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Electronic Supplementary Information

Contact Angle Measurement: A Preliminary Diagnostic Tool for Evaluating the Performance of $ZnFe_2O_4$ Nano-flake based Supercapacitors

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Supplementary Information

Contents:

1. Synthesis of $ZnFe_2O_4$ nano-grain thin films.

The conducting stainless steel (SS) substrates were cleaned prior to conventional chemical bath deposition (C-CBD) of $ZnFe_2O_4$ nano-grains as reported earlier. In typical experiments, the SS substrate immersed in an aqueous solution of zinc chloride (0.1 M, Merck) and iron (II) chloride (0.2 M, Merck) maintained at 55 °C without any rotation of substrates and the deposition was carried out for 3h. The SS substrates after completion of deposition were then annealed at 550 °C for 5h in a closed furnace under ambient air atmosphere and subsequently allowed to cool down naturally in the same atmosphere.

Figure captions

Fig. S1 Cyclic voltammograms (CV) at 10 mV s^{-1} scan rate b) Charge-discharge curves at 2 mA cm^{-2} current density of $ZnFe_2O_4$ nano-flakes thin film electrodes with varying concentration of KOH electrolyte.

Fig. S2 Correlative study of contact angle measurement (CA) and specific capacitances (F g^{-1}) of $ZnFe_2O_4$ nano-grain thin film electrodes using different aqueous electrolytes (1 M) and their mixture combination (1 M 1:1 v/v each electrolyte).

Fig. S3 Cyclic voltammograms (CV) at 10 mV s^{-1} scan rate b) Charge-discharge curves at 2 mA cm^{-2} current density c) Nyquist plots and d) Ragone plot of $ZnFe_2O_4$ nano-grain thin film electrodes using different aqueous electrolytes (1 M) and their mixture combination (1 M 1:1 v/v each electrolyte).

Figures

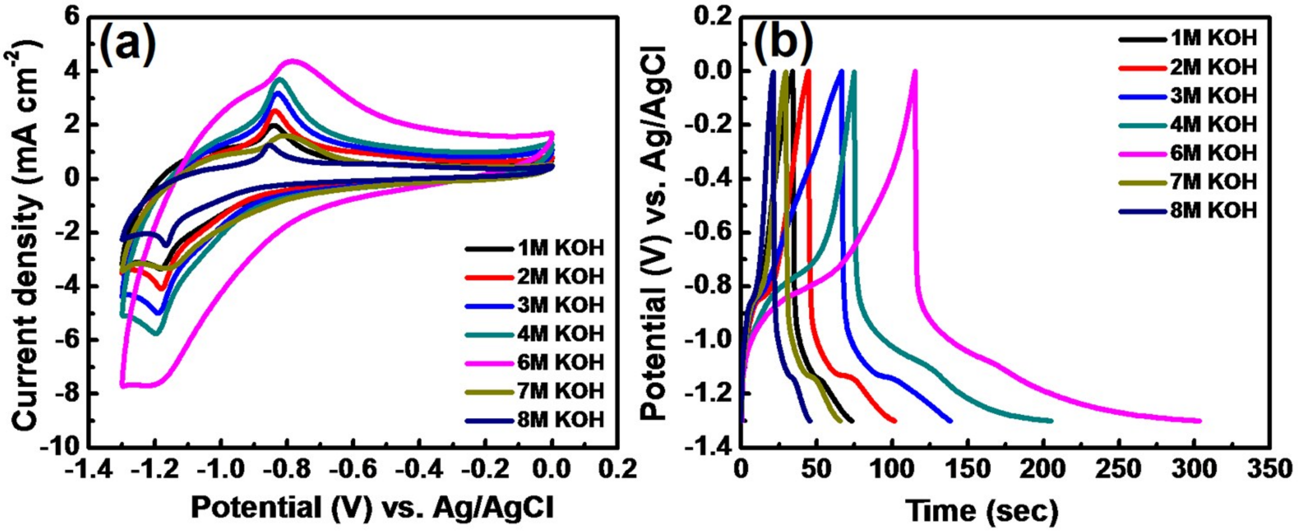

Fig. S1 Cyclic voltammograms (CV) at 10 mV s^{-1} scan rate b) Charge-discharge curves at 2 mA cm^{-2} current density of $ZnFe_2O_4$ nano-flakes thin film electrodes with varying concentration of KOH electrolyte.

