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g-C₃N₄/CuO and g-C₃N₄/Co₃O₄ nanohybrid structures as efficient electrode materials in symmetric supercapacitors

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Metal oxide dispersed graphitic carbon nitride hybrid nanocomposites (g-C₃N₄/CuO and g-C₃N₄/Co₃O₄) were prepared *via* a direct precipitation method. The materials were used as an electrode material in symmetric supercapacitors. The g-C₃N₄/Co₃O₄ electrode based device exhibited a specific capacitance of 201 F g⁻¹ which is substantially higher than those using g-C₃N₄/CuO (95 F g⁻¹) and bare g-C₃N₄ electrodes (72 F g⁻¹). At a constant power density of 1 kW kg⁻¹, the energy density given by g-C₃N₄/Co₃O₄ and g-C₃N₄/CuO devices is 27.9 W h kg⁻¹ and 13.2 W h kg⁻¹ 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-C₃N₄ matrix.

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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.¹ 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.^{2,3} Supercapacitors possess excellent performance recyclability due to the absence of any mass transfer between the electrodes.⁴ Carbon-based electrode materials have been used conventionally in supercapacitors owing to their high surface area and storage capacity.^{5,6} 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.⁷

Graphitic carbon nitride (g-C₃N₄) 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.⁸ The polymeric structure of g-C₃N₄ 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.⁹ However, the semiconducting nature, low surface area and the agglomerated layer structure limit its application as a supercapacitor electrode.¹⁰

As in other carbon electrodes, the charge storage in g-C₃N₄ 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).¹¹⁻¹⁵ Thus TMO with pseudocapacitive nature can be suitably coupled with g-C₃N₄ layer structure to mitigate the limitations of bare g-C₃N₄ electrodes.¹⁶

The commonly used transition metal oxides are ruthenium oxide,¹⁷ manganese dioxide,¹⁸ tungsten oxide,¹⁹ nickel oxide,²⁰ *etc.* Among them, Co₃O₄ and CuO have received a great deal of attention due to their economically viable and environmentally friendly nature.^{21,22} Moreover, as reported by Zhou *et al.* Co₃O₄ shows a very high theoretical capacitance of 3560 F g⁻¹ with an excellent shuttling between its Co²⁺ and Co³⁺ ions during electrochemical process.^{23,24} In a recent report by Zheng *et al.* mesoporous Co₃O₄ was anchored on the g-C₃N₄ surface, and the composite material showed a specific capacitance value of 780 F g⁻¹ at a current density of 1.25 A g⁻¹.²⁵ In another attempt, Shim *et al.* fabricated a supercapacitor from carbon and CuO anchored g-C₃N₄, which has given a specific capacitance value of 247.2 F g⁻¹ at a current density of 1 A g⁻¹.²⁶ 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-C₃N₄ and Co₃O₄, CuO nanohybrid systems.

In the present work pseudocapacitive Co₃O₄ and CuO metal oxides were grown on the surface of a 2D g-C₃N₄ phase. The hybrid materials were employed as electrode material in symmetric supercapacitors. The highlight of the present research is that the electrochemical properties of Co₃O₄ and CuO modified g-C₃N₄ 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-C₃N₄

g-C₃N₄ layer structure was prepared by the method reported elsewhere.⁴ 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-C₃N₄ phase was formed inside the crucible due to high-temperature self-polymerization of thiourea.

Synthesis of g-C₃N₄/CuO and g-C₃N₄/Co₃O₄ hybrid nanocomposites

Transition metal oxide (TMO) anchored g-C₃N₄ such as g-C₃N₄/Co₃O₄, g-C₃N₄/CuO hybrid nanocomposites, with g-C₃N₄ : TMO weight ratio of 7 : 3 was prepared by a simple precipitation technique. In this method, 0.06 g g-C₃N₄ was weighed out separately in two beakers and dispersed in 50 ml distilled water by ultrasonication. 0.045 g CuNO₃ and 0.06 g CoNO₃ were dissolved separately and mixed with g-C₃N₄ suspension by sonication for another 30 minutes. NH₄OH 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 α 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 α 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

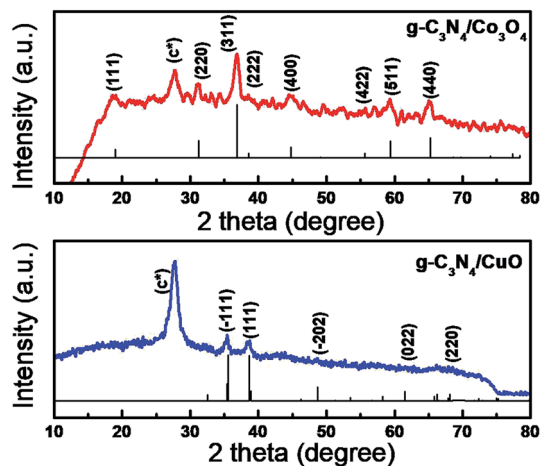


Fig. 1 XRD spectra of (a) g-C₃N₄/Co₃O₄ and (b) g-C₃N₄/CuO.

