



Cite this: *RSC Adv.*, 2019, 9, 38430

# g-C<sub>3</sub>N<sub>4</sub>/CuO and g-C<sub>3</sub>N<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub> nanohybrid structures as efficient electrode materials in symmetric supercapacitors

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Metal oxide dispersed graphitic carbon nitride hybrid nanocomposites (g-C<sub>3</sub>N<sub>4</sub>/CuO and g-C<sub>3</sub>N<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub>) were prepared *via* a direct precipitation method. The materials were used as an electrode material in symmetric supercapacitors. The g-C<sub>3</sub>N<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub> electrode based device exhibited a specific capacitance of 201 F g<sup>-1</sup> which is substantially higher than those using g-C<sub>3</sub>N<sub>4</sub>/CuO (95 F g<sup>-1</sup>) and bare g-C<sub>3</sub>N<sub>4</sub> electrodes (72 F g<sup>-1</sup>). At a constant power density of 1 kW kg<sup>-1</sup>, the energy density given by g-C<sub>3</sub>N<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CuO devices is 27.9 W h kg<sup>-1</sup> and 13.2 W h kg<sup>-1</sup> respectively. The enhancement of the electrochemical performance in the hybrid material is attributed to the pseudo capacitive nature of the metal oxide nanoparticles incorporated in the g-C<sub>3</sub>N<sub>4</sub> matrix.

Received 31st October 2019  
 Accepted 18th November 2019

DOI: 10.1039/c9ra08979a

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## Introduction

Renewable energy storage and its supply upon demand have been a major challenge for researchers owing to the short life span and poor power delivery of conventionally used lithium-ion batteries.<sup>1</sup> The supercapacitor has been recognized as a suitable storage device that can be used in combination with batteries to mitigate the power delivery problems associated with batteries.<sup>2,3</sup> Supercapacitors possess excellent performance recyclability due to the absence of any mass transfer between the electrodes.<sup>4</sup> Carbon-based electrode materials have been used conventionally in supercapacitors owing to their high surface area and storage capacity.<sup>5,6</sup> Nitrogen-doped carbon allotropes emerged recently as supercapacitor electrodes, which show excellent electrode electrolyte interaction due to the presence of lone pair electrons on the nitrogen atom.<sup>7</sup>

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is considered as an intrinsically nitrogen-rich system with lamellar structure. It is the most stable allotrope of carbon nitrides at ambient atmosphere, but it also has rich surface properties that are attractive for many applications including supercapacitor electrode and hydrogen evolution photocatalyst.<sup>8</sup> The polymeric structure of g-C<sub>3</sub>N<sub>4</sub> arises from the repetition of tri-s-triazine (symm. 1,3,5

triazine) units and the 2D lamellar structure arises from the weak van der-Waals interaction between the layers. The lone pair of electron on nitrogen could provide surface polarity on the electrode material and that could offer several binding sites for the electrolyte ions to interact with the electrode surface.<sup>9</sup> However, the semiconducting nature, low surface area and the agglomerated layer structure limit its application as a supercapacitor electrode.<sup>10</sup>

As in other carbon electrodes, the charge storage in g-C<sub>3</sub>N<sub>4</sub> is due the formation of electrical double layer at the electrode–electrolyte interface (EDLC) which is non-faradaic in nature. However the pseudo capacitive behavior in transition metal oxides (TMO), sulphides and conducting polymers arises due to the fast and reversible redox process between the electroactive material and electrolyte molecule (faradaic process).<sup>11–15</sup> Thus TMO with pseudocapacitive nature can be suitably coupled with g-C<sub>3</sub>N<sub>4</sub> layer structure to mitigate the limitations of bare g-C<sub>3</sub>N<sub>4</sub> electrodes.<sup>16</sup>

The commonly used transition metal oxides are ruthenium oxide,<sup>17</sup> manganese dioxide,<sup>18</sup> tungsten oxide,<sup>19</sup> nickel oxide,<sup>20</sup> *etc.* Among them, Co<sub>3</sub>O<sub>4</sub> and CuO have received a great deal of attention due to their economically viable and environmentally friendly nature.<sup>21,22</sup> Moreover, as reported by Zhou *et al.* Co<sub>3</sub>O<sub>4</sub> shows a very high theoretical capacitance of 3560 F g<sup>-1</sup> with an excellent shuttling between its Co<sup>2+</sup> and Co<sup>3+</sup> ions during electrochemical process.<sup>23,24</sup> In a recent report by Zheng *et al.* mesoporous Co<sub>3</sub>O<sub>4</sub> was anchored on the g-C<sub>3</sub>N<sub>4</sub> surface, and the composite material showed a specific capacitance value of 780 F g<sup>-1</sup> at a current density of 1.25 A g<sup>-1</sup>.<sup>25</sup> In another attempt, Shim *et al.* fabricated a supercapacitor from carbon and CuO anchored g-C<sub>3</sub>N<sub>4</sub>, which has given a specific capacitance value of 247.2 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>.<sup>26</sup> In the available reports, the electrochemical measurements were carried out in three electrode

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configuration. However, the actual performance of the device should be tested in two electrode configuration for practical applications. Only a very few reports are available in the literature based on the electrochemical properties of  $g\text{-C}_3\text{N}_4$  and  $\text{Co}_3\text{O}_4$ ,  $\text{CuO}$  nanohybrid systems.

In the present work pseudocapacitive  $\text{Co}_3\text{O}_4$  and  $\text{CuO}$  metal oxides were grown on the surface of a 2D  $g\text{-C}_3\text{N}_4$  phase. The hybrid materials were employed as electrode material in symmetric supercapacitors. The highlight of the present research is that the electrochemical properties of  $\text{Co}_3\text{O}_4$  and  $\text{CuO}$  modified  $g\text{-C}_3\text{N}_4$  were analyzed for the first time in symmetric two electrode configuration. The present research will be an excellent reference for the researchers working in the area of developing high energy density electrode materials with environmentally and economically benign nature.

