

Electronic Supplementary Information (ESI)

Synthesis, Characterization and theoretical studies on novel organic-inorganic hybrid ion-gel polymer thin films from $\gamma\text{-Fe}_2\text{O}_3$ doped polyvinylpyrrolidone - N-butylpyridinium tetrafluoroborate composite via intramolecular thermal polymerization

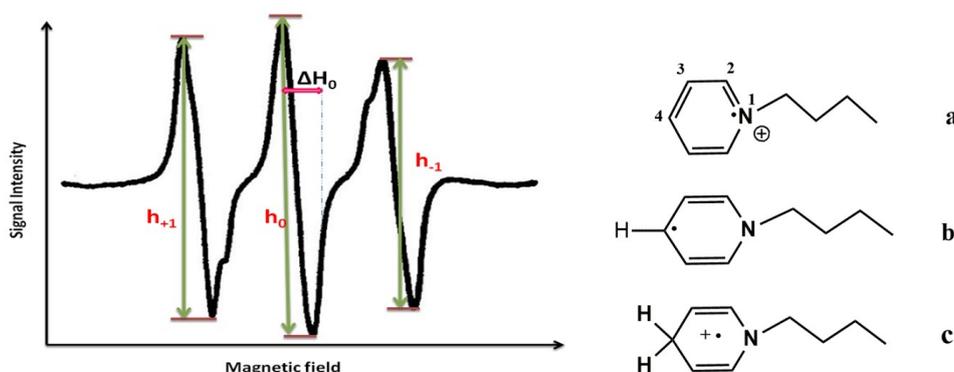
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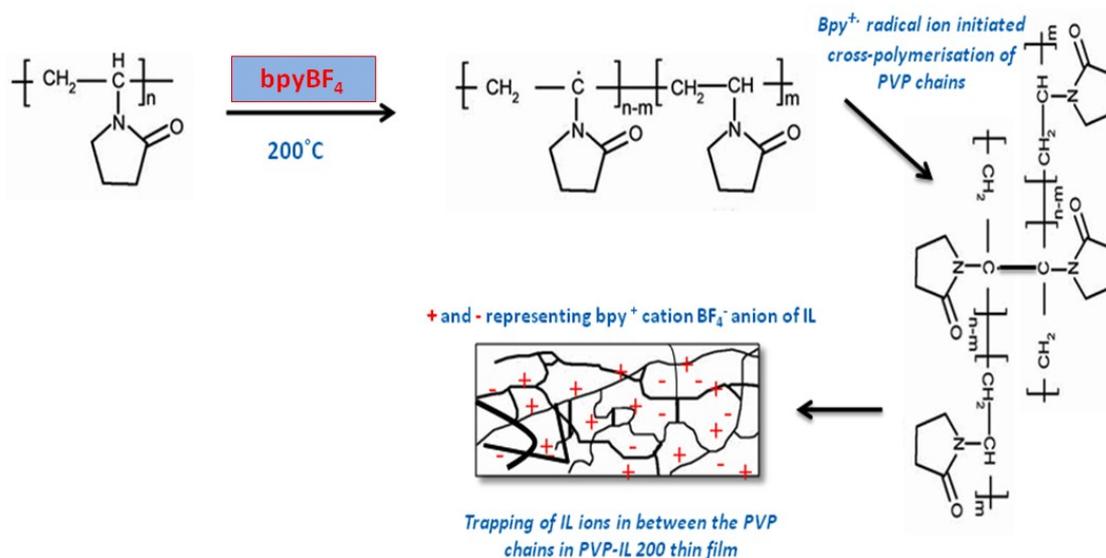
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Scheme 1: Representative of esr signal height h_{+1} , h_0 and h_{-1} in expression (1) and the possible radicals derived from bpy⁺ cation in 1:1 PVP-IL ion-gel.



Scheme 2: Schematic representation of the mechanism of IL free radical induced thermal polymerization of the PVP chains to form PVP-IL 200 thin film.

