

## Electronic Supplementary Information

### Synthesis of unique metal oxide/carbon composites via sealed-tube pyrolysis of metal acetylacetonates and the mechanism of their formation

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**Table 1: XRD crystallite size in nm of MnO and Fe<sub>3</sub>O<sub>4</sub> composites with temperature**

Temperature (°C)	MnO/C	Fe <sub>3</sub> O <sub>4</sub> /C
500	21.6	52.3
600	18.5	74.4
700	13.2	65.4

#### Thermal analysis of the STP samples

Thermogravimetric analysis (TGA) was carried out in oxygen ambient, at a heating rate of 10 °C/min to estimate the relative proportion of the constituents in STP products of Mn(acac)<sub>2</sub> and Fe(acac)<sub>3</sub>. In both cases, the resulting TG shows multiple-step weight loss due to the oxidation of carbon present in the sample; the corresponding exothermic peaks for the oxidation are detected in DTA. The temperature ranges over which weight loss occurs and the total weight loss percentage are tabulated in table 2. No major events corresponding to the oxidation of MnO and Fe<sub>3</sub>O<sub>4</sub> were observed.

In the “550°C sample”, an initial weight gain of 2% was seen (Figure. S1). It is surmised that, in this sample, oxidation of MnO occurs, accounting for the observed initial weight gain. This is probably because, at 550°C, there is not enough carbon formed to “shield” the MnO from oxidation. Multiple peaks present in the first derivative of the TGA curves show that weight loss occurs in different steps in the “650 °C sample”.

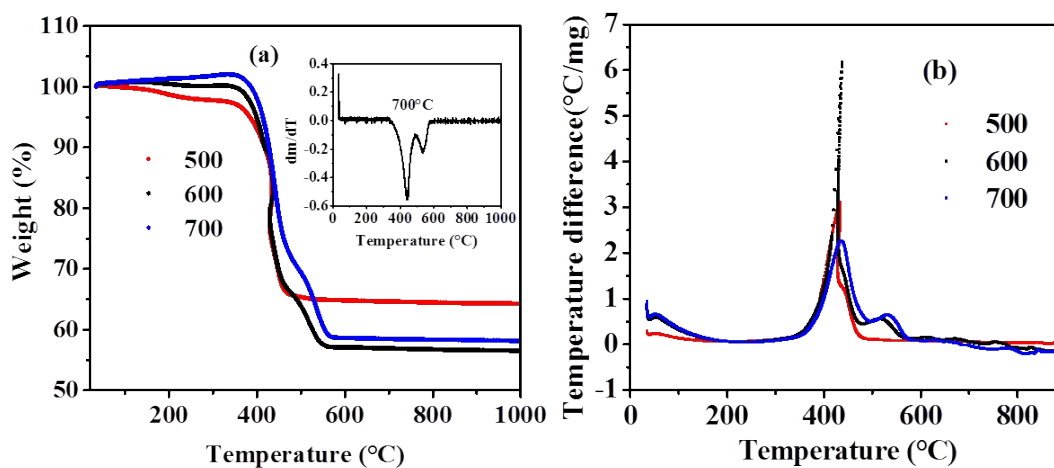
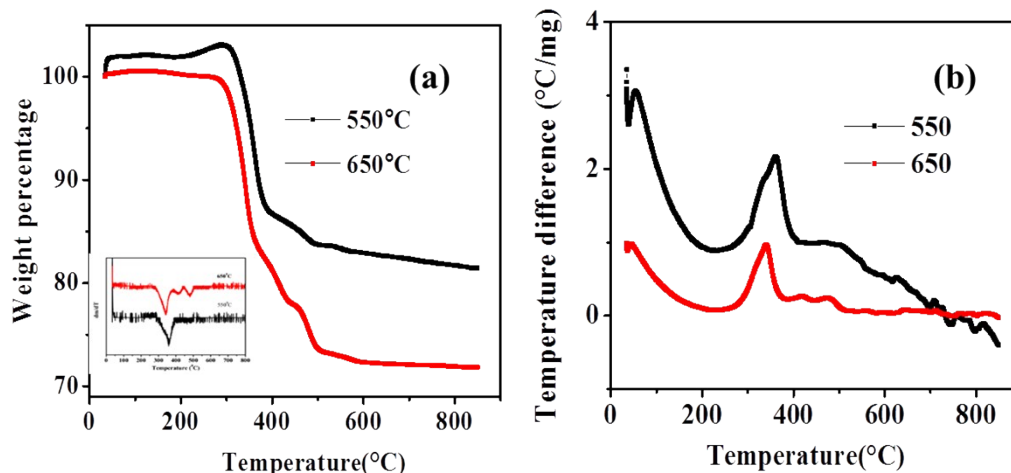


Figure. S2 (a) TGA and (b) DTA curves for STP products of  $\text{Fe}(\text{acac})_3$  synthesized at three different temperatures. Inset of (a) is obtained by differentiating the TGA curve for the “700°C sample”.

