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Supercapacitor and Photocatalytic Performances of Hydrothermally-derived Co<sub>3</sub>O<sub>4</sub>/CoO @ Carbon Nanocomposite

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Cobalt oxide ( $Co_3O_4/CoO$ ) nanoparticles-embedded carbon matrix ( $Co_3O_4/CoO$  @ carbon) was synthesized by pyrolysis of cobalt-salen complex ([Co(salen)]) followed by hydrothermal treatment. The X-ray diffraction, Raman and Fourier transformed infra-red spectroscopies confirmed the presence of  $Co_3O_4/CoO$  in the carbon matrix. The scanning electron microscope observation showed highly agglomerated spike-like grains. The TEM observation confirmed that the  $Co_3O_4/CoO$  grain are embedded in carbon matrix. The supercapacitor studies done on the  $Co_3O_4/CoO$  @ carbon matrix revealed a specific capacity of 324 C g <sup>-1</sup> at 1 A g <sup>-1</sup> in 1 M KOH. The  $Co_3O_4/CoO$  @ carbon electrode also exhibited long-term life cycle with high Coulombic efficiency of 96%. It is believed that the carbon present in the  $Co_3O_4/CoO$  @ carbon material was also tested for its catalytic property and it was found out that the prepared material exhibited excellent photocatalytic degradation of azure A dye.

## 1. Introduction

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Development of clean and renewable-energy technologies is indispensable for moving towards sustainable environment, as the use of conventional fossil fuels leads to adverse effects on the environmental ecosystem. The effective way of utilizing clean and renewable energies is to store them when available and use them when require. In this regard, much attention is being currently devoted towards development of an efficient energy-storage system. Electrochemical energy storage devices such as batteries and supercapacitor are the reliable devices to store energy and retrieve the same when required. Currently, the batteries and supercapacitors are developed with advanced electrode materials having robust energy as well as power densities and life cycle.<sup>1-4</sup> Being a portable storage-system, the supercapacitor technology is advancing to meet the energy and power demands of consumer electronics. Generally, supercapacitors are of two types viz., electrical double layer capacitors (EDLCs) and pseudocapacitors. The EDLCs store reversible charge separation the energy by at electrode/electrolyte interface (non-Faradaic), whereas the pseudocapacitors store charge by means of redox (Faradaic) reaction occurring on the surface of the electrode. Mostly, low cost and good conducting carbon-derived materials (ex. carbon nanofibers, carbon nanotube, reduced graphene-oxide etc.) with high surface area fall under the EDLC materials category.<sup>5-</sup> <sup>9</sup> These materials are generated in fascinating morphologies in

different dimensions which exhibit long-term life span but they failed in quantum of charge storage which limited their wide use. The transition-metal oxides, hydroxides and some redox polymers having fast reversible Faradaic reaction, are the most explored classes of materials for supercapacitor which can store maximum charge.<sup>10-17</sup>

The electron- and ion-transport efficiencies which are directly linked to charge storage ability of material, depends on its morphology, surface area, interaction with electrolyte etc. In this regard, current efforts are being devoted for designing and developing hybrid electrodes consisting of metal oxides (Faradic) and carbon nano networks (non-Faradic).18-19 The cobalt oxide is a semiconducting transition-metal oxide, one of the most exploited materials for various applications such as battery anode, catalysis, sensors etc. due to less band gap, ease of synthesis and large abundance.<sup>4,20</sup> Besides these admirable features, the cobalt oxide has high theoretical specific capacity (Co<sub>3</sub>O<sub>4</sub>: 404 C g<sup>-1</sup>, CoO: 1295 C g<sup>-1</sup>), adequate chemical and thermal stabilities.<sup>21-23</sup> One of the strategies to enhance the supercapacitor performance is infusing CoO to other metal oxides or conductive nano-network to generate high-energy density material by reducing diffusion length which will facilitate efficient charge transport.<sup>24-29</sup> Recently, ultra-small Sn nanoparticle embedded in nitrogen-doped porous carbon obtained by pyrolysis of [Sn(salen)] complex was used as anode material for lithium-ion battery (LIB). It was reported that the carbon network facilitated high performance of Sn anode for the LIB.<sup>30</sup> Poly-[Ni(salen)] derived from [Ni(salen)] complex was employed as supercapacitor electrode.31

By the way, among the various transition metal-oxides,  $Co_3O_4$  being a p-type semiconductor with efficient electronic and magnetic properties is considered as the most versatile oxide material for catalytic applications. Recently, Wang *et al.*,

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Electronic supplementary information (ESI) available: XRD, Raman and FT-IR spectra of acid leached sample,  $Co_3O_4/CoO$  @ carbon and pyrolysed salen complexes.