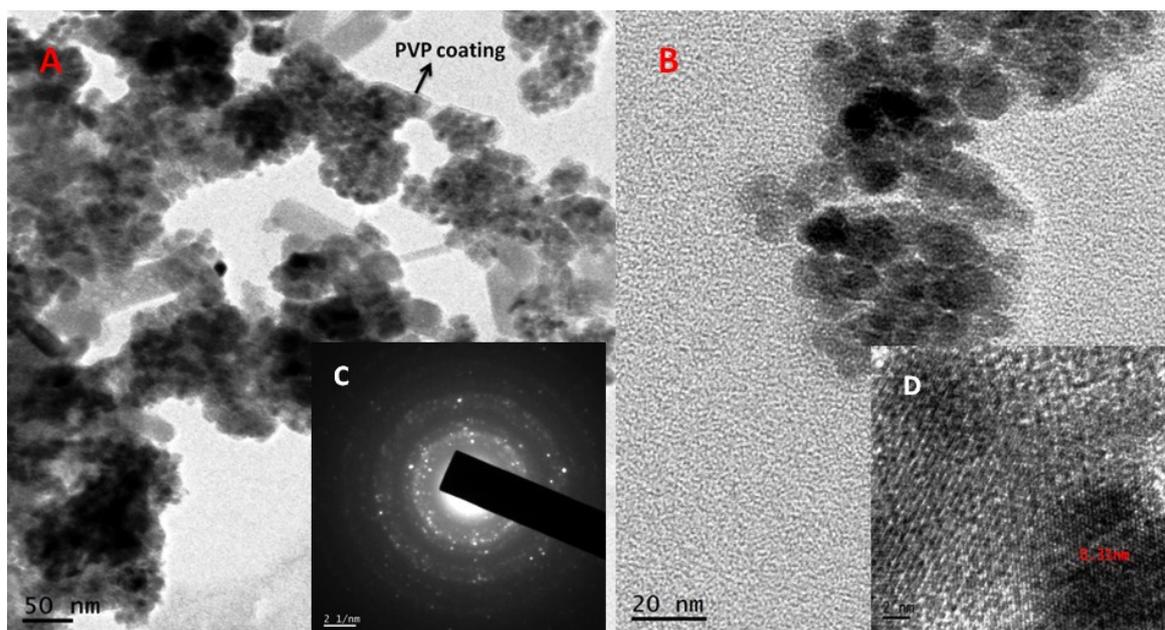


Fig. S1. The HR-TEM images of PVP coated γ -Fe₂O₃ nanoparticles is shown in A, B and D. The SAED pattern of PVP coated γ -Fe₂O₃ nanoparticles showing the poly nanocrystalline nature of γ -Fe₂O₃ nanoparticles due to the PVP coating is given in C.