## Experimental

### Synthesis of $g\text{-C}_3\text{N}_4$

$g\text{-C}_3\text{N}_4$  layer structure was prepared by the method reported elsewhere.<sup>4</sup> In a typical method, 5 g of thiourea was taken in a tightly closed silica crucible. The sample was heated to a temperature of 550 °C for 4 hours at a heating rate of two degrees per minute. The yellow colored  $g\text{-C}_3\text{N}_4$  phase was formed inside the crucible due to high-temperature self-polymerization of thiourea.

### Synthesis of $g\text{-C}_3\text{N}_4/\text{CuO}$ and $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ hybrid nanocomposites

Transition metal oxide (TMO) anchored  $g\text{-C}_3\text{N}_4$  such as  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ ,  $g\text{-C}_3\text{N}_4/\text{CuO}$  hybrid nanocomposites, with  $g\text{-C}_3\text{N}_4$  : TMO weight ratio of 7 : 3 was prepared by a simple precipitation technique. In this method, 0.06 g  $g\text{-C}_3\text{N}_4$  was weighed out separately in two beakers and dispersed in 50 ml distilled water by ultrasonication. 0.045 g  $\text{CuNO}_3$  and 0.06 g  $\text{CoNO}_3$  were dissolved separately and mixed with  $g\text{-C}_3\text{N}_4$  suspension by sonication for another 30 minutes.  $\text{NH}_4\text{OH}$  solution was added carefully to the suspension, and the pH was adjusted to 9. The precipitate of metal hydroxides so obtained was washed several times with de-ionised water, dried and calcined at a temperature of 300 °C for 2 h.

### General characterizations

The crystalline structure and phase formations of the materials were characterized by Bruker X-ray diffractometer using Copper  $K\alpha$  radiation ( $\lambda = 0.1546$  nm). Infrared spectra of the samples were recorded from Jasco-FT/IR-4100 spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out from Ultra Axis Kratos Analytical, UK, XPS instrument with an Al  $K\alpha$  X-ray source. The morphologies of the samples were characterized using field emission scanning electron microscope, Carl-Zeiss Gemini-300. Electrochemical studies of the samples were performed using VMP3 Biologic electrochemical workstation.

### Preparation of electrode and electrochemical analysis

The electrode preparation procedure for the fabrication of symmetric supercapacitor was given as follows. In a typical method

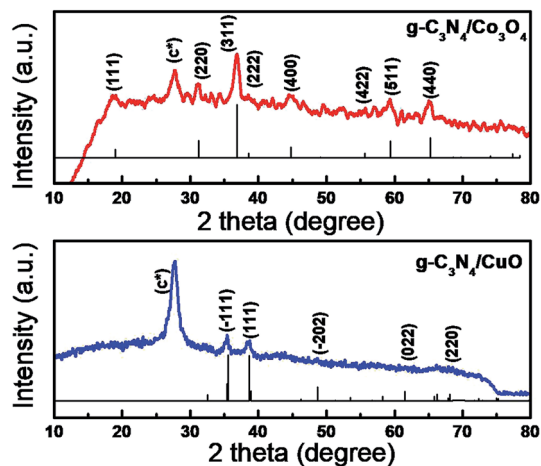


Fig. 1 XRD spectra of (a)  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and (b)  $g\text{-C}_3\text{N}_4/\text{CuO}$ .

8 : 1 : 1 ratio of the active material, PTFE binder, and the conducting material was mixed with ethanol and ultrasonicated for 30 minutes to obtain a uniform slurry. It was then coated uniformly on two conducting carbon cloth (ELAT, NuVant Systems Inc.) substrate having  $2 \times 2$  cm dimension and dried in a vacuum oven at 100 °C for 6 hours. The electrodes were then sandwiched on a separator (Celgard 3400), which was wetted with 30% KOH solution and placed carefully in an electrochemical test cell (ECC-std, EL-Cell GmbH).<sup>27</sup> The electrochemical measurements of the assembled device were performed in symmetric two electrode configuration by using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) by attaching the leads of the test cell to the electrochemical workstation (VMP3 Biologic).

## Results and discussions

### X-ray diffraction

The X-ray diffraction studies of the composite samples were carried out to analyze the phase formation of the component

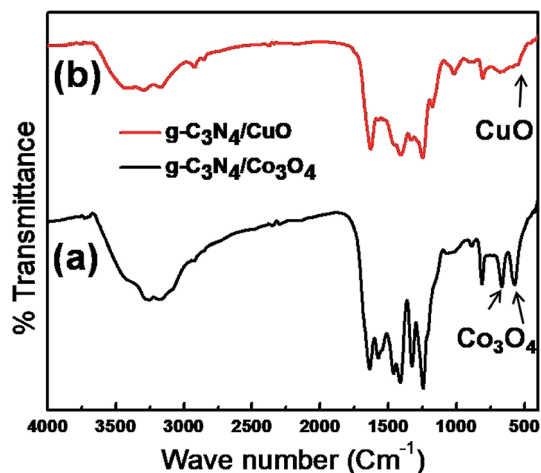


Fig. 2 FTIR spectra of (a)  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and (b)  $g\text{-C}_3\text{N}_4/\text{CuO}$ .