The study investigating the influence of concentration of KOH electrolyte on surface wettability (CA measurement) and thus the performance (specific capacitance) was performed in the concentration range of 1-8 M. The results show increasing trend of specific capacitance from 1M to 6M and beyond which decrease in specific capacitance was noted as a result of saturation. On the contrary, the CA value showed decreasing trend from 1M to 6M and beyond which increase in CA value was noted as shown in the Fig. 4 in main text. Fig. S1 shows electrochemical properties which are consistent with the CA and specific capacitance. All CV curves show redox peaks confirming the pseudocapacitive nature. The area under the CV curve increases with increase in concentration upto 6M. After 6M concentration, area under the CV curves and time of GCD discharging curves suddenly decreases which again supporting the observed trend of results.

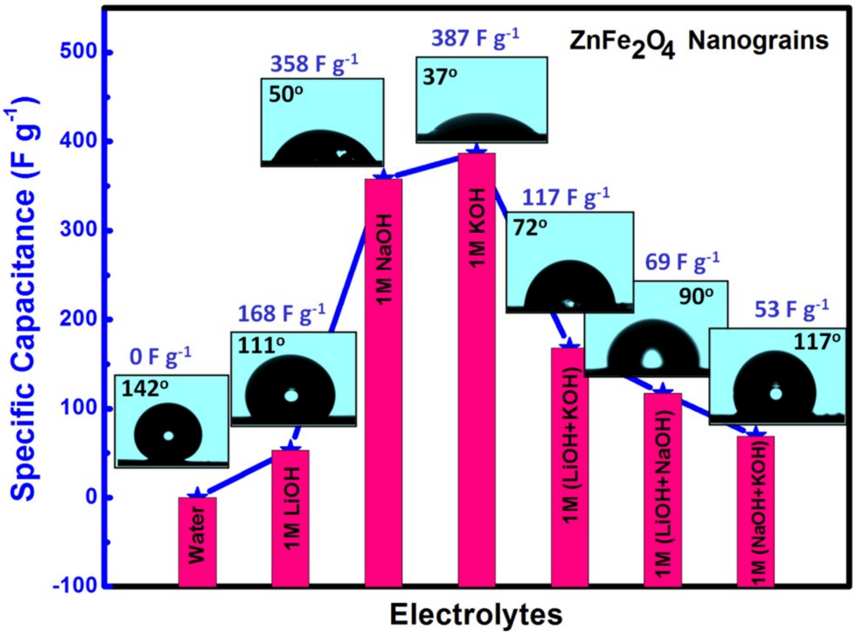

Fig. S2 Correlative study of contact angle measurement (CA) and specific capacitances (F g^{-1}) of $ZnFe_2O_4$ nano-grain thin film electrodes using different aqueous electrolytes (1 M) and their mixture combination (1 M 1:1 v/v each electrolyte).