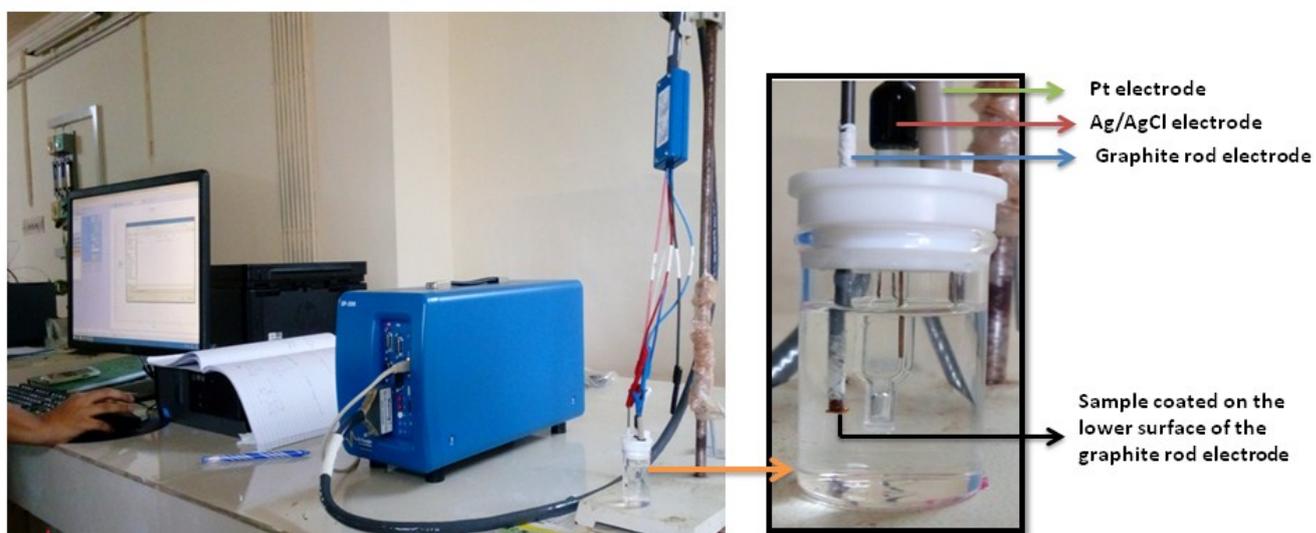


Fig. S2. The picture shows the Biologic SP-200 electrochemical workstation and customized three-electrode set-up used for electrochemical measurements.

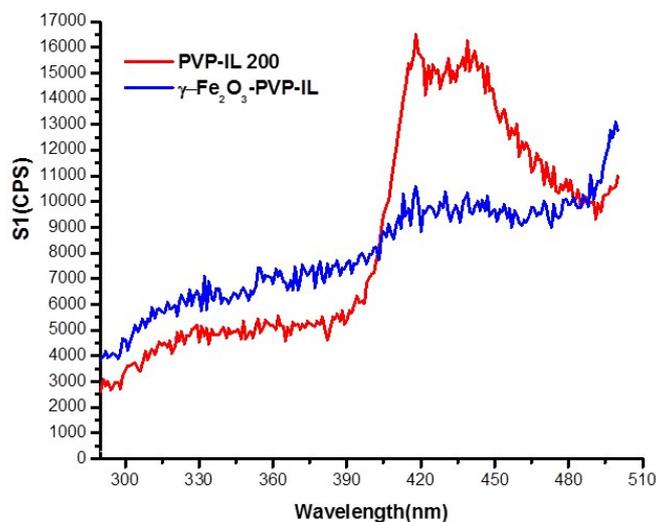


Fig. S3. Fluorescence spectra of IL-PVP thin film and Iron oxide incorporated IL-PVP magnetic thin film taken using 532 nm excitation wavelength.