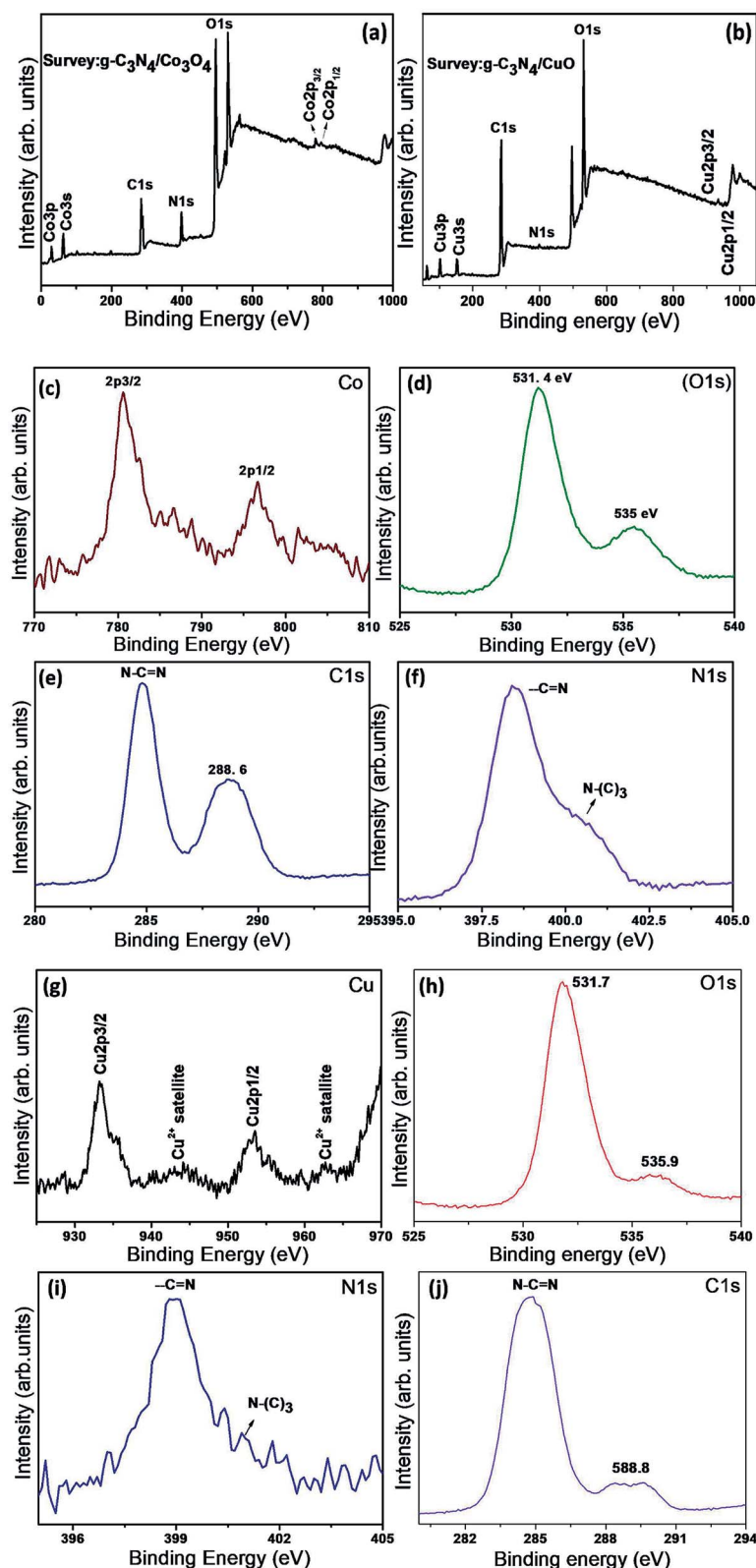


Fig. 3 Survey XPS spectrum of (a)  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and (b)  $g\text{-C}_3\text{N}_4/\text{CuO}$ . High resolution spectra of (c) Co 2p, (d) O 1s, (e) C 1s and (f) N 1s in  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ . High resolution spectra of (g) Cu 2p (h) O 1s (i) N 1s and (j) C 1s.

phases and were given as Fig. 1, the JCPDS card file is included along with XRD data for better understanding. In the XRD spectrum of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  (Fig. 1(a)), the peaks at  $2\theta$  values 18.9,

31.2, 36.9, 38.2, 44.7, 54.8, 59.4 and 65.3 corresponds to the diffraction from (111), (220), (311), (222), (400), (422), (511) and (440) planes of cubic phase of  $\text{Co}_3\text{O}_4$  (JCPDS no: 43-1003). The



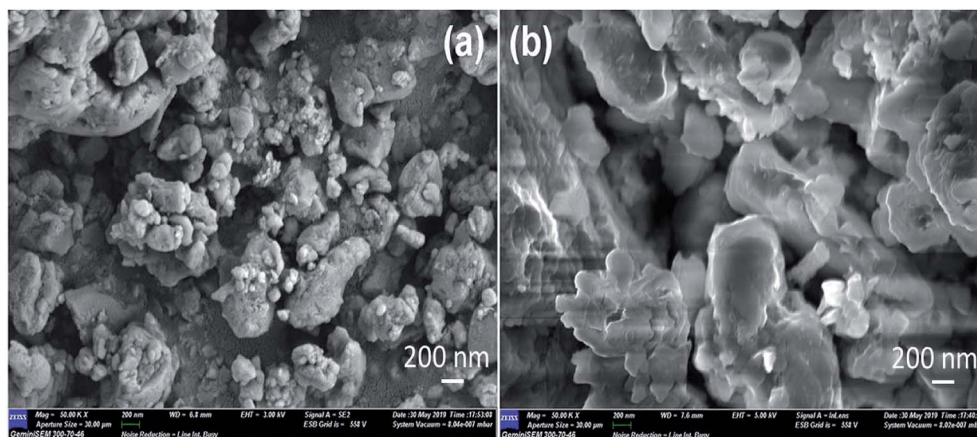


Fig. 4 (a) and (b) FESEM images of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and  $g\text{-C}_3\text{N}_4/\text{CuO}$  electrodes.

XRD spectrum of  $g\text{-C}_3\text{N}_4/\text{CuO}$  shows reflections at  $2\theta$  values 35.6, 38.5, 49.2, 66.6 and 68.2 corresponds to  $(-111)$ ,  $(111)$ ,  $(-202)$ ,  $(022)$  and  $(220)$  planes of the monoclinic phase of  $\text{CuO}$  (JCPDS no: 00-001-1117). The crystallite size of the particles calculated from Debye–Scherrer formula was 8–10 nm and 10–15 nm for  $g\text{-C}_3\text{N}_4/\text{CuO}$  and  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  respectively. The diffraction peaks marked as  $(C^*)$  is the characteristic peak of  $g\text{-C}_3\text{N}_4$

originated from the layer stacking arrangements in two-dimensional  $g\text{-C}_3\text{N}_4$  networks.