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reported the synergistic effect of Co<sub>3</sub>O<sub>4</sub> nanoparticles and graphene as catalysts for degradation orange II dye.<sup>32</sup> It was reported that the combination of Co<sub>3</sub>O<sub>4</sub> nanoparticles and graphene sheets provided much higher catalytic activity than that of pure Co<sub>3</sub>O<sub>4</sub>. In recent years, several efforts have been adopted to improve the catalytic efficiency of the Co<sub>3</sub>O<sub>4</sub> namely by preparing single, multi component and composite materials etc.<sup>32-38</sup> For example, Mohammad et al., have utilized nanostructured bicomponent cobalt metatitanate and cobalt oxides for effective degradation of triazo Direct Blue 71 dye under 250 W Hg light illumination.<sup>37</sup> Orange II dye was photocatalytically degraded to a large extent by using magnetic cobalt nanoparticles anchored on graphene nanosheets. It was reported that activation of graphene with peroxymonosulfate had a profound effect in efficient removal of Orange II dye from water.35

In this work,  $Co_3O_4/CoO$  nanoparticles embedded carbon matrix (hereafter known as,  $Co_3O_4/CoO$  @ carbon) was derived by hydrothermal treatment of chemically synthesized cobaltsalen complex ([Co(salen)]) and its electrochemical behavior is investigated with a target to achieve enhanced supercapacitor performance. We have also evaluated the photocatalytic ability of the  $Co_3O_4/CoO$  @ carbon matrix by monitoring the degradation of Azure A (AZA) dye. The detailed synthesis, characterization, electrochemical characteristics and photocatalytic property of the  $Co_3O_4/CoO$  @ carbon are reported here.

#### 2. Experimental

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#### 2.1. Material synthesis and characterization

Initially, (H<sub>2</sub>-salen) ligand was synthesized by reacting known quantities of salicylaldehyde (Sigma-Aldrich, India) and ethylene diamine (Sigma-Aldrich, India). Then, the [Co(salen)] complex was prepared by reacting the H<sub>2</sub>-salen ligand and cobalt acetate (Merck Pvt. Ltd., India) in a distilled ethanol in an appropriate amount.<sup>30,39,40</sup> The obtained [Co(salen)] complex was subjected to one spot pyrolysis at 800°C under argon (Ar) atmosphere for 5 h in a tubular furnace. Then, the pyrolyzed sample (0.2 g) was dispersed in 40 ml of distilled water by means of ultra-sonication. To this dispersed solution, 2 mM urea was added and stirred for 2 h. Then, the above solution was transferred into a Teflon-lined autoclave and kept in an air oven at 180°C for 12 h (hydrothermal treatment). After the treatment, the obtained sample was centrifuged, washed several times with ethanol and dried to obtain final product.

The obtained black powder was characterized by using X-ray diffraction (Bruker D8 advance Da vinci) employing Cu K<sub> $\alpha$ </sub> radiation source at a scan rate of 1° per minute, Raman spectroscopy (Witec Confocal Raman instrument with Ar ion laser 514.5 nm CRM200), Fourier transformed infra-red (Nicolet 6700) spectroscopy by means of KBr pellet method and Field emission scanning electron microscope (FE-SEM carl Zeiss SUPRA55VP) equipped with energy dispersive X-ray analysis (EDAX). High resolution transmission (HR-TEM, JEOL JEM 2100)

electron microscope analysis of the prepared material was carried at an operating voltage of 200 kV  $^{\rm DOI:\,10.1039/C7NJ04638C}$ 

#### 2.2. Electrochemical characterization

The supercapacitor studies of the sample were done in a three-electrode cell consisting of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon as working electrode, platinum (Pt) as counter electrode and Ag/AgCl as reference electrode. The working electrode was fabricated using the mixture of the  $Co_3O_4/CoO$  @ carbon (80 wt.%), carbon black (10 wt.%) and polyvinylidene fluoride (10 wt.%). The carbon black was used to increase the conductivity of the electrode material. The PVDF was used as binder in electrode fabrication to bind the electrode material on to the surface of nickel foam (NF) current collector (substrate). Nmethyl-2-pyrrolidone (NMP) was used as a solvent to obtain slurry. The slurry thus obtained was pasted on the NF (1 cm x 1 cm) and dried at 80 °C for overnight. The masses of the coated and uncoated electrodes were measured. The difference between the mass of coated and uncoated electrode was the active mass of the electrode. The active mass of the electrode was 2 mg cm<sup>-2</sup>. All the electrochemical tests were performed by using Biologics electrochemical workstation (SP-150). The cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) studies were carried out in a three electrode cell in 1M KOH. The EIS studies were carried out at several charge-discharge cycles in the frequency range of 100 KHz-0.01 Hz.

#### 2.3. Photocatalytic experiment

The photocatalytic performance of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon matrix was studied by examining the degradation of AZA dye (AZA is a product of SD-Fine Chemicals, India). The dye was purified and recrystallised as reported elsewhere.<sup>41</sup> The AZA solution was prepared by dissolving appropriate amount of the AZA in double distilled water to get a final concentration of 2.80  $\times$  10<sup>-5</sup> mol dm<sup>-3</sup>. Then, the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon (10 mg) was added to photocatalyst in 25 mL of aqueous AZA dye solution  $(2.80 \times 10^{-5} \text{ mol dm}^{-3}, \text{ pH=7})$ . The solution mixture was then stirred in dark for 1 h to achieve adsorption-desorption equilibrium. The photocatalytic degradation study was carried out in a Pyrex beaker under UV irradiation using a 250 W Philips UV lamp. The wavelength of the UV lamp was 360 nm and it is very much within the range of 250-400 nm. At specified time intervals, 2.5 mL of solution mixture were taken out of the beaker and filtered. The filtered solution was subjected to absorption spectral measurements by JASCO V-630 UV-visible spectrophotometer. Quartz cuvettes of path length 1 cm were used to record the absorption spectra in all case. The entire experiment was carried out in room temperature (24°C).