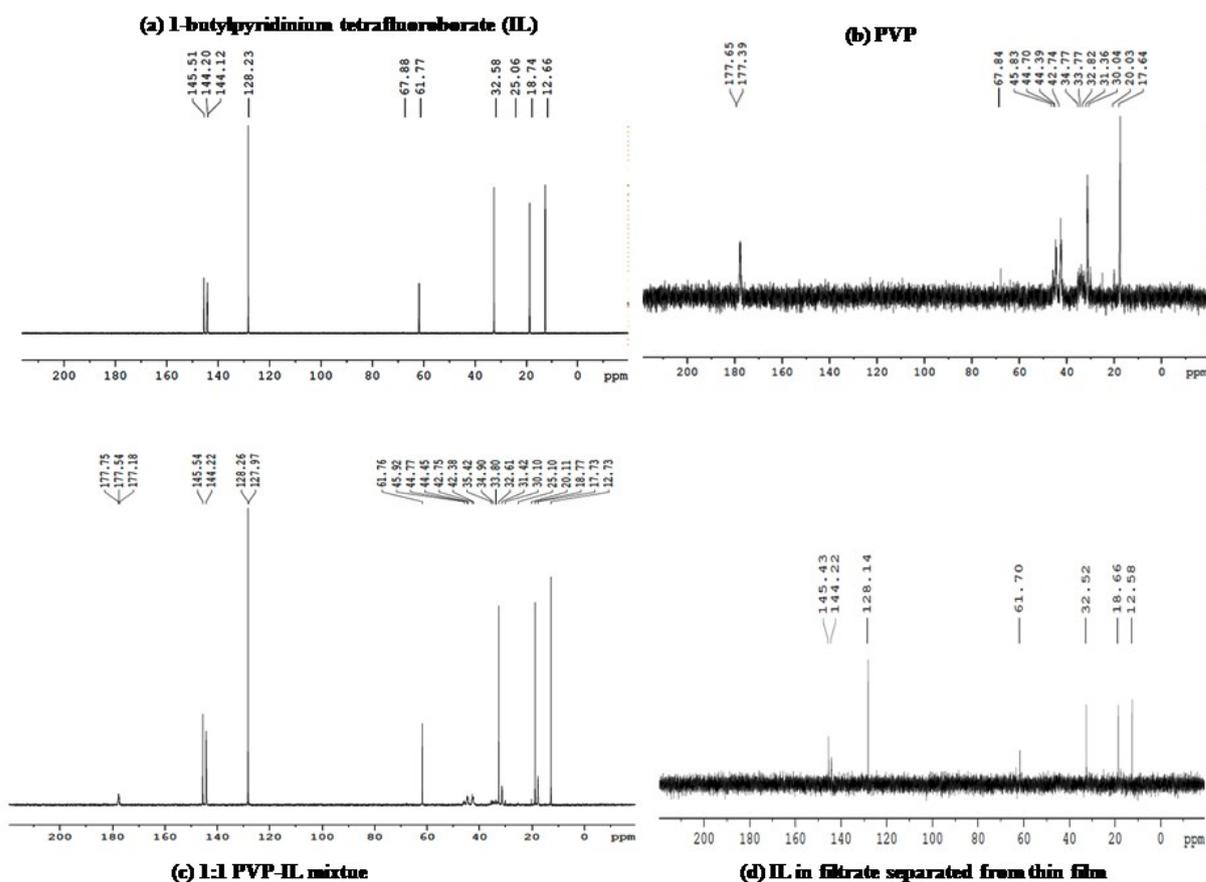


Fig. S4. Solution state C-13 NMR spectra of (a) N-Butylpyridinium tetrafluoroborate ionic liquid (IL), (b) pure PVP, (c) 1:1 mixture of N-Butylpyridinium tetrafluoroborate and PVP and (d) filtrate of the washed PVP-IL 200 thin film.

The C-13 NMR spectra of pure PVP (K30), pure IL (bpy[BF₄]), 1:1 mixture of IL and PVP, and the filtrate of thoroughly washed PVP-IL mixture heated at 200°C, all dissolved in D₂O solvent is shown in **Fig. S4**. In the solution

state C-13 spectra of PVP (Fig. S2(b)), the chemical shift of C=O is observed as a doublet at 177.65 and 177.39 ppm, resonance peaks of C-H in the PVP skeletal chain at 45.83, 44.70, and 44.39 ppm, resonance peaks of CH₂ in the PVP skeletal chain at 34.77, 33.77, 32.82, and 30.04 ppm, CH₂ peak near N atom in the pyrrolidone ring at 42.74 ppm, CH₂ peak near carbonyl group in the pyrrolidone ring at 31.36 ppm and the remaining CH₂ in the pyrrolidone ring at 17.64 ppm¹¹. The C-13 spectrum of 1-butyl pyridinium tetrafluoroborate shows peaks at 12.66, 18.74 and 32.58 due to CH₂ and CH₃ carbons in the butyl tail attached to pyridine ring and peaks at 128.23, 144.12, 144.20 and 145.51 ppm due to double bonded C atoms in the pyridine ring of the IL cation. In the C-13 spectrum of 1:1 mixture of PVP and IL, all the above mentioned peaks corresponding to both PVP and IL are observed. In addition to that, the C=O peak in 1:1 PVP-IL mixture is shows a triplet at 177.75, 177.54 and 177.18 ppm which indicates the splitting due to H-bonding interaction between the PVP and IL molecule. The analysis of the C-13 NMR (Fig. S4 (d)) of the filtrate obtained after washing the thin film revealed the peaks of IL only indicating that no chemical decomposition occurred in IL molecule while heating with PVP. The PVP carbonyl peak at 177ppm was completely absent in the C-13 spectra of the filtrate showing that no chemical bond formation occurred between PVP and IL molecules at 200°C and the interaction between PVP and IL was purely electrostatic attractive bonding. While the PVP matrix which cross polymerized in presence of IL was undissolvable in D₂O or any other solvents and hence, could be separated completely.

