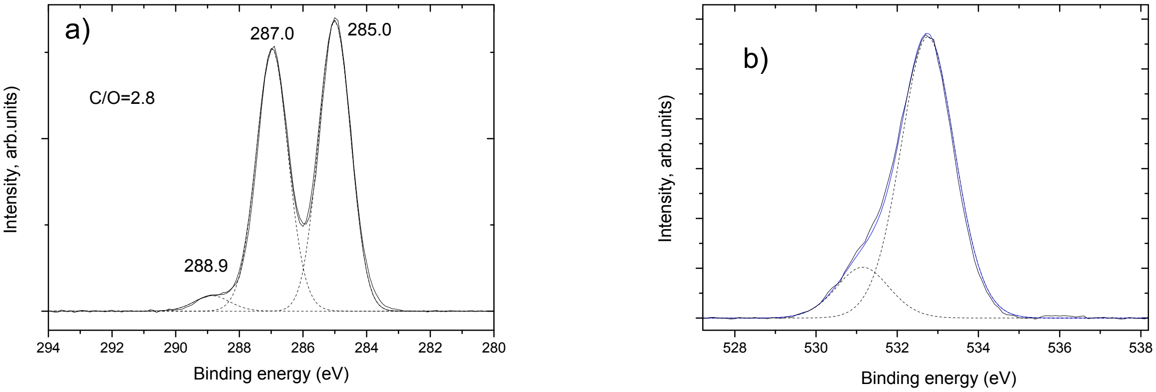

Fig. S8. XPS spectra of BGO powder: a) C1s and b) O1s

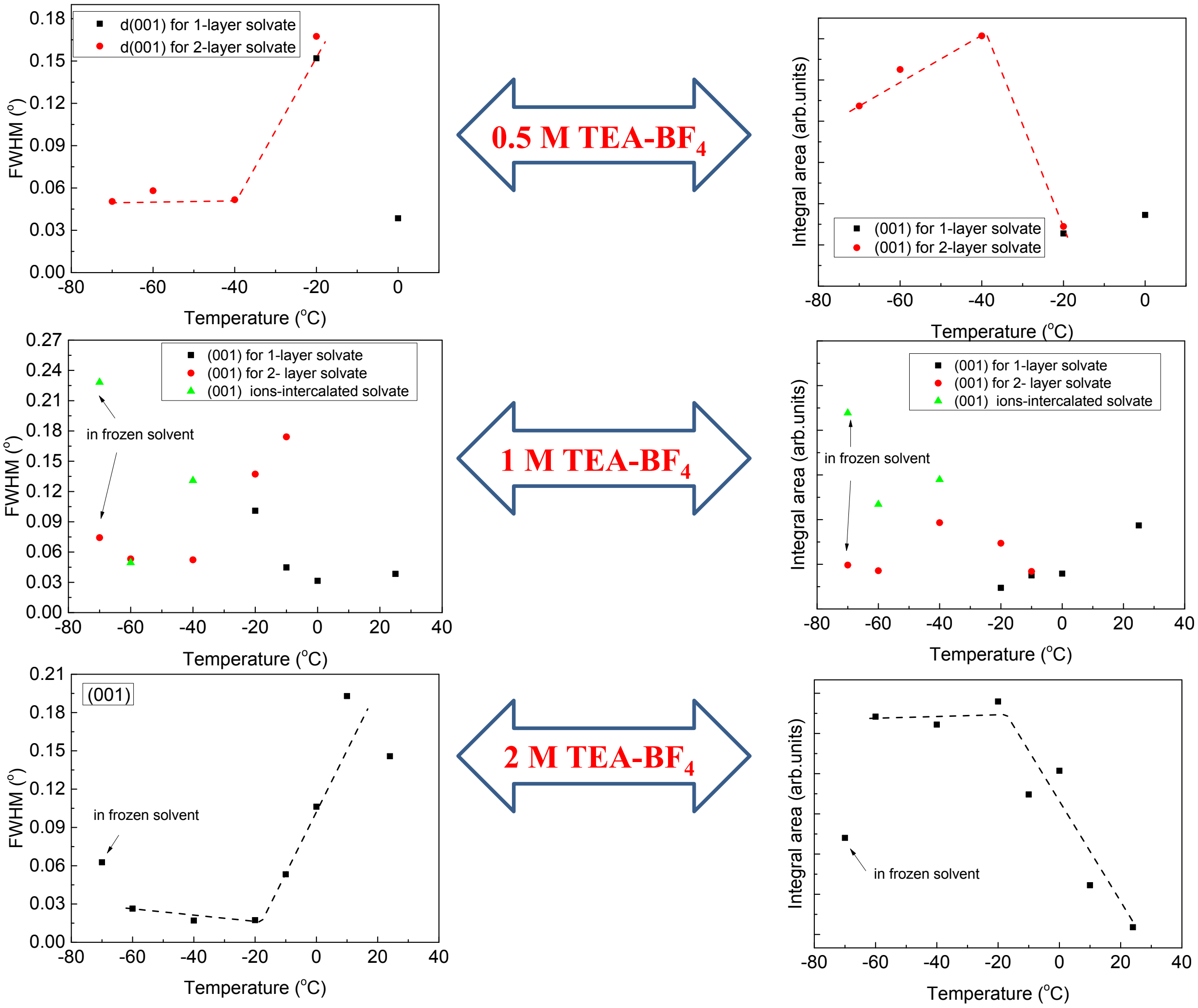

Fig. S9. Temperature vs FWHM and Temperature vs Integral intensity plots for BGO immersed in TEA-BF$_4$/acetonitrile electrolyte of 0.5 M, 1 M and 2 M concentrations**.** General trend observed in these graphs is increase of integrated intensity and decrease of FWHM for low temperature phases of BGO solvates. Acetonitrile is found to be frozen at -70 ^{0}C. The pattern recorded in frozen solvent shows the FWHM of (001) peak increased while the intensity of this peak found to be lower. The XRD patterns recorded for 1 M solution show the trends less clear. As it is often found for incomplete phase transformations, the ordering of BGO structure is less good when both 2-layered solvate and TEA-BF$_4$ intercalated solvates are co-existing below -10 ^{0}C.