#### FTIR spectra

FTIR analysis (Fig. 2) of the composite sample was done to analyze the phase formation of the constituent phases further

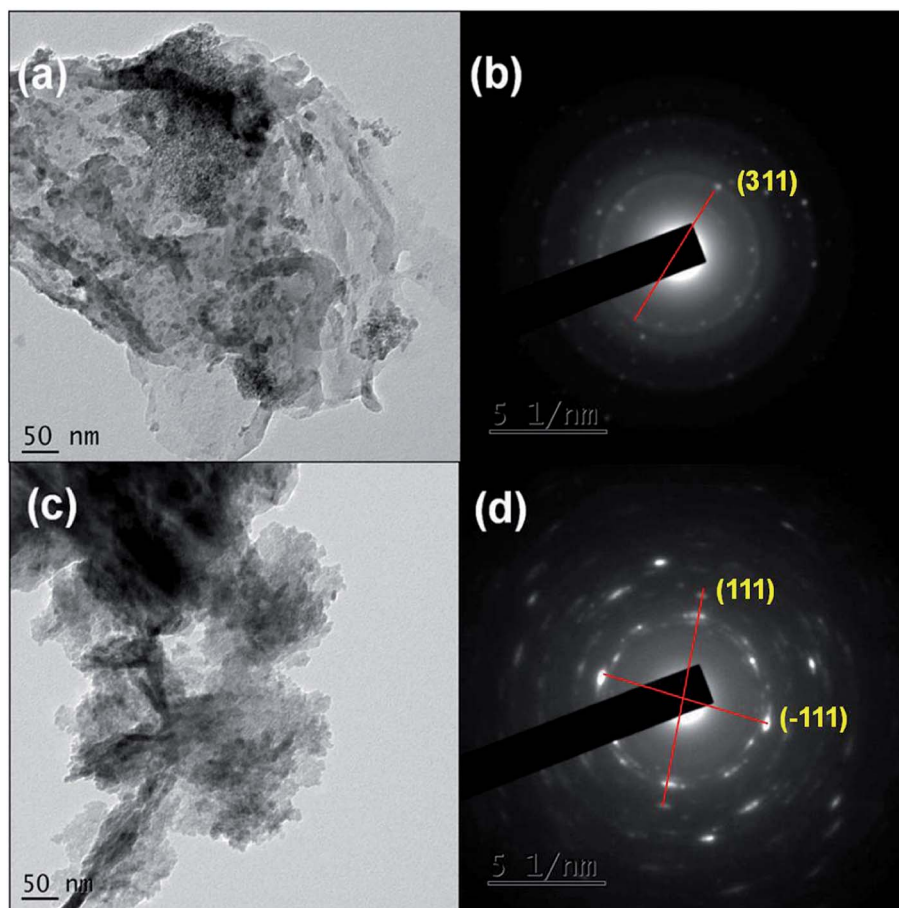


Fig. 5 (a) and (c) TEM images of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and  $g\text{-C}_3\text{N}_4/\text{CuO}$ ; (b) and (d) corresponding SAED patterns.



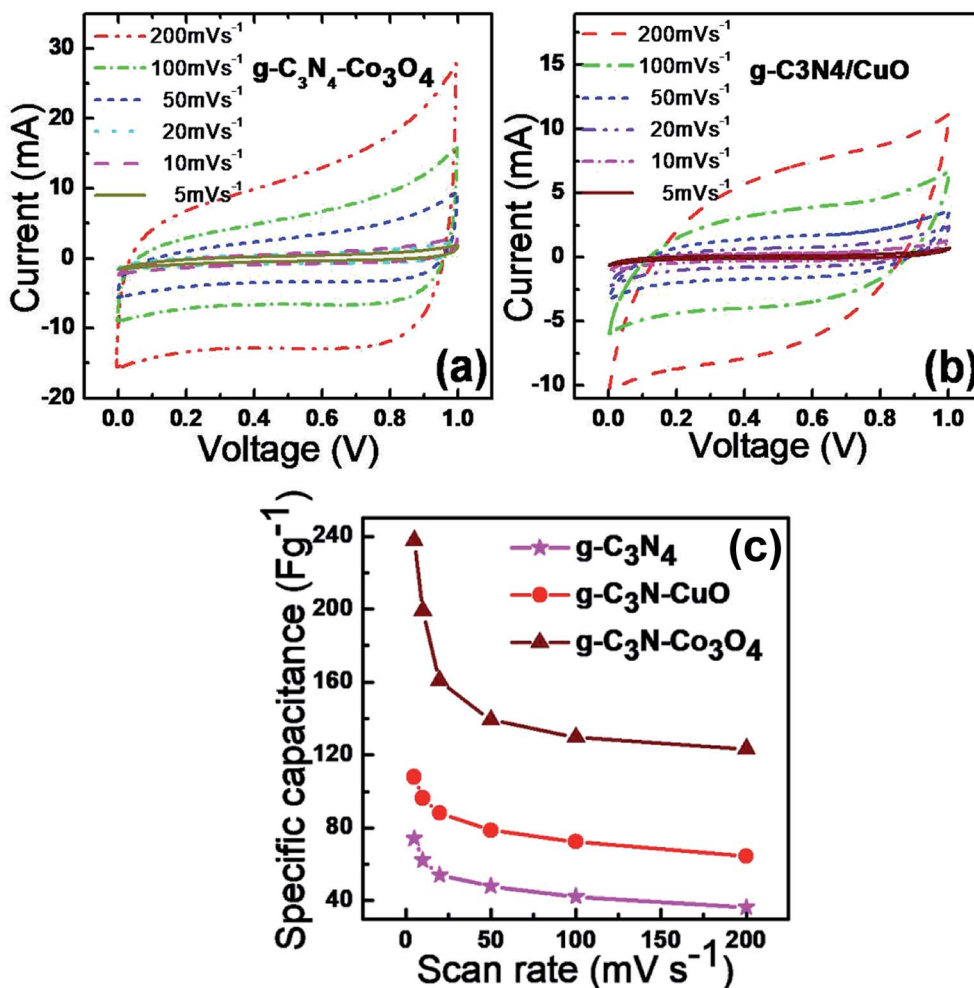


Fig. 6 Cyclic voltammograms of (a)  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and (b)  $g\text{-C}_3\text{N}_4/\text{CuO}$  at different scan rates. (c) Variation of specific capacitance of  $g\text{-C}_3\text{N}_4$ ,  $g\text{-C}_3\text{N}_4/\text{CuO}$  and  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  with scan rate.