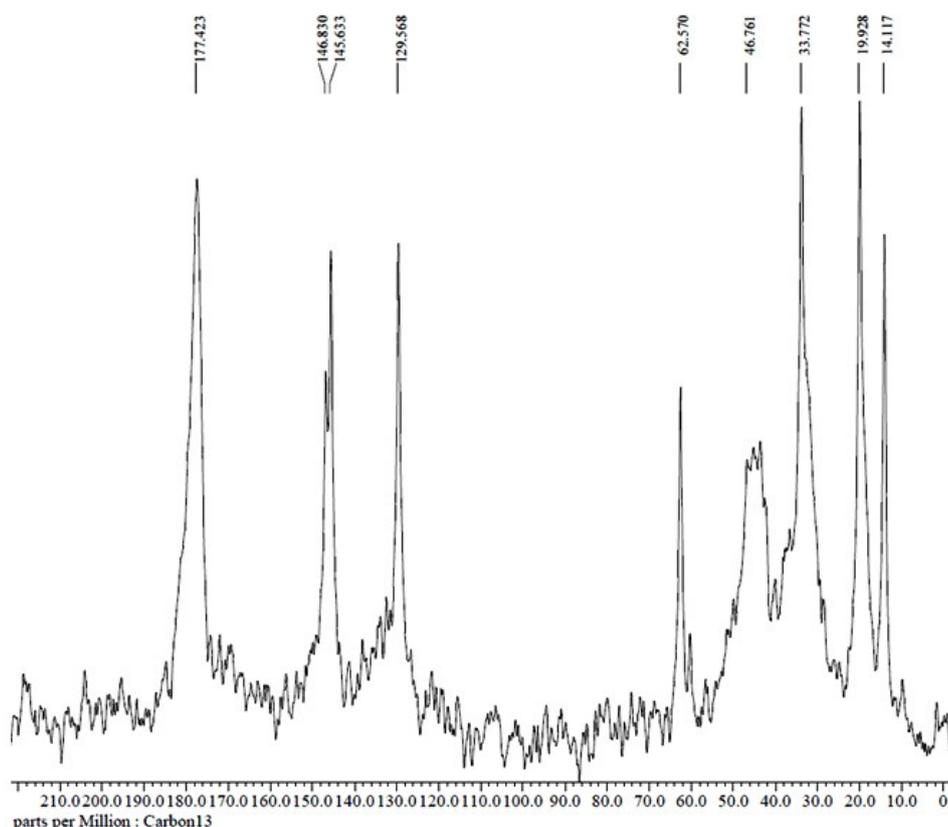


Fig. S5. Solid state C-13 NMR spectra of PVP-IL 200 thin film

The solid state C-13 NMR spectra of PVP-IL 200 thin film shown in Fig. S5 mainly exhibited the peaks corresponding to PVP and that of some trapped IL molecules after thermal polymerization. The chemical shift of the PVP C=O group is observed as a doublet at 177.423 ppm. The C-13 signals of CH₂ and CH₃ carbons in the butyl tail attached to pyridine ring in pure bpy[BF₄] at 12.66 and 18.74 ppm has been shifted to 14.117 and 19.928 ppm respectively, and peaks in pure IL at 128.23, 144.12, 144.20 and 146.83 ppm due to double bonded C atoms in the pyridine ring cation has been shifted to 129.568, 145.633 and 146.573 ppm, the peak at 61.77 ppm in pure IL due to CH₂-N< carbon has been shifted to 62.57ppm. The broad resonance peaks at 46.761 and 33.772 ppm is due to the CH and CH₂ carbons in the PVP skeletal chain.