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 × 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).²⁷ 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

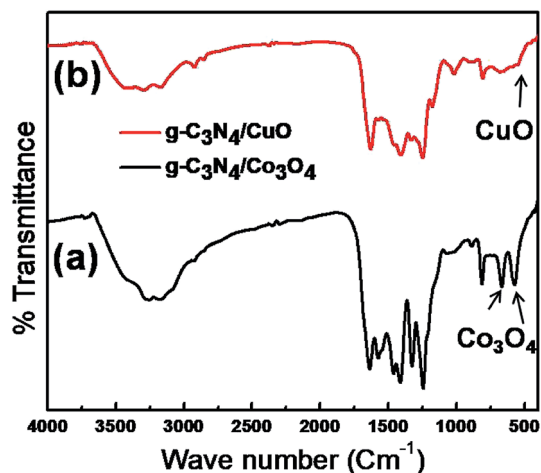


Fig. 2 FTIR spectra of (a) g-C₃N₄/Co₃O₄ and (b) g-C₃N₄/CuO.



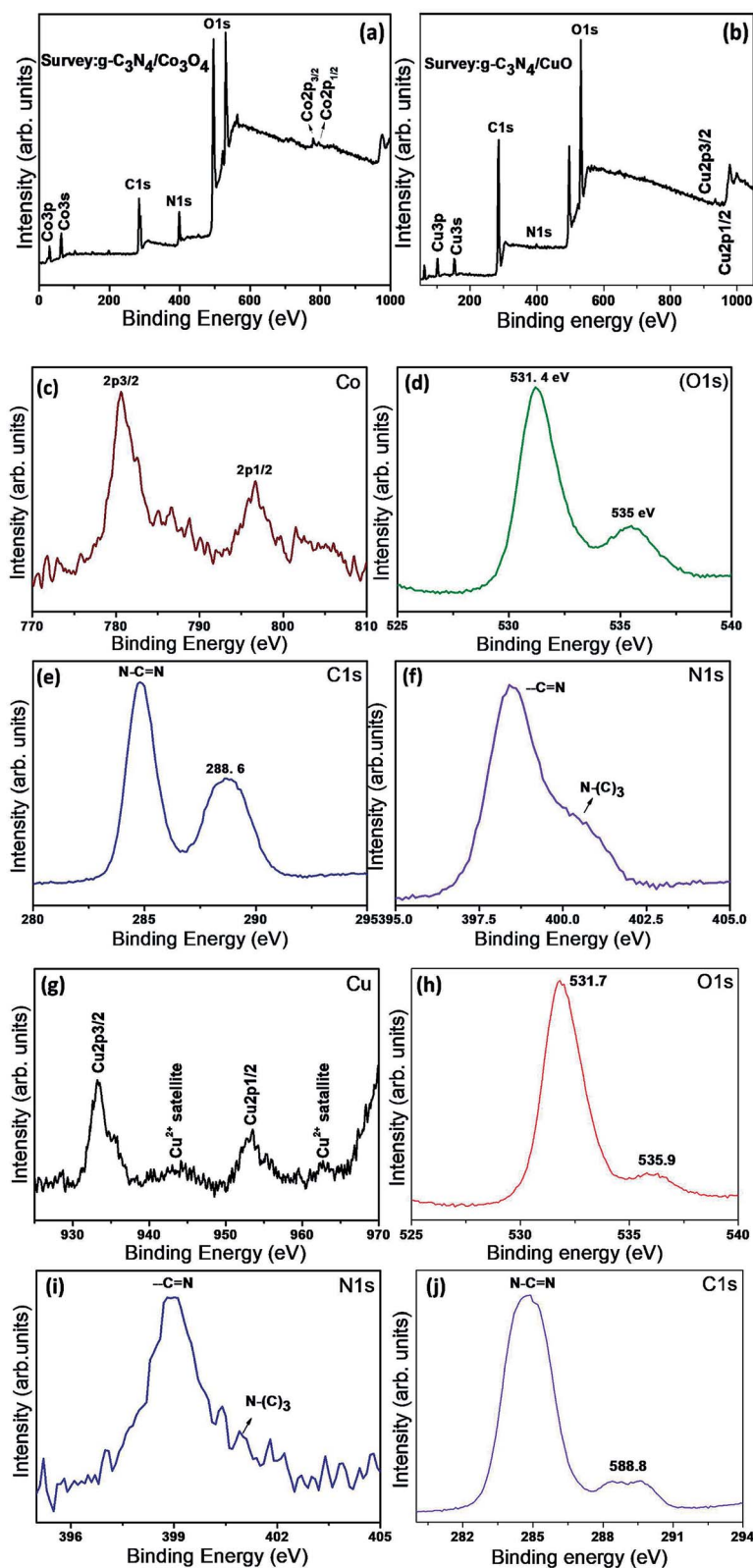


Fig. 3 Survey XPS spectrum of (a) $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ and (b) $g\text{-C}_3\text{N}_4/\text{CuO}$. High resolution spectra of (c) Co 2p, (d) O 1s, (e) C 1s and (f) N 1s in $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$. High resolution spectra of (g) Cu 2p (h) O 1s (i) N 1s 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 2θ 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 Co_3O_4 (JCPDS no: 43-1003). The



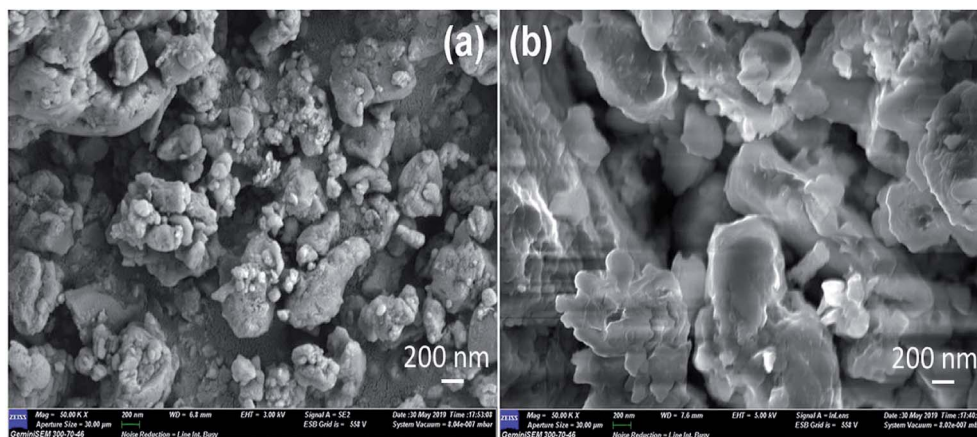


Fig. 4 (a) and (b) FESEM images of $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ and $g\text{-C}_3\text{N}_4/\text{CuO}$ electrodes.

XRD spectrum of $g\text{-C}_3\text{N}_4/\text{CuO}$ shows reflections at 2θ 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 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