and to determine the presence of a functional group attached to the surface of the electrode material. The common peaks in both the spectra of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and  $g\text{-C}_3\text{N}_4/\text{CuO}$  are due to the contribution from the  $g\text{-C}_3\text{N}_4$  phase. The peaks at the region of  $1200\text{--}1600\text{ cm}^{-1}$  arise from the  $\text{-CN}$  stretching vibrations of the heterocyclic rings of  $s$ -triazine units. The sharp at  $810\text{ cm}^{-1}$  is the characteristic peak originating from the breathing mode vibrations of triazine ring.<sup>28</sup> The peaks around  $1000\text{--}1100\text{ cm}^{-1}$  arise due to the bending vibrations of  $\text{-OH}$  functional groups and the broad peaks around  $3200\text{--}3600\text{ cm}^{-1}$  originate from the stretching vibrations of  $\text{H}_2\text{O}$  molecules adsorbed on the surface of the electrode material. The existence of spinel  $\text{Co}_3\text{O}_4$  nanoparticles on the electrode sample can be confirmed from the presence of sharp characteristic peaks in Fig. 2(a) at  $575\text{ cm}^{-1}$  and  $665\text{ cm}^{-1}$ , respectively.<sup>12</sup> The peak at  $537\text{ cm}^{-1}$  in Fig. 2(b) is the stretching vibrational band of  $\text{Cu-O}$  bond in monoclinic  $\text{CuO}$  crystal.<sup>22</sup>

#### X-ray photoelectron spectroscopy (XPS)

XPS spectra of the hybrid nanostructures  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and  $g\text{-C}_3\text{N}_4/\text{CuO}$  were recorded in order to analyze the chemical

composition and the electronic environment of the electrode materials. The survey XPS spectra of the samples were given as Fig. 3(a) and (b). The survey spectrum confirms the presence of constituent phases in the composite sample. Binding energy values in all the spectra were carbon corrected by comparing with C 1s value of  $284.8\text{ eV}$ . The high resolution XPS spectra of Co in Fig. 3(c) exhibit well defined peaks at  $780$  and  $796\text{ eV}$  corresponding to the  $\text{Co } 2p_{3/2}$  and  $\text{Co } 2p_{1/2}$  spin states with a spin separation of  $16\text{ eV}$ , which are the characteristics of  $\text{Co}_3\text{O}_4$  phase. Two weak satellite peaks at  $788$  and  $804\text{ eV}$  are the features of spinel structure in which  $+3$  ion occupy octahedral site and  $+2$  ion at the tetrahedral sites.<sup>29</sup> The O 1s peak at  $531.2\text{ eV}$  in Fig. 3(d) is the characteristic peak of spinel  $\text{Co}_3\text{O}_4$  structure which arises due to the presence of lattice oxygen. Second O 1s peak at  $535.9\text{ eV}$  is due to the presence of defective oxygen on the surface of the  $\text{Co}_3\text{O}_4$  phase. The two major peaks of C 1s in Fig. 3(e) at  $284.8$  and  $288.6\text{ eV}$  are originated from the  $\text{sp}^2$  hybridised  $\text{N-C=N}$  structure of  $g\text{-C}_3\text{N}_4$  network. The N 1s peaks in Fig. 3(f) at  $398.4$  and  $400.5\text{ eV}$  are attributed to the N atom from  $\text{N-C=N}$  and  $\text{N-(C)}_3$  structural units of  $g\text{-C}_3\text{N}_4$ .



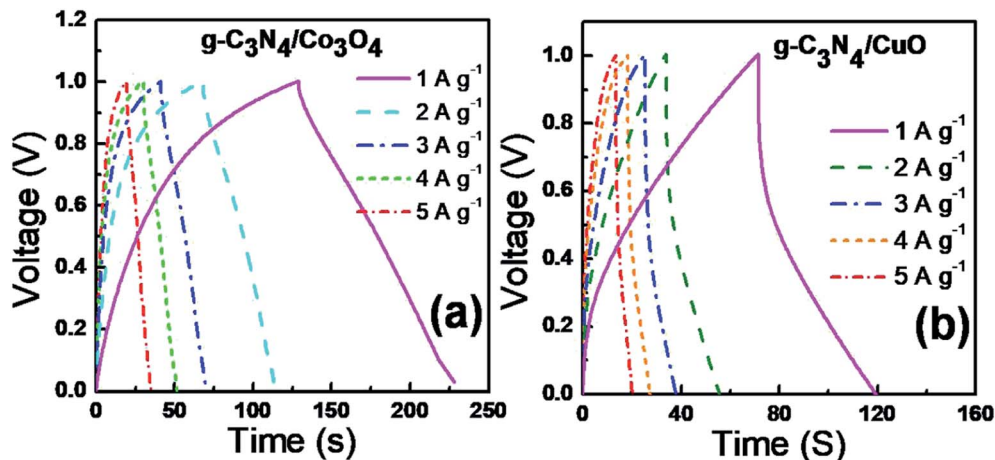


Fig. 7 GCD curves of (a)  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and (b)  $g\text{-C}_3\text{N}_4/\text{CuO}$  based supercapacitors at a constant current density of  $1 \text{ A g}^{-1}$  in  $2 \text{ M KOH}$  electrolyte.