#### 3. Results and Discussions

#### 3.1. Crystal structure and morphology

Fig. 1a shows the XRD pattern recorded for the  $Co_3O_4/CoO$ @ carbon matrix sample obtained from pyrolysis of the [Co(salen)] complex followed by hydrothermal treatment. The

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set of Bragg peaks located at diffraction angles (20), 46.5, 62.3, 66.2 and 70.5° could be indexed to the cubic phase of CoO as per the JCPDS PDF # 89-2803. The set of diffraction peaks present at 32.8, 38.5, 51.6 and 54.2° are assigned to  $Co_3O_4$  as per the JCPDS PDF# 65-3103. In addition, the XRD pattern also has peaks at 25.1, 26.4 and 44.2° which confirm presence of graphitic carbon as per JCPDS PDF# 89-8487.<sup>42-44</sup> The presence of asymmetric peak at 44.2° confirmed the turbostatic nature of the disordered carbon layer in the graphitic carbon. Thus, the XRD data indicate that the hydrothermally-derived sample consists of CoO,  $Co_3O_4$  and carbon. The XRD results have been substantiated by the Raman and IR spectral data.



Fig. 1 (a) XRD pattern, (b) Raman spectrum and (c) FT-IR spectrum recorded for the hydrothermally-derived Co $_3O_4/CoO$  @ carbon matrix.

Fig. 1b shows the Raman spectrum obtained for the hydrothermally-derived  $Co_3O_4/CoO$  @ carbon sample. Distinct four bands located at Raman shifts 513, 1330, 1603 and 2204 cm<sup>-1</sup> are clearly seen. The Raman shifts observed at 1330 and 1603 cm<sup>-1</sup> correspond to the D and G bands of graphitic carbon. The appearance of the D band originates from the edges of defected carbon layers due to breakdown of translational symmetry, while the G band is attributed to the second order

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scattering of graphitic carbon.44 It is well known that the disorder in the structure is measured by the Intensity ratio of the D and G bands  $(I_D/I_G)$ . The observed  $(I_D/I_G)$  of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon sample is 0.95 which is very close to 1. Such a high (I<sub>D</sub>/I<sub>G</sub>) ratio indicates the presence of large amount of defects in the graphitic carbon. Additionally, a distinct peak at 2204 cm<sup>-1</sup> is seen. This peak is attributed to the laser scribed graphene (LSG). The appearance of this 2D peak indicates the presence of lower structural defect in the sp<sup>3</sup> carbon of the carbon matrix. The peak at 517 cm<sup>-1</sup> corresponds to Co-O bond. The Raman spectroscopy data have been substantiated by the FT-IR data shown in Fig. 1c. The IR spectrum of the sample has low intense two sharp peaks at 3625 and 3737 cm<sup>-1</sup> which are assigned to N-H bonds. The peaks at 1565 and 1345 cm<sup>-1</sup> are ascribed to C=C and C=N bonds, respectively. The strong band observed at 1095 cm<sup>-1</sup> is due to C-N-C bond. The peak present at 950 cm<sup>-1</sup> is corresponding to C-H bond. In addition, sharp peak at 665 and intense peak at 510 cm<sup>-1</sup> are also present which are ascribed to Co<sup>3+</sup>-O and Co<sup>2+</sup>-O bonds, respectively. The appearance of Co<sup>3+</sup>-O and Co<sup>2+</sup>-O bonds confirms that the hydrothermally-derived sample consists of CoO and Co<sub>3</sub>O<sub>4</sub>. It is well known that in the Co<sub>3</sub>O<sub>4</sub> spinel, Co<sup>3+</sup> is in the octahedral environment, while Co<sup>2+</sup> is in the tetrahedral environment. <sup>45,46</sup> The detailed description of FT-IR of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon matrix and pyrolyzed salen complex has been given in Supplementary materials (Fig. S2). Fig. 2 (a-f) shows the surface morphology of the hydrothermally-derived Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon sample obtained from FE-SEM taken at different magnifications. The morphology consists of largely agglomerated spike-like grains with the thickness about 80 nm. In addition, the matrix also consists of different shape and size grains. Usually, a flat-smooth surface will result in for the carbon material. In the present case, the smooth surface has been lost, this could be due to the presence of the  $Co_3O_4/CoO$  grains. To identify the elements present in the sample, EDX profile was recorded. The Fig. 2g shows the obtained EDX profile. The presence of carbon, oxygen and cobalt is clearly visible. From the intensities of the peaks, the estimated amounts of C, O and Co are 64, 12 and 24 wt.%, respectively. The rich carbon content would have resulted from the decomposition of [Co(salen)] complex during the adopted synthetic route. The EDX data have been supported by the elemental mappings shown in Fig. 2(h-j). It can be seen that all the three elements are homogeneously distributed throughout the matrix. The high density of the elemental mapping is observed for 'C', indicating its presence in the sample. To substantiate the EDX results and to quantify the amount of carbon and oxide composition, known quantity of the prepared sample (50 mg) was subjected to acid leaching in conc.HNO<sub>3</sub>, 24 h to dissolve the cobalt oxide. It was seen that the solution was magenta color and the residue was black in color. After complete dissolution, the formed magenta color solution was decanted and the residue was washed with the distilled water several times, and finally dried at 110 °C for overnight. Then, the mass of obtained residue was weighed using electronic balance. It was found that  $\approx$ 30 mg of the residue was obtained. This accounts for 60% of the residue. Further, the residue was