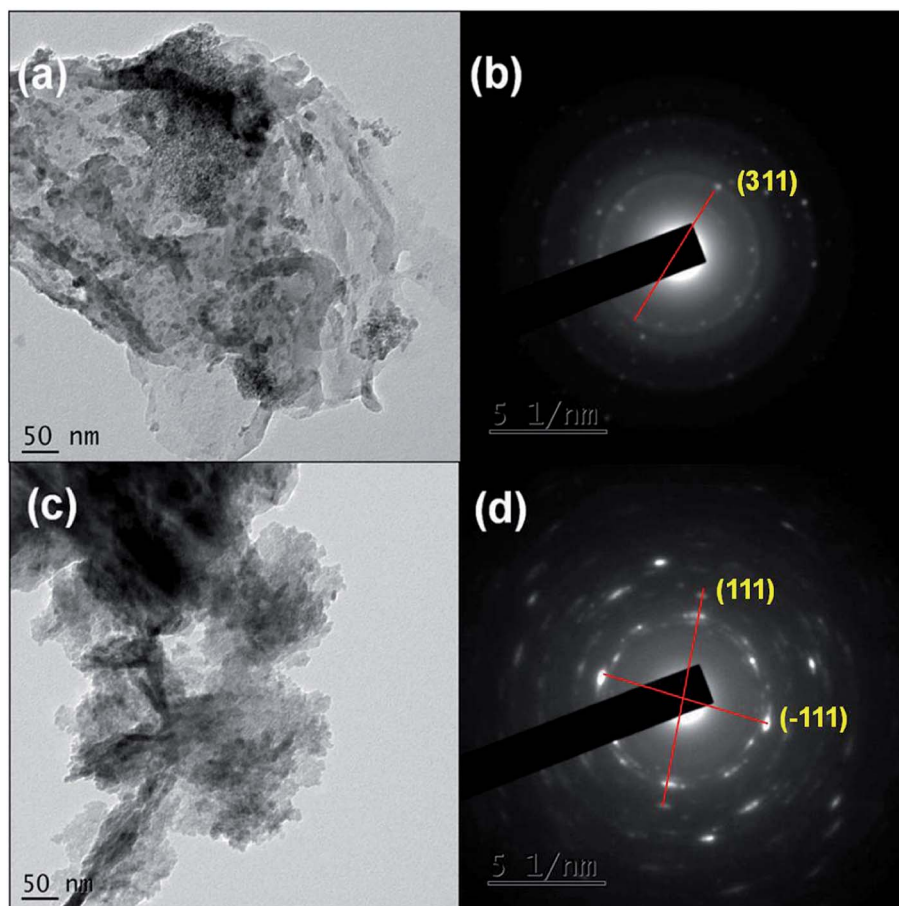


Fig. 5 (a) and (c) TEM images of $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ and $g\text{-C}_3\text{N}_4/\text{CuO}$; (b) and (d) corresponding SAED patterns.



