Band gap modified boron doped NiO/Fe₃O₄ nanostructure as the positive electrode for high energy asymmetric supercapacitor

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Figure S1. XRD plot of F1N2, FN and F2N1.

The peaks at $2\theta = 30.05$, 35.47, 43.02, 57.03 and 62.35° were related to the Fe₃O₄ (JCPDS card 65-3107). ^{1,2,3} The peaks related to the 38.19, 44.07 and 78.04 ° were related to the NiO (JCPDS card 71-1179). ^{4,5,6} The relative intensity of NiO related peaks increased (for FN and FN2) with increasing the concentration of NiSO₄ in the precursor. The most intense peak of Fe₃O₄ at $2\theta = 35.47^{\circ}$ was related to the (311) plane.² The NiO showed the most intense peak at 44.07 ° related to the (200) plane.⁴



Figure S2. High resolution FE-SEM image of (a) F1N1, (b) FN and (c) F2N1.



Figure S3. CV of solo Fe_3O_4 , NiO and FN (NiO/ Fe_3O_4 composite) at 10 mV s⁻¹ scan rate.



Figure S4. CV of (a) F2N1, (b) FN and (c) F1N2 at different scan rate. The CV was measured in three electrode system with 6 M KOH electrolyte.



Figure S5. Retention of specific capacitance of F1N2, FN and F2N1 with scan rate. F2N1 has only 25% capacitance retention at a scan rate of 200 mV s⁻¹ compare to 10 mVs⁻¹. FN shows and F1N2 show 43 and 52 % capacitance retention at a scan rate of 200 mV s⁻¹.



Figure S6. The UV-visible absorption spectra of F1N2B, F1N2B1, F1N2B2 and F1N2B3. F1N2 represents the multi metal composite without boron doping. The concentration of boron increases for F1N2B1, F1N2B2 and F1N2B3 respectively.



Figure S7. (a) FE-SEM and (b) TEM image of F1N2B2.



Figure S8. (a) The CD of F1N2B2 at different current density and (b) the variation of specific capacitance of F1N2B2 with different current density.



Figure S9. Variation of specific capacitance of ASS with (a) scan rate and (b) current density.

Relation between diffusion time constant and activation energy

The Warburg impedance (W) is arise due to the diffusion and can be represented by the equation

$$W = W_R \frac{\tanh\sqrt{j\omega W_T}}{\sqrt{j\omega W_T}} \tag{1}$$

Where W_R is the Warburg resistance and W_T is the Warburg diffusion time constant. ^[7]The W_R and W_T can be obtained from the ZView software.

The diffusion path (L) and the diffusion time constant (W_T) are related by the equation

$$L^2 = 2DW_T \tag{2}$$

Where D is the diffusion coefficient. ^[8,9]

The activation energy (*Ea*) can be calculated from the electrical conductivity (σ) following the equation

$$\sigma = A \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

Where *A*, *R* and *T* denote frequency factor, activation energy, gas constant, and absolute temperature, respectively. ^[8,9] *Ea* can be calculated from the slope of the $ln(\sigma)$ vs. 1/T plot

$$E_a = R \times Slope \tag{4}$$

Slope being negative the activation energy will be positive. ^[9]

The jump frequency (η) of an atom and the diffusion coefficient within the solid are related by the equation

$$D = B \eta a^2 \tag{5}$$

Where *B* is the coordination factor and *a* is the lattice parameter of the solid. [7]

The jump frequency (η) depends on the activation energy (Ea) by the equation

$$\eta = \frac{KT}{h} \exp\left(-\frac{E_a}{KT}\right) \tag{6}$$

Where h is the Plank constant and K is the Boltzmann constant. ^[7]

From equation 5 and 6

$$D = \frac{BKTa^2}{h} \exp\left(-\frac{E_a}{KT}\right)$$
(7)

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