Fig. 2 (a-f) SEM images at various magnifications, (f, g) EDX profile and (h-j) elemental mappings taken on the surface of the hydrothermally-derived  $Co_3O_4/CoO$  @ carbon sample.

subjected to XRD and Raman analysis. The obtained XRD and Raman data of the residue are given in supplementary material (Fig. S1). It can be seen that the XRD pattern consists of Bragg angles, at 26.4 and 44.2°. These Bragg peaks correspond to carbon as per the standard XRD pattern (PDF # 89-8487). Thus, the  $Co_3O_4/CoO$  has gone in to the solution when the sample is dissolved in conc. HNO<sub>3</sub> and carbon remained as residue in the leached sample. The XRD results have been corroborated by the Raman data (supplementary materials, Fig. S1b). It is seen that the Raman spectrum of the acid-leached sample has characteristic carbon bands at 1312, 1586 and 2613 cm<sup>-1</sup> which corresponds to D, G and 2D bands of graphene. It is noteworthy that the characteristic Raman shift of the Co-O at 675 cm<sup>-1</sup> is absent. This clearly confirms that cobalt oxide is completely leached out from the carbon matrix upon acid treatment followed by washing with water. Thus, based on the aforementioned XRD, Raman, FT-IR and SEM/EDX data, it is confirmed that the hydrothermally-derived sample is composed of Co<sub>3</sub>O<sub>4</sub>/CoO and carbon in 40% and 60% proportions, respectively.

Fig. 3a and 3b show the TEM images of the  $Co_3O_4/CoO$  @ carbon matrix. It is confirmed that the  $Co_3O_4/CoO$  grains are embedded in the carbon matrix. Boundary between the oxide grains and carbon is seen. Fig. 3c shows the lattice fringes observed for the  $Co_3O_4/CoO$  @ carbon sample. The presence of  $Co_3O_4$  (440) peaks has been confirmed (Fig. 3c). The selected area electron diffraction pattern (SAED) of the hydrothermally-derived  $Co_3O_4/CoO$  @ carbon is shown in Fig. 3d. It can be seen that the SAED pattern shows well-defined spots and rings. The appearance of well-defined spots and rings in the SAED pattern reveals that the hydrothermally-derived  $Co_3O_4/CoO$  @ carbon sample is highly crystalline in nature. The d-spacing values of the  $Co_3O_4$  [PDF # 65-3103] and the CoO [PDF # 89-2803], Substantiating the above discussed XRD data.



Fig. 3 (a-b) TEM images, (c) Lattice fringes and (d) SAED pattern recorded for the hydrothermally-derived Co $_3O_4/CoO$  @ carbon matrix

It is believed that during the hydrothermal process, urea decomposes to give hydroxyl ion which can increase pH of the content in the Teflon autoclave leading to form  $Co(OH)_2$  which on dehydration lead to formation of CoO and  $Co_3O_4$  nanoparticles as shown below. It is also believed that the  $Co_3O_4/CoO$  nanoparticles are embedded in the carbon matrix during the grain growth. Prior to the hydrothermal treatment, the pyrolysis of [Co(salen)] complex was done to generate carbon matrix.

$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$	(1)
$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$	(2)
$Co^{2+} + OH^{-} \rightarrow Co(OH)_2$	(3)
$Co(OH)_2 \rightarrow CoO + H_2O$	(4)
$3 \operatorname{Co}(OH)_2 + \frac{1}{2}O_2 \rightarrow \operatorname{Co}_3O_4 + 3H_2O$	(5)

Thus, the salen complex having abundance of carbon source, yielded as high as 60% carbon in the  $Co_3O_4/CoO$  @ carbon sample. The formed carbon nanonetwork is expected to increase conductivity of the sample and decrease the diffusion path. Such an enhanced conductivity as well as reduced



 $\label{eq:scheme 1. Schematic representation of the hydrothermally-derived Co_3O_4/CoO @ carbon matrix showing Co_3O_4/CoO grains are anchored on to the carbon.$ 

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diffusion path is expected to deliver excellent supercapacitor and photocatalytic performances. Based on the results obtained here, schematically the material can be best described as shown in Scheme 1.

#### 3.2. Supercapacitor performances

The electrochemical activity of the hydrothermally-derived Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon was investigated using cyclic voltammetry and galvanostatic charge-discharge studies in 1 M KOH in the potential range of 0-0.5 V vs. Ag/AgCl for application in supercapacitors. Fig. 4a. shows the CV curves recorded for the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon sample in the potential range of 0-0.5 V at various scan rate of 2, 5, 10, 20, 50 mV s<sup>-1</sup> in 1 M KOH. A pair of redox peaks is clearly seen in all the cases suggesting the electrochemically active nature of the prepared material and demonstrating the conventional behaviour of a battery-type electrode. For comparison, the CV curve recorded on the bare nickel foam (NF) substrate is also given. It is seen that the bare substrate did not show any significant current in 1 M KOH, indicating it is electrochemically inert and provides only support for the active material. Thus, the charge storage is dominated by the Faradaic reaction. The anodic oxidation peak appears at 0.33 V and the cathodic reduction peak occurs at 0.25 V with the peak potential separation of about 80 mV at 2 mV s<sup>-1</sup> scan rate. The peak potential separation observed here is slightly higher value than the value of an ideal reversible reaction (59 mV), implying the redox reaction is quasi reversible. The following electrochemical reactions are responsible for the appearance of current peaks in KOH:<sup>23, 47</sup>