Table 2: TG-DTA results for STP products of  $\text{Fe}(\text{acac})_3$  and  $\text{Mn}(\text{acac})_2$

	STP temperature (°C)	Total Weight loss temperature range (°C)	Total weight loss (%)
$\text{Fe}_3\text{O}_4/\text{C}$	500	340-495	42.6
	600	340-560	43
	700	340-560	31.5
$\text{MnO}/\text{C}$	550	280-504	18.7
	650	220- 528	28

Since the powders contain such a large proportion of carbon, the weight loss due to the oxidation of carbon and weight gain due to the oxidation of  $\text{Fe}_3\text{O}_4$  might be superimposed, complicating the analysis. TG-DTA, therefore, can only provide a rough guide to the nature of pyrolysis products.

#### Effect of reaction duration on sealed-tube pyrolysis

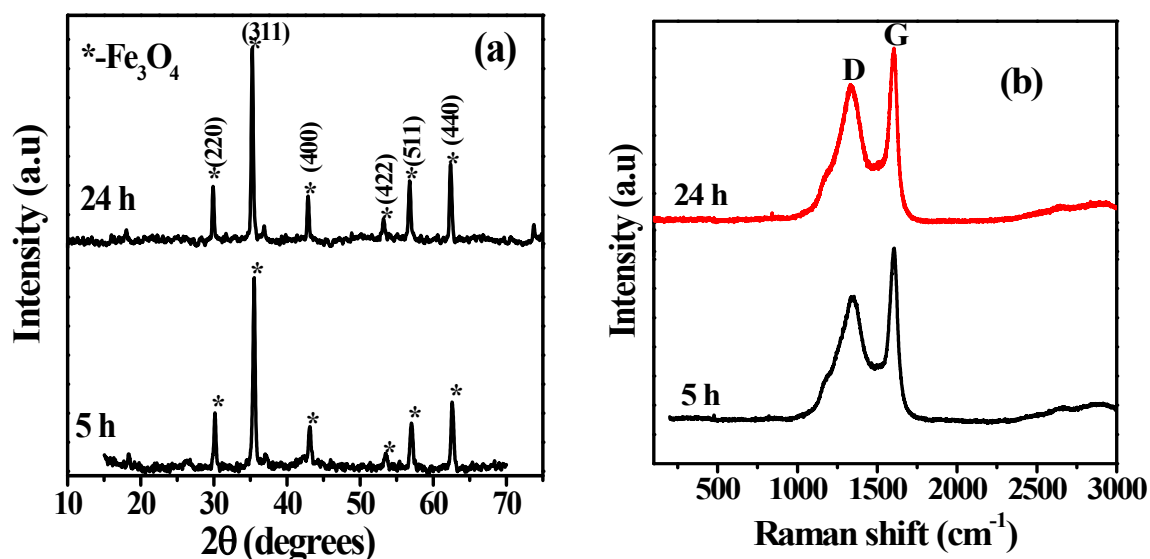


Figure. S3 (a) XRD and (b) Raman spectrum of  $\text{Fe}_3\text{O}_4/\text{C}$  powders obtained at 700 °C for STP reaction duration of 5 and 24 hours where no changes were recorded eventhough cognizable changes occurred in the microstructure of the product

#### TG-DTA for the complex $\text{Mn}(\text{acac})_2$ used as the CVD precursor to $\text{MnO}/\text{C}$

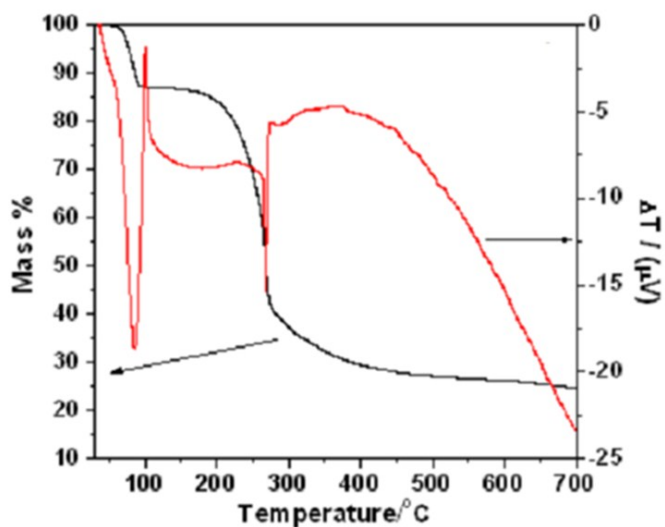


Figure. S4 TG-DTA of  $\text{Mn}(\text{acac})_2$  in nitrogen ambient at a heating rate of 10 $^{\circ}\text{C}/\text{min}$

## Electrochemical studies

(a) *MnO/C*: Electrochemical measurements were conducted using 0.1M Na<sub>2</sub>SO<sub>4</sub> and KOH as electrolyte. The sample prepared at 650°C displayed best capacitive characteristics among all. In sodium sulphate, they exhibited capacitance upto 50 F/g .