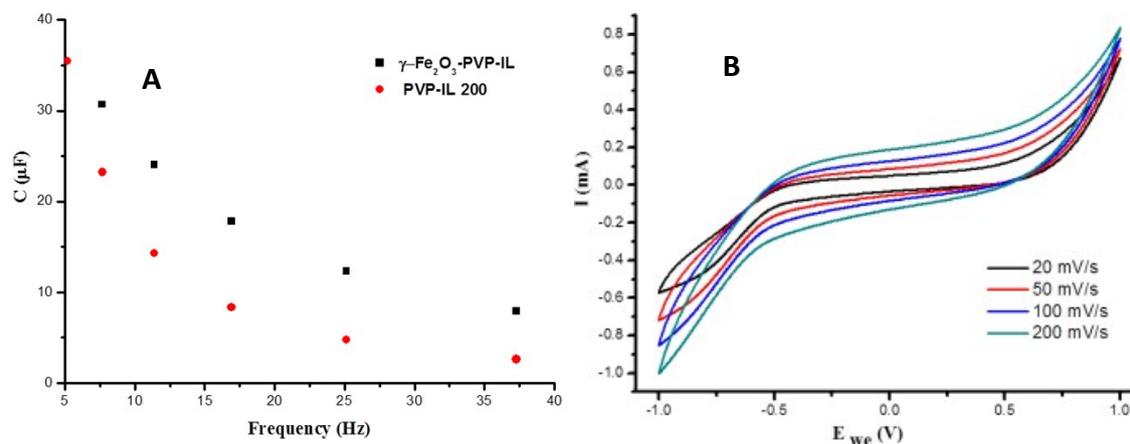


Fig. S6. (A) Comparative plot of Capacitance versus Frequency for PVP-IL 200 and $\gamma\text{-Fe}_2\text{O}_3$ doped PVP-IL 200. **(B)** Cyclic voltametric curves of PVP-IL 200 measured at different scanning rates.

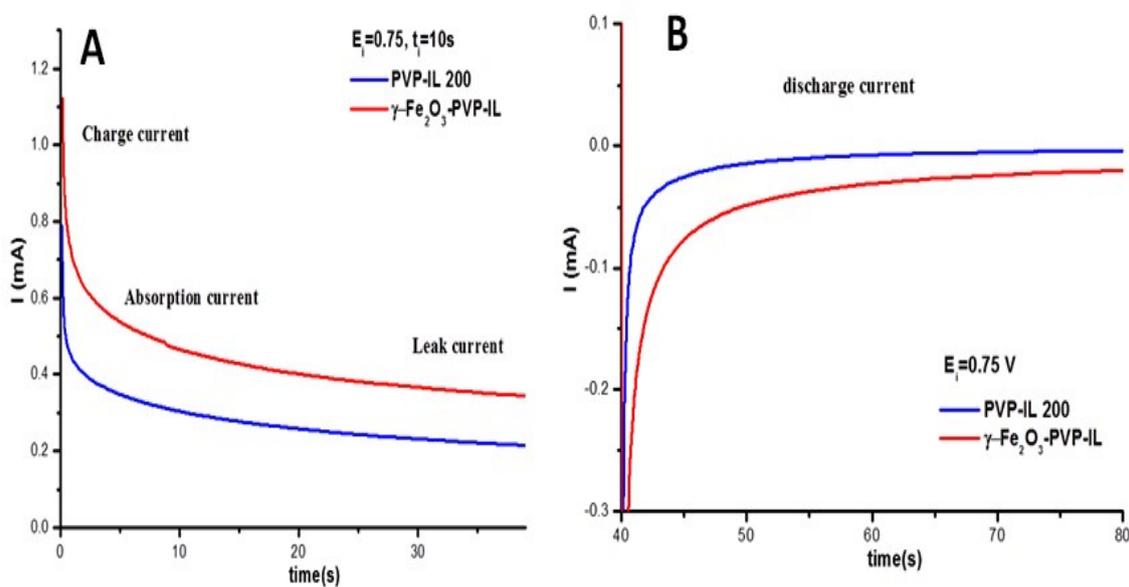


Fig. S7. Plots of Charging **(A)** and discharging **(B)** behaviour of PVP-IL 200 and $\gamma\text{-Fe}_2\text{O}_3\text{-PVP-IL}$ measured using chronoamperometry at a constant potential of 0.75 V (E_i) applied for 10s (t_i).