$2 \text{ CoO} + 2\text{OH}^{-} \leftrightarrow \text{H}_2\text{O} + \text{Co}_2\text{O}_3 + 2 \text{ e}^{-}$	(6)
CoO + OH⁻ ↔ CoOOH + e⁻	(7)
$Co_3O_4 + OH^- + H_2O \leftrightarrow 3 CoOOH + e^-$	(8)

In addition to the peak at 0.25 V, it is noted that a shoulder peak appears at 0.05 V. The appearance of such a shoulder peak implies that more than one redox reaction is proceeding on the electrode. The appearance of anodic peak is due to the oxidation of  $Co^{2+}$  to  $Co^{3+}$  and the cathodic peak corresponds to the reduction to lower oxidation state of  $Co^{3+}$ . Thus, it is believed that both CoO and  $Co_3O_4$  are undergoing redox reaction with the KOH. It is seen that as the scan rate increased, the peak current also increased, as it has been usually observed for a battery-type electrode.<sup>48</sup> Fig. 4b shows the variation of anodic and cathodic peak currents with the square root of scan rate (known as Randles-Sevcik plot). In both cases, the peak current varies linearly with the square root of the scan rate which is characteristics of a diffusion controlled fast reversible Faradaic reaction.<sup>49</sup>

Fig. 5a shows the galvanostatic charge  $\mathbb{P}$ discharge profiles recorded for the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon electrode at current densities of 1, 2, 3, 4, 5 and 10 A g<sup>-1</sup> in a potential window of 0 to 0.45 V. It can be seen that the charge-discharge profiles are nearly mirror images revealing that the Faradaic reactions are reversible. Interestingly, it is noted that for the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon electrode, clear plateau region is seen in the potential



6 7 d (b) Randles plot obtained for le in 1 M KOH. substantiating the y confirms that the

Fig. 4 Cyclic voltammetry curves at different scan rates and (b) Randles plot obtained for the hydrothermally-derived  $Co_3O_4/CoO$  @ carbon electrode in 1 M KOH.

range of 0.25–0.4 V vs. Ag/AgCl substantiating the aforementioned CV data, which clearly confirms that the Faradaic process is a typical battery-type electrode. In addition, the  $Co_3O_4/CoO$  @ carbon electrode exhibits high charge/discharge times; this validate the role of carbon matrix in the sample. The carbon matrix facilitates the charge transport providing an efficient conductive pathway leading to enhance the battery-type characteristics of the  $Co_3O_4/CoO$  @ carbon electrode was estimated from the charge-discharge curves using the following formula:<sup>50</sup>

$$E_s = I t/m C g^{-1}$$
 (9)

where,  $E_s$  is the specific capacity (C g<sup>-1</sup>), t is the discharge time (s), I is the constant discharge current (A), m is the active mass of the electrodes (g). The uniformity in shape of all the charge-discharge profiles confirms that the redox reactions are highly reversible.

(a)

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0.5

0.4

0.3

0.2

0.1

0.0

500

400

300

200

100

250

Potential (V)

0

200

0 L 0

Specific Capacity (C g<sup>-1</sup>)

⊃otential (V) vs. Ag/AgCI

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Fig. 5b shows the dependence of specific capacity on the

current density. The specific capacity decreases with increase of

current rate. At lower current, high specific capacity and at high

Fig. 5 (a) Galvanostatic charge-discharge profiles at different currents. (b) Dependence of specific capacity on the current densities and (c) Cycle-life data as well as Coulombic efficiency at 10 A  $g^{-1}$  recorded for the hydrothermally-derived Co<sub>2</sub>O<sub>4</sub>/CoO @ carbon sample in 1 M KOH. Inset: first three and last three cycles of charge-discharge profiles recorded at a current density of 10 A g<sup>-1</sup>

600

Cycle number

800

1000

400

current lower specific capacity have been resulted which is a characteristic of a battery-type material. The fast chargingdischarging process at high current density is always associated with poor utilization of the active mass resulting in low capacity. The specific capacity of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon electrode estimated at 1 A g<sup>-1</sup> 1 M KOH was as high as 324 C g<sup>-1</sup>. It is noted that even at a high current of 10 A g<sup>-1</sup>, the Co<sub>3</sub>O<sub>4</sub> /CoO @ carbon electrode exhibits specific capacity of about 207 Cag-1 The specific capacity in the range of 75-300 C gal: has been heported for the CoO or Co<sub>3</sub>O<sub>4</sub> as shown in Table 1. Interestingly, the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon electrode exhibits much better specific capacity than several available reports, implying that the Co<sub>3</sub>O<sub>4</sub>/CoO@ carbon can be a potential electrode for supercapacitor application.