Fig. S5 (a) shows the cyclic voltammograms obtained in 0.1M KOH at various scan rates for powders prepared at 650°C. Measurements were carried out over the potential range of -0.7 V - 0.6 V, and minor peaks corresponding to diffusion-related reactions were observed. Galvanostatic charge-discharge curves (Fig. S5 (b)) exhibited linear voltage-time behaviour.

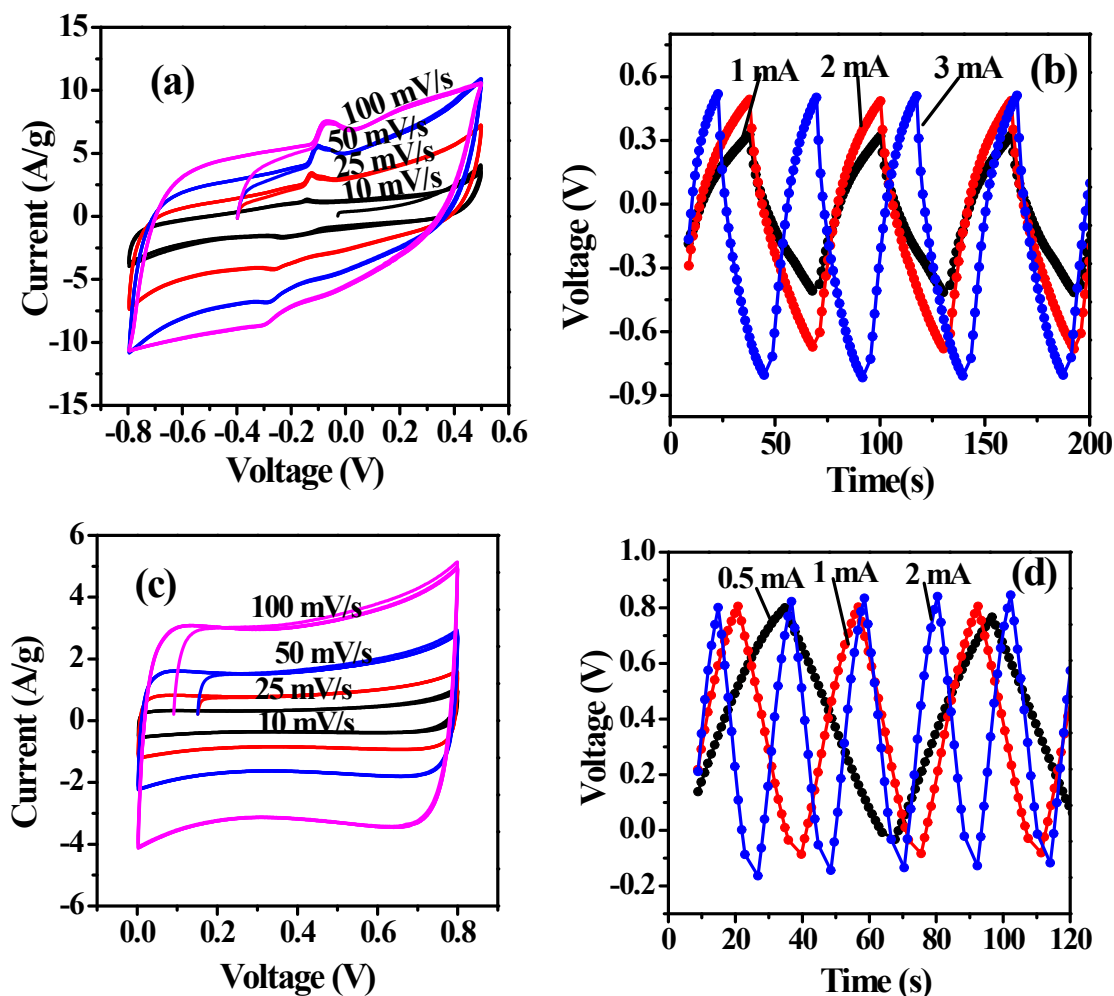
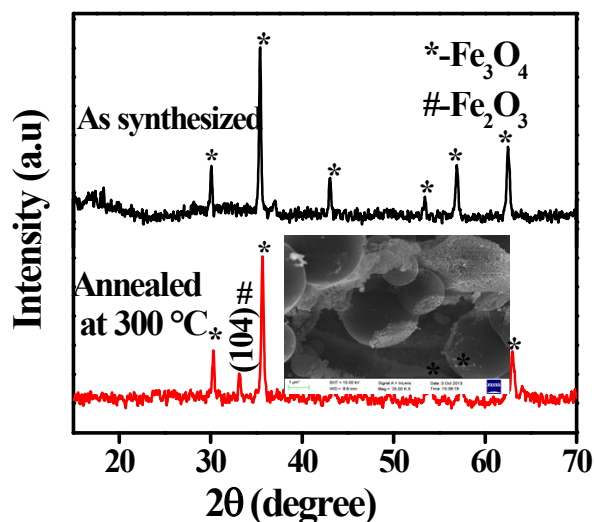