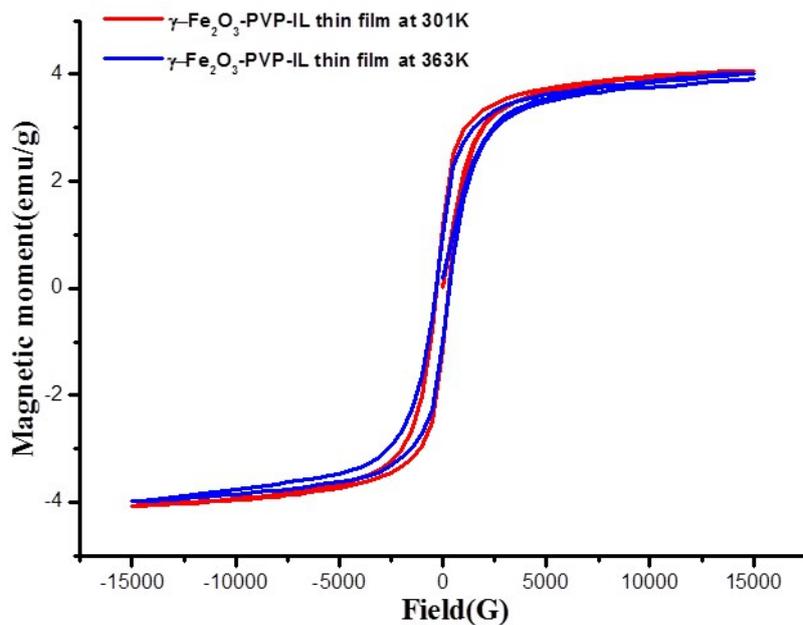


Fig. S8. Comparison of M-H curves of γ - Fe_2O_3 doped PVP-IL magnetic thin film at 301 and 363K.

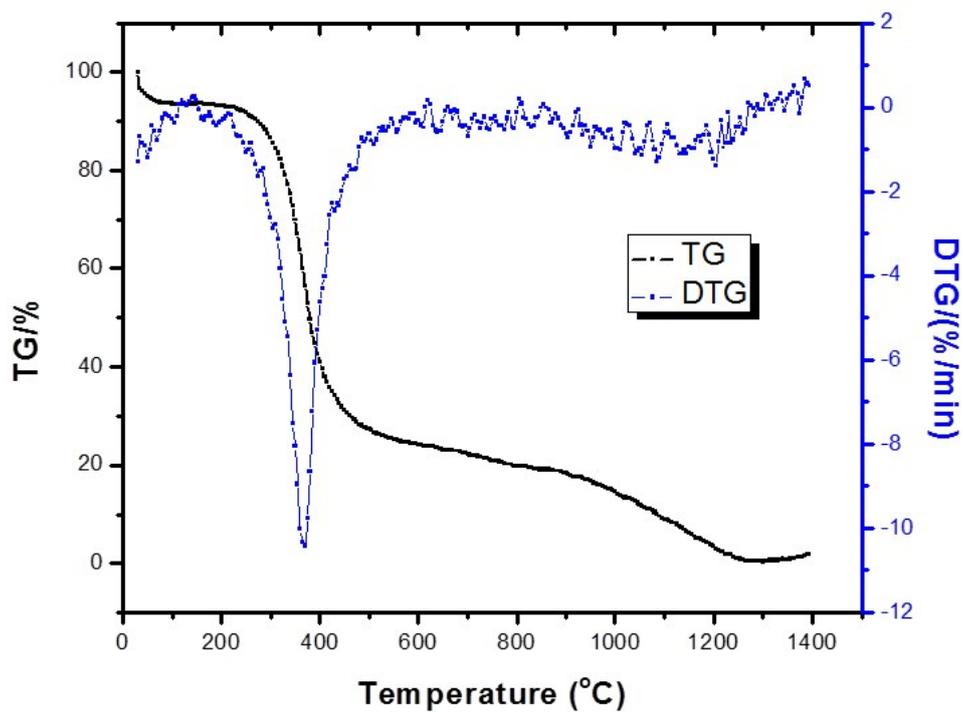


Fig. S9. a) TG-DTG of PVP:IL thin film prepared at 200°C.