High stability is one of the vital parameters of a supercapacitor for an actual application. Thus, the glavanostatic charge-discharge cycles were done for 1000 cycles at a current of 10 A g<sup>-1</sup>. In each cycle, the specific capacity and Coulombic efficiency were calculated by using the following formula:

$$q = Q_D / Q_C \qquad (10)$$

where,  $Q_D$  is the discharge capacity and  $Q_C$  is the charge capacity. Fig. 5c shows the cycling stability and Coulombic efficiency obtained for the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon electrode. The Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon electrode exhibits specific capacity of 207 C g<sup>-1</sup> at the first cycle and 192 C g<sup>-1</sup> at the end of  $1000^{th}$  cycle. Thus, the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon electrode retained over 91% of charge even at 1000<sup>th</sup> cycle. Interestingly, the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon matrix also exhibited high Columbic efficiency of 96 % even at 1000<sup>th</sup> charge-discharge cycle. It can be seen that the charge-discharge profiles at the first cycle and the 1000<sup>th</sup> cycle are nearly similar, exhibiting excellent stability (inset of Fig. 5c). It is believed that such an excellent stability and high Coulombic efficiency could be due to the presence of conductive carbon nano-network which would have facilitated the charge storage efficiently by reducing diffusion path. The merits of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon over other oxides are its excellent batterytype behaviour and stability due to non-dissolution of metal ions in the aqueous electrolyte which are very important for developing a practical hybrid energy-storage device.

Table 1 Specific capacity reported for cobalt oxide-based materials

S. No.	Name of sample	Method	Specific capacity (C g <sup>-1</sup> )	Reference
1	$\alpha$ -Co(OH) <sub>2</sub> and CoO	Radiation	195 in	[12]
		induced	1M KOH	
		method		
2	Co <sub>3</sub> O <sub>4</sub> /carbon	Low	200 in	[18]
	microspheres	temperature	2M KOH	
		solution route		
3	Co <sub>3</sub> O <sub>4</sub> and CoO	Solution	160 in	[23]
		combustion	6M KOH	
4	CoO	Ball milling	300 in	[48]
			1M KOH	
5	CoO/RGO	Microwave	180 in 2	[49]
		synthesis	М КОН	
6	CoO/graphene foam	Hydrothermal	140 in 3	[51]
			M NaOH	
7	CoO on grapheme	Hydrothermal	220 in	[52]
			ЗМ КОН	
8	CoO/Co <sub>3</sub> O <sub>4</sub> @carbon	Hydrothermal	324 C g <sup>-1</sup>	This work
			in 1 M	
			КОН	

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To understand the kinetics of ion and electron transports in the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon matrix, the EIS studies were done for freshly assembled cell as well as at the end of several chargedischarge cycles. Fig. 6a shows the Nyquist plots obtained for the representative charge-discharge cycles. Each plot consists of a depressed semicircle in the high-frequency region and an extended spike (Warburg element) in the low-frequency region. Similar Nyquist plot has been reported elsewhere.<sup>50,51</sup> It is noted that as the number of charge-discharge cycle increases, the diameter of the semicircle increases and the spike shifts to higher resistance value. The presence of Warburg element implies the dominance of diffusion controlled Faradaic reaction, especially at higher number of charge-discharge cycles. The obtained Nyquist plots were fit into an equivalent circuit as shown in inset of Fig. 6b. The equivalent circuit consists of solution resistance ( $R_s$ ), charge-transfer resistance ( $R_{ct}$ ) of a Faradaic reaction occurring on the electroactive surface, constant phase element (Cpe) and Warburg component (W).49-51 From the best fit, the  $R_s$  and  $R_{ct}$  values were obtained for the representative charge-discharge cycles. It was found that both R<sub>s</sub> and R<sub>ct</sub> increased as the number of charge-discharge cycle increased. This means the increase of intrinsic resistance of the electrode material due to interaction with the OH ions. Thus, the electrode exhibited decreased specific capacity at higher charge-discharge cycle. This has been substantiated by the conductivity of the electrode matrix estimated from the Rs value as shown in Fig. 6c. The conductivity of the electrode was estimated using the following equation:52

 $\sigma_{s} = I / R_{s} \times A$  S cm<sup>-1</sup> (11)

where,  $\sigma_s$  is electrode conductivity (S cm<sup>-1</sup>), I is the distance between the two electrodes (cm), R<sub>s</sub> is the solution resistance (Ohm), A is the area of electrode interacting with electrolyte (cm<sup>2</sup>). It is seen that as we move from 1<sup>st</sup> cycle to 1000<sup>th</sup> cycle, the conductivity decreases significantly. Fig. 6d shows the Bode plot recorded at the representative charge-discharge cycles.

Fig. 6 Nyquist plots (a) full range, (b) high frequency region at representative chargedischarge cycles, (c) variation of conductivity with the cycle number and (d) Bode plots

at different cycle numbers obtained for the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon matrix electrode in 1 View Article Online DOI: 10.1039/C7NJ04638C

It is noted that the phase angle at high-frequency region is low due to high electrode/electrolyte resistance, supporting lower specific capacity at higher charge-discharge cycles.

#### 3.3. Photocatalytic degradation of AZA dye

The photocatalytic property of the  $Co_3O_4/CoO$  @ carbon material was analyzed in terms of the decoloration of the AZA dye in aqueous solution under UV irradiation. The aqueous solution of AZA exhibits absorption maxima at 625 nm owing to its monomeric form.<sup>53</sup> The degradation of the dye was studied by monitoring the changes in the absorption maxima of the AZA with respect to the irradiation time.