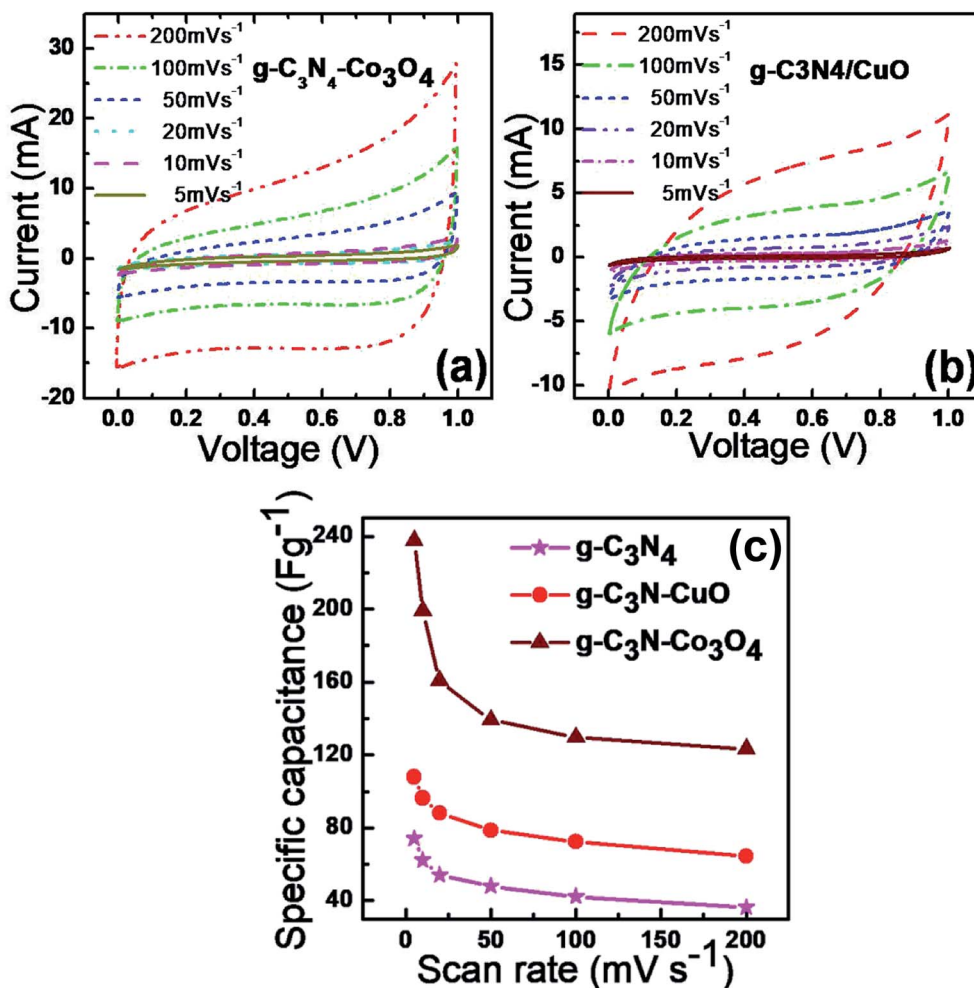


Fig. 6 Cyclic voltammograms of (a) $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ and (b) $g\text{-C}_3\text{N}_4/\text{CuO}$ at different scan rates. (c) Variation of specific capacitance of $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4/\text{CuO}$ and $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ 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 -CN stretching vibrations of the heterocyclic rings of *s*-triazine units. The sharp at 810 cm^{-1} is the characteristic peak originating from the breathing mode vibrations of triazine ring.²⁸ The peaks around $1000\text{--}1100\text{ cm}^{-1}$ arise due to the bending vibrations of -OH functional groups and the broad peaks around $3200\text{--}3600\text{ cm}^{-1}$ originate from the stretching vibrations of H_2O molecules adsorbed on the surface of the electrode material. The existence of spinel Co_3O_4 nanoparticles on the electrode sample can be confirmed from the presence of sharp characteristic peaks in Fig. 2(a) at 575 cm^{-1} and 665 cm^{-1} , respectively.¹² The peak at 537 cm^{-1} in Fig. 2(b) is the stretching vibrational band of Cu-O bond in monoclinic CuO crystal.²²