The high resolution XPS spectra of Cu in  $g\text{-C}_3\text{N}_4/\text{CuO}$  is depicted in Fig. 3(g). The peaks at 933.2 and 953.3 eV are the characteristic signal of Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  respectively and the satellite peaks of  $\text{Cu}^{2+}$  at higher binding energy region are also visible.<sup>29</sup> The O 1s give spectra at 531.4 and 536.1 eV which is the characteristics of lattice and defective oxygen respectively (Fig. 3(h)). C 1s peaks at (Fig. 3(i)) 284.7 eV, 288.8 eV and the N 1s peaks (Fig. 3(j)) 398.9 eV and 400.9 eV are the characteristic peaks of  $g\text{-C}_3\text{N}_4$  as discussed in the case of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ .<sup>4</sup>

### Morphology analysis

The surface morphology of the composite electrodes  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and  $g\text{-C}_3\text{N}_4/\text{CuO}$  were depicted as Fig. 4(a) and (b).  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  sample exhibited a spherical morphology with porous nature, however in  $g\text{-C}_3\text{N}_4/\text{CuO}$  the particles aggregated together to form large grains which is unfavorable for the penetration of electrolyte molecules during electrochemical process. The crystalline nature of the materials were further analysed using TEM. As can be seen from Fig. 5(a) the  $\text{Co}_3\text{O}_4$  particles were uniformly distributed in the network of  $g\text{-C}_3\text{N}_4$  with a clear boundary between the constituent phases; however, in the case of  $g\text{-C}_3\text{N}_4/\text{CuO}$  (Fig. 5(c)), the distribution of CuO in  $g\text{-C}_3\text{N}_4$  matrix is non-homogeneous with a small aggregation of metal oxide phases in the matrix. The SAED patterns of the composite sample indicated that in  $g\text{-C}_3\text{N}_4/\text{CuO}$  (Fig. 5(d)), the metal oxide phases are more crystalline with bright spots than in  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  (Fig. 5(b)). The crystalline phases usually reduce the performance of an electrochemical device by decreasing the accessible surfaces for the electrolyte molecule to interact with the electrode surface. It is also seen from SAED pattern that the diffraction patterns are obtained from the highly populated planes of  $\text{Co}_3\text{O}_4$  (311) and CuO (111) & (-111) in the composite material.

### Cyclic voltammogram (CV)

The CV profiles of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and  $g\text{-C}_3\text{N}_4/\text{CuO}$  electrodes are shown in Fig. 6(a) and (b) respectively. The CV curve of an ideal

supercapacitor material is expected to have a rectangular shape. In current ( $i$ )-voltage ( $v$ ) curve, the value of current [ $i = C(v/t)$ ] should be constant since the scan rate ' $v/t$ ' and capacitance ' $C$ ' are constant.<sup>18</sup> In Fig. 6(a), the CV profiles of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  electrodes show a nearly rectangular type CV and an excellent current response, which are the characteristic features of an ideal capacitor. The CV profile of the symmetric supercapacitor based on  $g\text{-C}_3\text{N}_4/\text{CuO}$  electrodes Fig. 6(b) shows a small deviation from ideal capacitive behavior as compared to the  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  electrode. The calculated value of specific capacitance ( $C_{sp}$ ) from CV profile for  $g\text{-C}_3\text{N}_4/\text{CuO}$  and  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  at a scan rate of  $5 \text{ mV s}^{-1}$  was found to be  $238 \text{ F g}^{-1}$  and  $108 \text{ F g}^{-1}$  respectively which is far greater than the  $C_{sp}$  of bare  $g\text{-C}_3\text{N}_4$  ( $74 \text{ F g}^{-1}$ ). The variation in specific capacitance was compared in Fig. 6(c) with the scan rate for both the electrodes, with the electrochemical properties of bare  $g\text{-C}_3\text{N}_4$ . The  $C_{sp}$  value of all the electrodes was high at lower scan rate since the electrolyte molecule get more time for their interaction with the electrode surface. Compared to the electrochemical

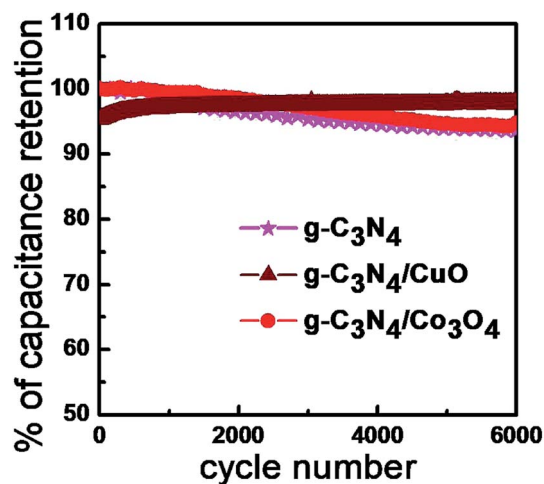


Fig. 8 Cycling stability curve of the supercapacitors at a constant current density of  $5 \text{ A g}^{-1}$ .