Absorption profiles of the AZA solution in the presence of catalyst was recorded under UV radiation exposed from 0 to 70 min. The obtained absorption profiles are displayed in Fig. 7a. For comparison, the absorption profile of the AZA dye solution in the absence of the catalyst was also recorded and presented in Fig. 7a. It is seen that in all cases, the absorption maximum is centred at 625 nm which is characteristic of the AZA absorption. It is noteworthy that the absorbance recorded for the AZA dye solution in the absence of catalyst is about 1.2. Upon addition of the catalyst, the absorbance of the AZA dye decreased to nearly half (0.6 at 0 min). The decreases in intensity soon after the addition of the catalyst could be due to the adsorption of the AZA dye molecules on the surface of the catalyst. Such an adsorption can facilitate effective degradation.54 It can be noticed from Fig. 7a that the absorbance of the AZA dye steadily decreases with increasing UV irradiation time in the presence of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon catalyst. The absorption spectral change is accompanied by simultaneous colour fading of the AZA dye from blue to colourless and such colour fading is often associated with gradual decomposition of chromophoric group of the dye molecule.<sup>34,53</sup> To confirm the degradation of the AZA dye in the presence of the catalyst, the absorption profile of the AZA dye solution in the absence of the catalyst was recorded under UV radiation exposure 0 to 70 min. The obtained absorption profiles are shown in Fig.7b. It is noted that the absorption maximum is centred at 625 nm in all examined period with the absorbance value of in the range of 1 - 1.2 even after 1h of UV exposure. The formation of free radicals and selfaggregation of the AZA dye have resulted in the decrease of absorption intensity upon UV irradiation. Similar observation has been reported for photoactive phenothiazine dye elsewhere.<sup>38</sup> The data obtained from absorption spectral studies were utilized to calculate the decomposition rate  $(C_t/C_0)$ of the AZA dye as a function of UV irradiation time and the obtained plot is displayed in Fig. 7c. The  $C_0$  and  $C_t$  are the concentrations of AZA dye before and after UV light irradiation, respectively. The degradation (%) of the AZA was found to be 95% and it is obvious from Fig. 7 (b and c). that in the absence of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon catalyst, the decomposition of the AZA dye under the same UV light irradiation conditions was found to be insignificant, confirming the excellent photo

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degradation performance of the dye on the  $Co_3O_4/CoO$  @ carbon material. The change in absorption spectra of the AZA dye upon equilibrating with the catalyst in dark is given in Fig. 7d. It is obvious from Fig. 7d that upon



Co3O4/CoO @ carbon catalyst (c) under dark condition at 0 and 70 min.

incubation in the dark even upto 70 min, the spectral profile of the AZA dye remains unperturbed which clearly rules out the possibility of any dark reactions. It is worth mentioning that the amount of added catalyst and the irradiation time showed a prominent effect on the degradation rate. However, we have optimized the photoreaction in such a way that the amount of the  $Co_3O_4/CoO$  @ carbon is kept minimal for cost-effective performance.

To understand the reaction kinetics involved in the degradation reaction of the AZA dye, we analyzed the absorption spectral data of degraded dyes over a specified period of time by the pseudo-first order kinetic model using equation,<sup>55</sup>

$$ln(C_t) = ln(C_0) - K_r t$$
 (12)

where,  $C_0$  is the initial concentration of the AZA and  $C_t$  represents the concentration of the AZA at a time t and  $k_r$  is the rate constant of the pseudo-first order reaction. The kinetic plot for the photocatalytic degradation of the AZA is displayed in the inset of Fig. 7c. As shown in the inset of Fig. 7c, the plot of  $ln(C_t/C_0)$  vs t obeys a linear regression with a slope value equal to rate constant  $k_r$ . It is well known that a linear plot is indicative of the existence of first order reaction kinetics.

If the order of the reaction is anything other than one (second (2) or third (3) order) then the graph of  $\ln(C_t/C_0)$  vs t will be a curve (not a straight line).<sup>56</sup> Thus, from the above observation it is inferred that the photocatalytic degradation of the AZA in the presence of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon catalyst follows first order rate kinetics and the rate constants for the photocatalytic degradation of the AZA was found to be 0.023 min<sup>-1</sup>. It is worth mentioning that the photocatalytic

performance of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon  $v_i$ material number of the previously Peported TON catalyst for the degradation of phenothiazine dyes.<sup>38</sup>

#### 3.4. Product analysis of degraded AZA

The analysis of the photodegraded AZA dye was done by using UV-Vis and FT-IR spectroscopies. Fig. 8a shows the obtained UV-Vis spectra of the AZA dye before and after the photocatalytic treatment. It is evident that before photocatalytic degradation, the AZA exhibits two well-resolved maxima at 245 nm and 289 nm in the UV region and an intense absorption maximum at 625 nm in the visible region.57 The presence of conjugated system arising out of the dimethylamine substituted aromatic rings through the sulfur and nitrogen is responsible for the appearance of intense peak at 625 nm, whereas the small bands in the UV region (centered at 245 nm and 289 nm) are attributed to the substituted benzene rings.<sup>57</sup> As is seen, after the photocatalytic degradation, all the three characteristic absorption peaks of the AZA dye are completely disappeared. No significant absorption peak was observed. Thus, it is evident that the AZA dye has undergone complete mineralization owing to the photodegradation in the presence of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon catalyst under UV radaition. The degraded product did not have any significant functional group.