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 eV . The high resolution XPS spectra of Co in Fig. 3(c) exhibit well defined peaks at 780 and 796 eV corresponding to the $\text{Co } 2p_{3/2}$ and $\text{Co } 2p_{1/2}$ spin states with a spin separation of 16 eV , which are the characteristics of Co_3O_4 phase. Two weak satellite peaks at 788 and 804 eV are the features of spinel structure in which $+3$ ion occupy octahedral site and $+2$ ion at the tetrahedral sites.²⁹ The O 1s peak at 531.2 eV in Fig. 3(d) is the characteristic peak of spinel Co_3O_4 structure which arises due to the presence of lattice oxygen. Second O 1s peak at 535.9 eV is due to the presence of defective oxygen on the surface of the Co_3O_4 phase. The two major peaks of C 1s in Fig. 3(e) at 284.8 and 288.6 eV are originated from the sp^2 hybridised 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 eV are attributed to the N atom from N-C=N and N-(C)_3 structural units of $g\text{-C}_3\text{N}_4$.



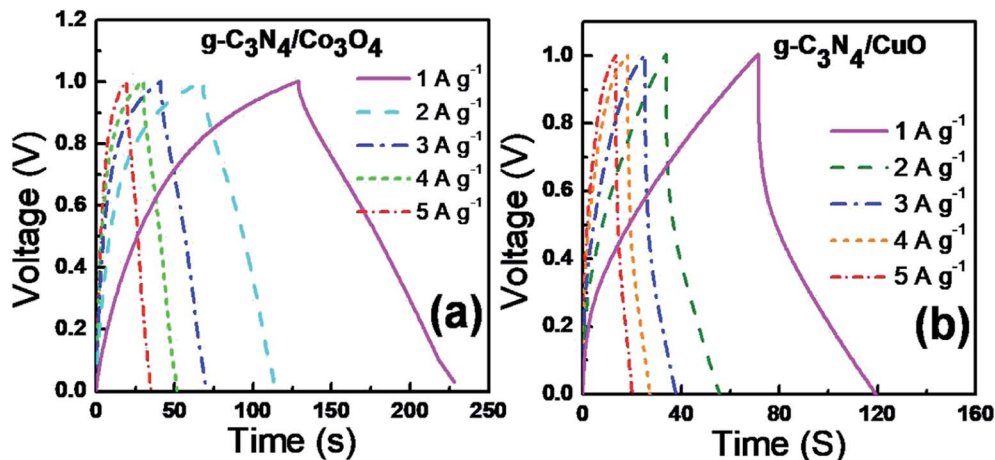


Fig. 7 GCD curves of (a) $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ and (b) $g\text{-C}_3\text{N}_4/\text{CuO}$ based supercapacitors at a constant current density of 1 A g^{-1} in 2 M KOH electrolyte.