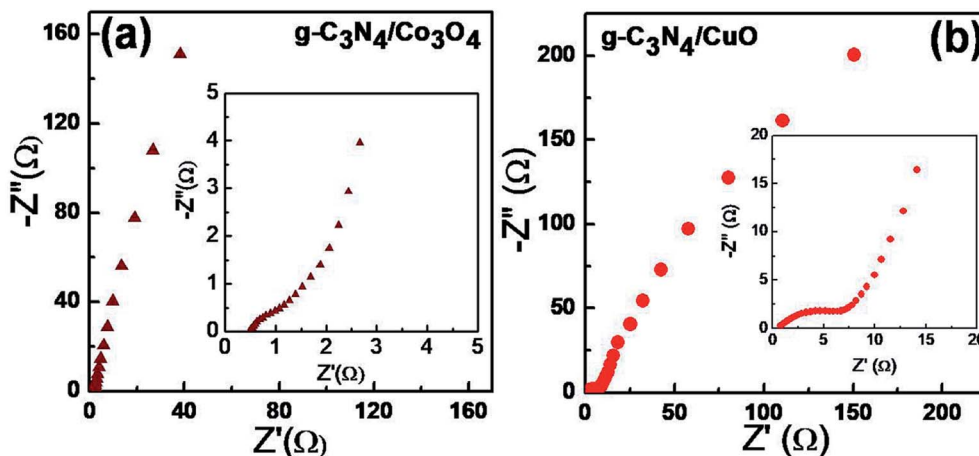


Fig. 9 Nyquist plots for (a)  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and (b)  $g\text{-C}_3\text{N}_4/\text{CuO}$  based supercapacitors over the frequency range from 100 kHz and 1 MHz.

performance of bare  $g\text{-C}_3\text{N}_4$ , the composite samples,  $g\text{-C}_3\text{N}_4/\text{CuO}$  and  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  have shown excellent performance due to the pseudocapacitive contribution from  $\text{CuO}$  and  $\text{Co}_3\text{O}_4$  nanocrystals.<sup>21</sup>

### Galvanostatic charge–discharge (GCD)

The actual device performance of the supercapacitor can be analyzed from the GCD experiments.<sup>30</sup> The GCD profile was performed in 1 M KOH solution at different current densities of 1, 2, 3, 4, and 5  $\text{A g}^{-1}$  and is shown in Fig. 7. Compared to  $g\text{-C}_3\text{N}_4/\text{CuO}$  (Fig. 7(b));  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  (Fig. 7(a)) supercapacitor electrodes exhibited an almost rectangular type GCD curve indicating an excellent efficiency for the charge–discharge process. The IR drop at the beginning of the GCD curve indicates the internal resistance of the electrode materials arising from electrical contact resistance, bulk solution resistance, and resistance from ion migration. Compared to  $g\text{-C}_3\text{N}_4/\text{CuO}$ , the IR drop value of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  is significantly lower, which indicates excellent charge efficiency for  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  supercapacitor. The specific capacitance value of the devices were calculated from the GCD profiles using the equation,

$$C_{\text{sp}} = \frac{2I}{m} \left( \frac{\Delta t}{\Delta v} \right);$$

where  $I$  is the discharge current,  $m$  is the mass loading of active material in a single electrode,  $\Delta t$  is the discharge time, and  $\Delta v$  is the cell potential range after IR drop. The  $C_{\text{sp}}$  value of  $g\text{-C}_3\text{N}_4/\text{CuO}$  and  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  electrodes at a current density of 1  $\text{A g}^{-1}$  was found to be 95  $\text{F g}^{-1}$  and 201  $\text{F g}^{-1}$ , respectively. At high current densities, the  $C_{\text{sp}}$  value of the devices decreases due to the limited interaction of the ions at the electrode–electrolyte interface.<sup>31</sup>

The cyclic stabilities of the supercapacitors were analyzed from the charge–discharge measurements under an applied current density of 5  $\text{A g}^{-1}$  for 6000 cycles and given as Fig. 8. The  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  based device exhibited excellent cyclic stability of 97% even after 6000 cycles. However, the stability of  $g\text{-C}_3\text{N}_4/\text{CuO}$  and  $g\text{-C}_3\text{N}_4$  based supercapacitors was found to be, 94% and 93% respectively. The agglomeration of the electrode material

during the electrochemical process could be a reason for the reduced cyclic stability in  $g\text{-C}_3\text{N}_4/\text{CuO}$  and  $g\text{-C}_3\text{N}_4$  electrodes.

The energy density and power density values of the devices were calculated from the GCD profile by the relation;  $E = \frac{1}{2} C_{\text{sp}} V^2$  and  $P = E/\Delta t$ . At a constant power density of 1  $\text{kW kg}^{-1}$ , the energy densities possessed by  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and  $g\text{-C}_3\text{N}_4/\text{CuO}$  based devices are 27.9  $\text{W h kg}^{-1}$  and 13.2  $\text{W h kg}^{-1}$  respectively.

### Electrochemical impedance spectra (EIS)

EIS measurements were carried out to further analyze the performance of the devices (Fig. 9). The EIS spectra or the Nyquist plots consist of a semicircle at the high-frequency area and a vertical line at the low-frequency area. The radius of the semicircle ( $R_{\text{ct}}$ ) gives the value of charge transport resistance of the electrode material. A small arc radius in EIS spectra indicates a better charge transport at the electrode–electrolyte interface.<sup>32</sup> EIS results show that the  $R_{\text{ct}}$  value of  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  (Fig. 9(a)) is very small compared to  $g\text{-C}_3\text{N}_4/\text{CuO}$  (Fig. 9(b)) electrodes indicating an excellent charge transport in the  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  electrode. The low-frequency region of the impedance spectra is associated with the ionic diffusion from the bulk of the solution towards the electrode surface. A vertical line parallel to the y-axis of the plot is the ideal condition for a supercapacitor material. It can be seen that for  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  electrodes, the straight line at the low-frequency region is more vertical than the other electrode. Moreover, the length of the straight line is very small (less imaginary part) in  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  electrodes designating a lower resistance for ion diffusion from the bulk of the solution.<sup>33</sup>

## Conclusions

In summary, pseudocapacitive  $\text{Co}_3\text{O}_4$  and  $\text{CuO}$  nano structures were anchored on the surface of the two dimensional  $g\text{-C}_3\text{N}_4$  by direct precipitation method. The hybrid materials,  $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$  and  $g\text{-C}_3\text{N}_4/\text{CuO}$  were used as electrode materials in symmetric supercapacitors. The electrochemical performance



of g-C<sub>3</sub>N<sub>4</sub> exhibited significant enhancement by coupling with Co<sub>3</sub>O<sub>4</sub> and CuO with a specific capacitance of 201 F g<sup>-1</sup> and 95 F g<sup>-1</sup> for g-C<sub>3</sub>N<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>/CuO composite materials respectively. The enhancement in electrochemical properties in the composites can be attributed to the presence of pseudocapacitive metal oxide phases. The g-C<sub>3</sub>N<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub> exhibited a cycling stability of 97% even after 6000 cycles with an energy density of 27.9 W h kg<sup>-1</sup>.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

R. B. Rakhi acknowledges the financial support from Ram-anujan Fellowship (SB/S2/RJN-098/2015) from DST-SERB, Government of India. Jithesh Kavil is grateful to University Grants Commission, Govt. of India for FDP fellowship.