To substantiate the UV-Vis spectral data as well as to get better insights into the final degradation pattern of the AZA dye, FT-IR analysis of the AZA dye before and after photodegradation under catalyst, was performed. It is obvious from Fig. 8b that the FT-IR spectra of the AZA before degradation exhibits band at 3421 cm <sup>-1</sup> corresponding to N-H stretching modes. The asymmetric and symmetric bending vibrations of dimethylamino are observed at 1483 and 1392 cm<sup>-1</sup>, respectively. The most intense band in the IR spectrum at 1609 cm<sup>-1</sup> is caused by the tangential C=C stretching vibration. The strong band at 1484 cm<sup>-1</sup> is attributed to the C–N–C asymmetric stretching vibration of the central ring and phenyl ring. The ringstretching mode of C-N bond vibration is observed as a strong band at 1336 cm<sup>-1</sup>. The strong and medium bands at 897 and 872 cm<sup>-1</sup> are assigned to C–S–C stretching vibrations of the central ring coupled with phenyl ring deformation modes and the wagging mode of the amino group, respectively.57 Interestingly, the FT-IR spectrum of the photodegraded AZA dye exhibited bands corresponding to OH stretching at 3280 cm<sup>-1</sup>, OH bending vibrations at 1632 cm<sup>-1</sup> and the band at 1051 cm<sup>-1</sup> is ascribed to C-C bond arising out of trace carbon elements, respectively. The absence of characteristic N-H stretching, C-S-C stretching, phenyl ring-N (C–N) stretching and dimethylamino bending stretching vibrations in the FT-IR data suggests that the aromatic ring of the AZA dye is completely degraded.

It has been reported that oxidative mineralisation of thiazine dyes (Note: AZA is a thiazine dye) involves a series of pathway involving demethylation (formation of azure C and thionine) and ring opening products (amino-diol, sulfonic acid and aniline).<sup>58</sup> The absence of characteristic peaks of the aforementioned intermediates in the absorption and FT-IR spectral data of the degraded AZA dye, clearly implies that the AZA dye got completely mineralised. The process of complete



Fig. 8 (a) Absorption profiles and (b) FT-IR spectra recorded for the AZA dye before and after photodegradation in the presence of  $Co_3O_4/CoO$  @ carbon catalyst.

mineralisation of thiazine dyes in the presence of photocatalyst is driven by oxidative process involving both the hydroxide and super oxide radicals generated at the interface of the  $Co_3O_4/CoO$  @ carbon catalyst.<sup>58</sup> Thus, from the UV-Vis absorption and FT-IR spectral analysis, it is confirmed that the AZA dye gets mineralised under photodegradation in the presence of the  $Co_3O_4/CoO$  @ carbon catalyst. The degradation pattern of the AZA can be depicted as shown in the Scheme 2 below:



Scheme 2 Plausible degradation mechanism of the AZA dye under UV radiation in the presence of  $Co_3O_4/CoO$  @ carbon catalyst.

#### 3.5. Explanation for Photocatalytic degradation of AZA-dyeticle Online

DOI: 10.1039/C7NJ04638C The ability of semiconductor nanoparticles to generate electron-hole pairs play a vital role in the photocatalytic degradation of dye molecules.<sup>32,38</sup> Upon the interaction of the UV light with the  $Co_3O_4/CoO$  @ carbon catalyst, an electron in the valence band of the catalyst material is excited to the conduction band with the simultaneous generation of a hole in the valence band. The holes that are accumulated on oxide surface will oxidize water or surface hydroxyls to form reactive hydroxide radicals (OH<sup>-</sup>). Whereas, the photogenerated electrons will react with oxygen to produce super oxide radicals  $(O_2^{-})$ , which then reacts with the adsorbed AZA dye molecules to produce oxidized species or decomposed products. In addition to the above factors, the synergistic effect of the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon material is expected to have a significant effect on the photocatalytic degradation of the AZA. For instance, the decrease in the recombination of the photogenerated electrons and holes allows them to take part in the photocatalytic reaction. The presence of the carbon matrix around the Co<sub>3</sub>O<sub>4</sub>/CoO acts as a good supporting material for the catalyst by reducing diffusion path and ensures the adsorption of more amount of the AZA dye molecules over the catalyst surfaces for efficient catalytic performance. Thus, the Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon can be a potential dye degradation material for practical application. Owing to the wide spread use of the AZA in pigments, insecticides and staining agent, the AZA dye is extensively discharged to the nearby vicinity, heavily polluting water and soil on the environmental eco-system. The developed catalyst can be utilized for degradation of the AZA in these places to mitigate any adverse effects caused due to the discharge of the dye in the environment.

#### Conclusions

The Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon electrode exhibited a specific capacity of 324 C g<sup>-1</sup> at 1 A g<sup>-1</sup> with high Coulombic efficiency as well as excellent long-term stability. It is believed that the carbon present in the Co<sub>3</sub>O<sub>4</sub>/CoO acted as conductive nanonetwork by reducing diffusion path which lead to such a high supercapacitor performance. The Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon material also exhibited high photocatalytic activity for the degradation of the AZA dye under UV illumination and the degradation percentage of AZA dye was found to be as high as 95% with short duration. Thus, the hydrothermally-derived Co<sub>3</sub>O<sub>4</sub>/CoO @ carbon can be a potential material for supercapacitor application and can function as efficient photocatalyst.

## Conflicts of interest

There are no conflicts to declare.

#### Acknowledgements

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## Supercapacitor and Photocatalytic Performances of Hydrothermally-derived

Co<sub>3</sub>O<sub>4</sub> / CoO @ Carbon Nanocomposite

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Hydrothermally-derived Co<sub>3</sub>O<sub>4</sub>/CoO @ Carbon Nanocomposite with spike-like cobalt oxide anchored on conductive carbon network showed excellent supercapacitor and photocatalytic performance