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 Cu^{2+} at higher binding energy region are also visible.²⁹ 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 $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$.⁴

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 Co_3O_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 Co_3O_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.¹⁸ 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 mV s^{-1} was found to be 238 F g^{-1} and 108 F g^{-1} respectively which is far greater than the C_{sp} of bare $g\text{-C}_3\text{N}_4$ (74 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

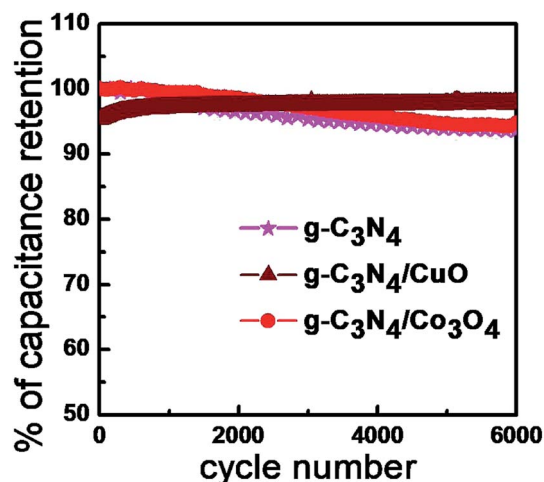


Fig. 8 Cycling stability curve of the supercapacitors at a constant current density of 5 A g^{-1} .



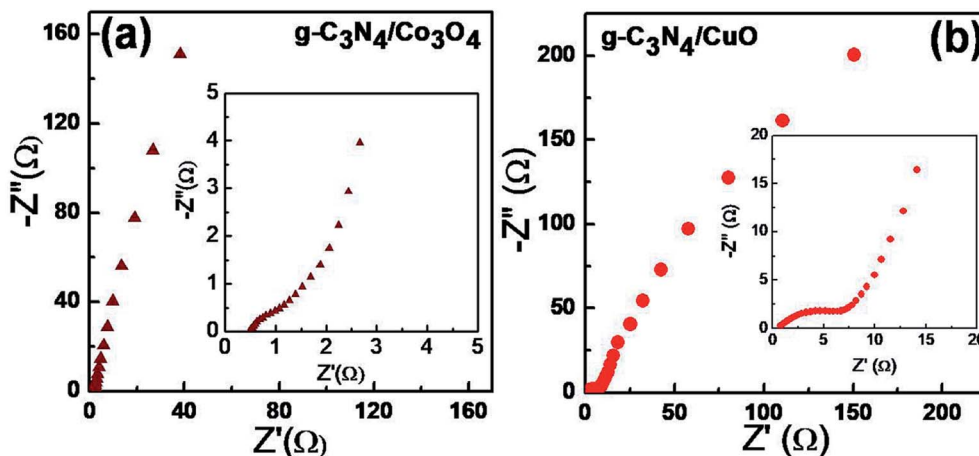


Fig. 9 Nyquist plots for (a) $g\text{-C}_3\text{N}_4/\text{Co}_3\text{O}_4$ and (b) $g\text{-C}_3\text{N}_4/\text{CuO}$ based supercapacitors over the frequency range from 100 kHz and 1 MHz.

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 CuO and Co_3O_4 nanocrystals.²¹

Galvanostatic charge–discharge (GCD)

The actual device performance of the supercapacitor can be analyzed from the GCD experiments.³⁰ The GCD profile was performed in 1 M KOH solution at different current densities of 1, 2, 3, 4, and 5 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, Δt is the discharge time, and Δv is the cell potential range after IR drop. The C_{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 A g^{-1} was found to be 95 F g^{-1} and 201 F g^{-1} , respectively. At high current densities, the C_{sp} value of the devices decreases due to the limited interaction of the ions at the electrode–electrolyte interface.³¹

The cyclic stabilities of the supercapacitors were analyzed from the charge–discharge measurements under an applied current density of 5 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 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 W h kg^{-1} and 13.2 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_{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.³² EIS results show that the R_{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.³³

Conclusions

In summary, pseudocapacitive Co_3O_4 and 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-C₃N₄ exhibited significant enhancement by coupling with Co₃O₄ and CuO with a specific capacitance of 201 F g⁻¹ and 95 F g⁻¹ for g-C₃N₄/Co₃O₄ and g-C₃N₄/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-C₃N₄/Co₃O₄ exhibited a cycling stability of 97% even after 6000 cycles with an energy density of 27.9 W h kg⁻¹.

Conflicts of interest

There are no conflicts to declare.

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