## References

- M. R. Palacín and A. de Guibert, *Science*, 2016, **351**, 1253292.
- M. D. Stoller and R. S. Ruoff, *Energy Environ. Sci.*, 2010, **3**, 1294–1301.
- D. Guo, L. Lai, A. Cao, H. Liu, S. Dou and J. Ma, *RSC Adv.*, 2015, **5**, 55856–55869.
- J. Kavil, P. Anjana, C. Roshni, P. Periyat, K. G. Raj and R. Rakhi, *Appl. Surf. Sci.*, 2019, **487**, 109–115.
- L. L. Zhang and X. Zhao, *Chem. Soc. Rev.*, 2009, **38**, 2520–2531.
- C. Huang, Y. Ding, C. Hao, S. Zhou, X. Wang, H. Gao, L. Zhu and J. Wu, *Chem. Eng. J.*, 2019, **378**, 122202.
- L.-F. Chen, X.-D. Zhang, H.-W. Liang, M. Kong, Q.-F. Guan, P. Chen, Z.-Y. Wu and S.-H. Yu, *ACS Nano*, 2012, **6**, 7092–7102.
- S. P. Vattikuti, A. K. R. Police, J. Shim and C. Byon, *Appl. Surf. Sci.*, 2018, **447**, 740–756.
- Y. Gong, M. Li and Y. Wang, *ChemSusChem*, 2015, **8**, 931–946.
- J. Kavil, P. Anjana, P. Periyat and R. Rakhi, *J. Mater. Sci.: Mater. Electron.*, 2018, **29**, 16598–16608.
- A. B. Bhalerao, R. N. Bulakhe, P. R. Deshmukh, J.-J. Shim, K. N. Nandurkar, B. G. Wagh, S. P. Vattikuti and C. D. Lokhande, *J. Mater. Sci.: Mater. Electron.*, 2018, **29**, 15699–15707.
- S. P. Vattikuti, A. K. R. Police, J. Shim and C. Byon, *Sci. Rep.*, 2018, **8**, 4194.
- S. P. Vattikuti, P. Nagajyothi, P. Anil Kumar Reddy, M. Kotes Kumar, J. Shim and C. Byon, *Mater. Res. Lett.*, 2018, **6**, 432–441.
- H. Gao, X. Wang, G. Wang, C. Hao, S. Zhou and C. Huang, *Nanoscale*, 2018, **10**, 10190–10202.
- D. Wang, Y. Xiao, X. Luo, Z. Wu, Y.-J. Wang and B. Fang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 2509–2515.
- J. Kavil, P. Anjana, P. Periyat and R. Rakhi, *Sustainable Energy Fuels*, 2018, **2**, 2244–2251.
- F. Amir, V. Pham and J. Dickerson, *RSC Adv.*, 2015, **5**, 67638–67645.
- P. Suktha, P. Chiochan, A. Krittayavathananon, S. Sarawutanukul, S. Sethuraman and M. Sawangphruk, *RSC Adv.*, 2019, **9**, 28569–28575.
- J. Xu, C. Li, L. Chen, Z. Li and P. Bing, *RSC Adv.*, 2019, **9**, 28793–28798.
- K. Han, Y. Liu, H. Huang, Q. Gong, Z. Zhang and G. Zhou, *RSC Adv.*, 2019, **9**, 21608–21615.
- Q. Guan, J. Cheng, B. Wang, W. Ni, G. Gu, X. Li, L. Huang, G. Yang and F. Nie, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7626–7632.
- A. Pendashteh, M. F. Mousavi and M. S. Rahmanifar, *Electrochim. Acta*, 2013, **88**, 347–357.
- S. Zhou, Z. Ye, S. Hu, C. Hao, X. Wang, C. Huang and F. Wu, *Nanoscale*, 2018, **10**, 15771–15781.
- S. Zhou, C. Hao, J. Wang, X. Wang and H. Gao, *Chem. Eng. J.*, 2018, **351**, 74–84.
- H.-L. Zhu and Y.-Q. Zheng, *Electrochim. Acta*, 2018, **265**, 372–378.
- S. P. Vattikuti, B. P. Reddy, C. Byon and J. Shim, *J. Solid State Chem.*, 2018, **262**, 106–111.
- R. Rakhi, D. Cha, W. Chen and H. N. Alshareef, *J. Phys. Chem. C*, 2011, **115**, 14392–14399.
- G. Liao, S. Chen, X. Quan, H. Yu and H. Zhao, *J. Mater. Chem.*, 2012, **22**, 2721–2726.
- M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717–2730.
- B. Babu, S. G. Ullattil, R. Prasannachandran, J. Kavil, P. Periyat and M. M. Shaijumon, *ACS Sustainable Chem. Eng.*, 2018, **6**, 5401–5412.
- D. Jiang, Q. Xu, S. Meng, C. Xia and M. Chen, *J. Alloys Compd.*, 2017, **706**, 41–47.
- R. B. Rakhi, B. Ahmed, D. Anjum and H. N. Alshareef, *ACS Appl. Mater. Interfaces*, 2016, **8**, 18806–18814.
- W. Qi, R. Lv, B. Na, H. Liu, Y. He and N. Yu, *ACS Sustainable Chem. Eng.*, 2018, **6**, 4739–4745.