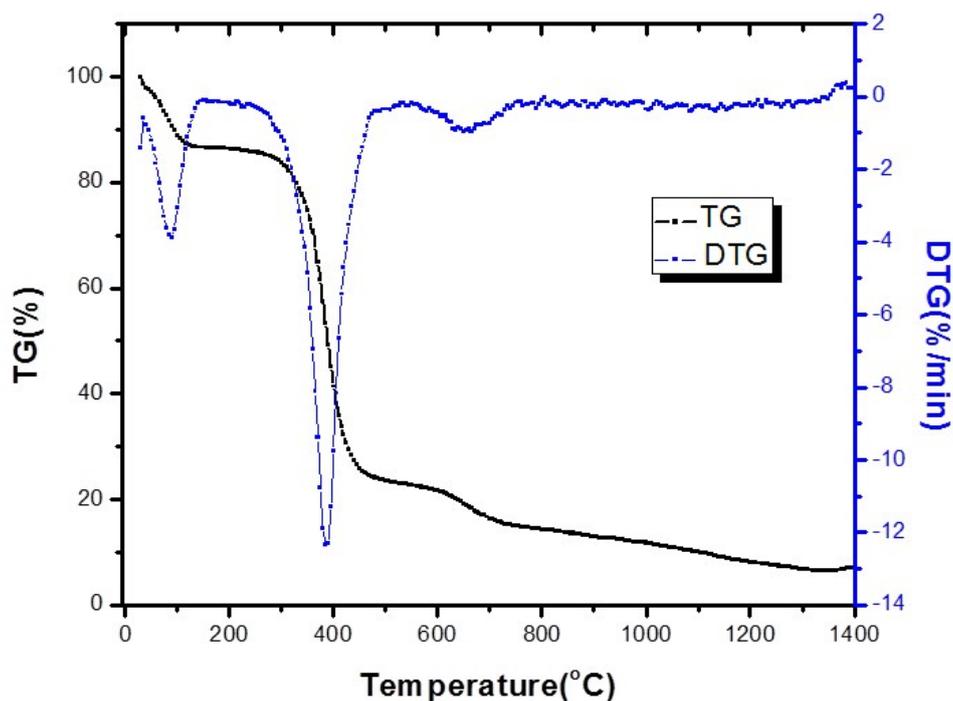


Fig. S10. b) TG-DTG of γ -Fe₂O₃-PVP-IL thin film prepared at 200°C.

Fig. S9 shows the thermal behaviours of the PVP-IL thin film prepared at 200°C determined by TG-DTG at a heating rate of 10°C/min in a temperature range from 28 to 1400°C in nitrogen atmosphere. The PVP-IL thin film maintained stable thermal behaviours up to 360 °C, and a major weight loss occurred at about 368 °C due to the thermal decomposition of the organic materials. In the corresponding DTG curve, a strong endothermic curve is observed sharply at 368°C. **Fig. S10** shows the thermal behaviours of γ -Fe₂O₃-PVP-IL thin films prepared at 200°C. The thermal behaviour of γ -Fe₂O₃-PVP-IL thin film was different. According to the heat flow, exothermic peaks appeared at 88, 388 and 640 °C. Water molecules adsorbed on the surface fine grained iron oxide are lost between 100-200°C and loss of structural OH groups in iron oxides as water molecules occurs through dehydroxylation reaction: $2\text{OH}^- \rightarrow \text{O}^{2-} + \text{H}_2\text{O}$ at 250-400°C². In **Fig. S10**, the DTG peak corresponding to small weight loss due to the removal of adsorbed water molecules on the γ -Fe₂O₃ MNP doped PVP-IL film was observed to be at 88°C, the major peak at 388°C is due to the thermal decomposition of organic matter as well as loss of structural OH and small broad peak at 640°C is due to the possible phase changes in nano iron oxide.

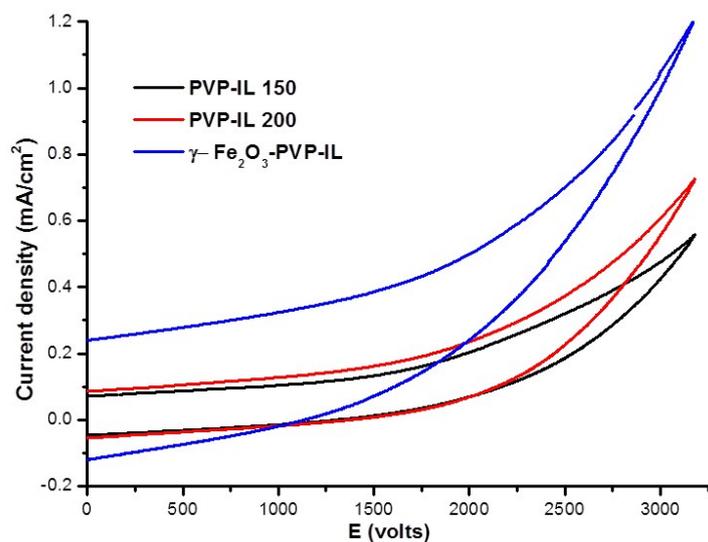


Fig. S11. Comparative plot of current density vs potential measured for PVP-IL 150, PVP-IL 200 and γ -Fe₂O₃-PVP-IL.

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