Figure. S5 Cyclic voltammogram and galvanostatic charge –discharge curves- (a) and (b) for MnO/C sample prepared at 650°C (c) and (d) for Fe<sub>3</sub>O<sub>4</sub>/C sample prepared at 600°C

The specific capacitance calculated from these data were consistent with the values obtained from cyclic voltammetry. A highest measured value of capacitance of 95 F/g was observed for the 650°C sample.

**(b)  $Fe_3O_4/C$ -** Fig. S5 (c) and (d) shows the cyclic voltammograms and charge–discharge behaviour for the sample prepared at 600°C in 0.1M  $Na_2SO_4$ , which displayed best capacitive characteristics among the STP powders prepared at various temperatures. Electrode capacitance calculated from the slope of the charge-discharge curve is 55 F/g.

Attempts were made to enhance specific surface area by heating the  $MnO/C$  and  $Fe_3O_4/C$  samples in air at 300°C. The heating in air resulted in the partial oxidation of magnetite to  $\alpha$ - $Fe_2O_3$  and partially broken carbon spheres due to oxidation (ESI S6). The cyclic voltammogram obtained in 0.1M  $NaSO_4$  for the oxidized STP sample shows increase in specific capacitance. Furthermore, the increase in capacitance occurs without changing the internal resistance of the material, as shown by the Nyquist plot in the inset (Fig. S7 (b)).



**Figure. S6 XRD pattern of as obtained  $Fe_3O_4/C$  before and after heating in air, illustrating the partial oxidation of magnetite to hematite, along with partly oxidized carbon spheres**

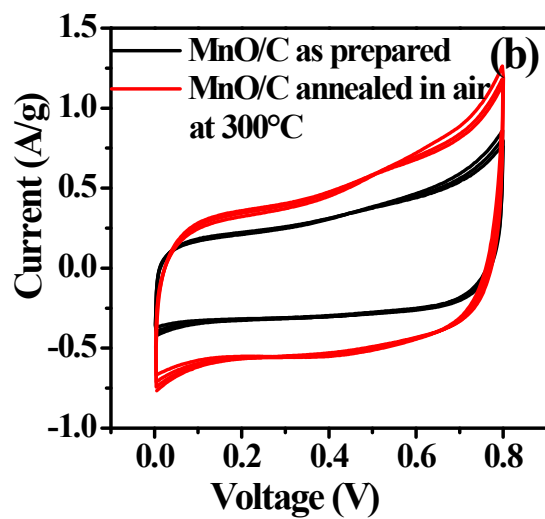
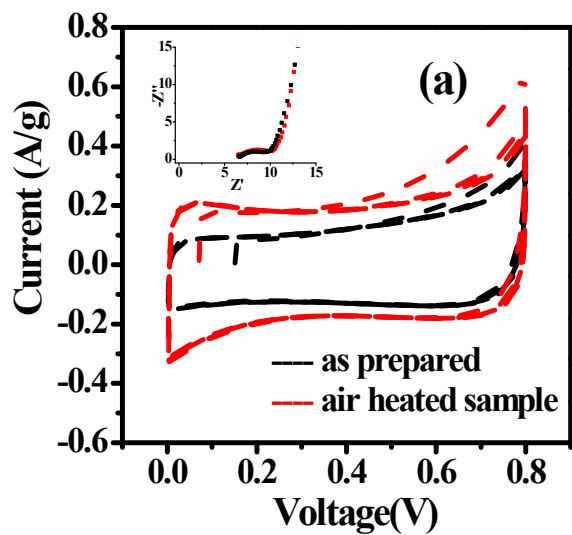


Fig. S7. Comparison of CV in 0.1M  $\text{Na}_2\text{SO}_4$  before and after heating in air for (b)  $\text{Fe}_3\text{O}_4/\text{C}$  (c)  $\text{MnO}/\text{C}$ , showing enhanced capacitance