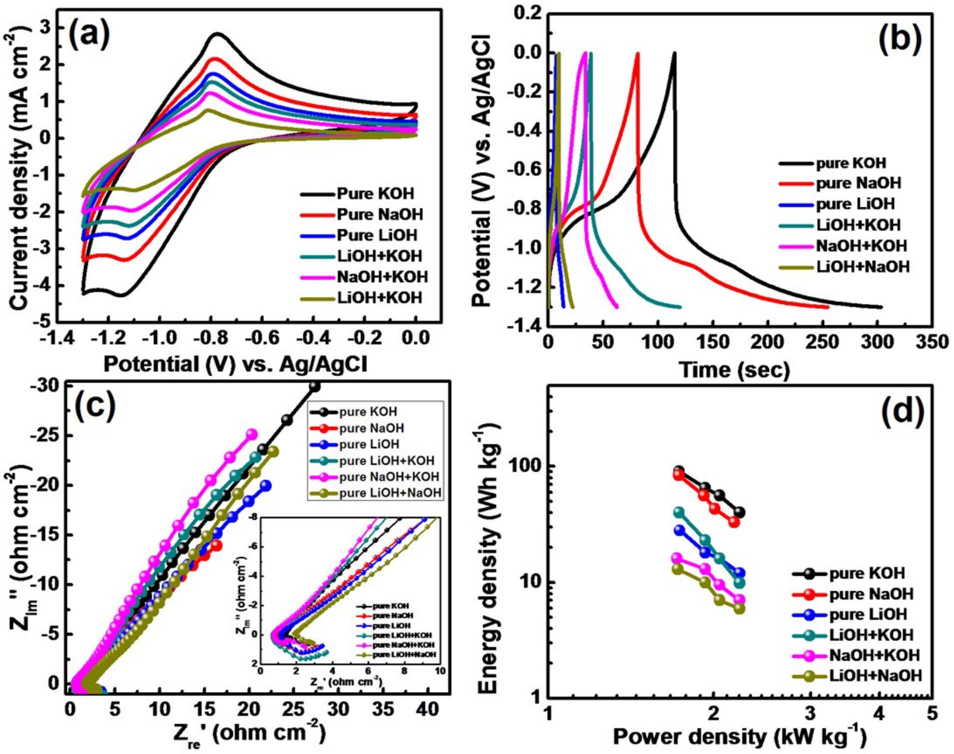

Fig. S3 Cyclic voltammograms (CV) at 10 mV s^{-1} scan rate b) Charge-discharge curves at 2 mA cm^{-2} current density c) Nyquist plots and d) Ragone plot of $ZnFe_2O_4$ nano-grain thin film electrodes using different aqueous electrolytes (1 M) and their mixture combination (1 M 1:1 v/v each electrolyte).

Fig. S2 shows the CA photographs and contact angles of different electrolytes in contact with the bare nano-grain $ZnFe_2O_4$/SS electrode, which demonstrates the extent of permitted intercalation of electrolytic ions, their corresponding specific capacitance. Similar correlative trends in CA and specific capacitance were observed for the $ZnFe_2O_4$ nano-grains based electrode in comparison with $ZnFe_2O_4$ nano-flakes based electrode reported in the main manuscript. The result of $ZnFe_2O_4$ nano-grains based electrodes show good reproducibility.

Fig. S3(a) shows the cyclic voltammograms (CV) of $ZnFe_2O_4$ nano-grains electrode with 1M KOH, NaOH, LiOH and their mixture combination LiOH+KOH, NaOH+KOH and LiOH+NaOH (1M 1:1v/v of each electrolyte). All the CV curves exhibited pair of redox peaks within the potential window (0.0V to -1.3 V) indicating the fact that $ZnFe_2O_4$ nano-grain thin films also shows pseudocapacitive behaviour in aqueous electrolytes or their mixtures. Furthermore, the larger area under the CV curves for 1M KOH electrolyte indicates the fast intercalation and deintercalation of small hydrated K^+ ion within the open pores and voids of the nano-grain network and thus high specific capacitance. This is in good agreement with the smaller CA value of 37^o (hydrophilic).

The area under the curves for 1M NaOH and 1M LiOH showed decreasing trend same as that observed for specific capacitance which indicates that the size of the hydrated ions of Na^+ and Li^+ increases thereby retarding the intercalation and de-intercalation events. This is further supported by the observed increasing trend of CA values of 50^o (NaOH) < 111^o (LiOH) trending towards hydrophobic nature than that for 1M KOH electrolyte.

In order to find the effect of hydrated ions on specific capacitance and CA values, combined mixture of each electrolyte LiOH+KOH, NaOH+KOH and LiOH+NaOH was also studied. Fig. S3 shows CV curves obtained when combined mixture of electrolyte LiOH+KOH, NaOH+KOH and LiOH+NaOH. It is observed that the mixture of LiOH+KOH shows maximum area under the CV curve than NaOH+KOH and LiOH+NaOH electrolyte combination, which indicates that the hydrated impurity ions directly affects the performance of supercapacitors. The results were further confirmed by measuring the CA values of each individual electrolyte and mixture combination and found to be in good agreement with the observed trends as shown in Fig. S2. Further investigation of supercapacitive properties, the galvanostatic charge-discharge (GCD) measurements were carried out in the same aqueous electrolytes and their combined mixture of electrolytes at constant current density of 2 mA cm^{-2} between the potential windows 0.0 to -1.3 V as shown in Fig. S3 (b). From the figure it is observed that the triangular shape of GCD curves are in good agreements with CV curves by showing pseudocapacitive behaviour. The specific capacitances (F g^{-1}) were calculated using discharging curves. The calculated specific capacitance of $ZnFe_2O_4$ nano-flake for the electrolyte and mixture combination at the constant current density of 2 mA cm^{-2} showed decreasing trend (KOH (387 F g^{-1}) > NaOH (358 F g^{-1}) > LiOH (168 F g^{-1}) and LiOH+KOH (117 F g^{-1}) > NaOH+KOH (69 F g^{-1}) > LiOH+NaOH (53 F g^{-1})), respectively. While the CA measurements showed contrary trend of increase in CA values with decreasing specific capacitance as shown in Fig. S2. The observed variation in mixed combination of electrolytes can be attributed to combined effect of hydrated ions and or competition for abstraction of hydrated species.