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Facile synthesis of cobalt oxide and graphene nanosheets nanocomposite for aqueous supercapacitor application

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A B S T R A C T

The present work includes the fabrication and electrochemical characterization of cobalt oxide (Co_3O_4)/graphene nanosheets nanocomposite as efficient electrode for supercapacitor application. The characterization techniques involved in this work are scanning electron microscopy and transmission electron microscopy for surface morphology, Raman spectroscopy and X-Ray diffraction for structural analysis. The specific capacitance of Co_3O_4 with multilayer graphene nanocomposite was determined to be 140 F/g (28 mF/cm^2) at scan rate of 20 mV/s. The composite electrode can deliver a power density of 856 W/kg with maintaining energy density of 2.38 Wh/kg. The better performance is due to the synergistic effect of graphene and Co_3O_4 in the composite.

1. Introduction

The growing demand of energy requires new energy sources and their storage devices. Battery is being considered as a potential candidate as it can store large amount of energy. However, the short life, low power density and maintenance cost are the drawbacks associated with a battery. In this context, supercapacitor has become a promising candidate as an energy storage device because of its high power density, fast charge- discharge, excellent cyclic efficiency and lower maintenance [1–5]. The properties of supercapacitor depend on electrode materials, so finding or synthesizing electrode material with advanced properties has become a challenge to make an advanced supercapacitor to fulfil the present and future requirements [5–10]. Supercapacitor can be categorized in two types based on its energy storage working principles; they are electric double layer capacitor (EDLC) and pseudo-capacitor [3,4,6]. Different types of carbon materials are used in EDLCs, while in pseudocapacitor the metal oxides are used as electrodes.

Different metal oxide nanoparticles have been synthesized with dramatic characteristics [7–10]. Nanocomposites with different combination of metal oxide and carbon have been fabricated by different methods in order to get optimum performance from the supercapacitor [7–15]. This is an attempt to make an electrode of multilayer graphene nanosheet nanocomposite with bismuth iron oxide for supercapacitor application to improve the capacitance value as well as other electrochemical properties [5]. The composites have been a preferential choice for any device to improve the performance [16–20]. As graphene has larger surface area and electrical conductivity, the graphene sheets improve the electrochemical properties of the composite electrode. L. Tao et al. [4] have used cobalt oxide (Co_3O_4)/graphene nanotube in battery to improve the reversible capacity and cyclic stability. There have been many attempts made to enhance electrochemical properties and energy ofCo_3O_4 based supercapacitor [11–17].

Co_3O_4 with low cost, non-toxic, easy synthesis and environmental friendly nature is being considered as promising material to be used in supercapacitor application. In this manner, Co_3O_4 has been mixed with carbon nanotubes in order to prepare hybrid nanocomposite as electrode with improving the capacitance of the electrode [21–22]. It is required to fabricate a supercapacitor with high power and energy density for practical applications. This could be achieved from a nanocomposite consisting of the materials which are used in EDL and pseudocapacitors. A composite electrode was designed by depositing Co_3O_4 on multiwall carbon nan-

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otubes by a chemical deposition method [23]. In that electrode, carbon nanotubes with excellent mechanical flexibility and high electrical conductivity can work as matrices for structural stability and electron transfer.

Co_3O_4 has been extensively investigated in order to obtain the excellent properties of electrode. Co_3O_4 nanocomposites have been fabricated with graphene [24], nickel foam [25–26], carbon nanotubes [21–22] and ITO films [27] to improve the electrochemical properties of supercapacitor. Nickel foam was utilized to prepare freely standing Co_3O_4 nanowire arrays via template-free growth followed by thermal treatment [26]. A flexible and transparent supercapacitor has been demonstrated using ultrafine Co_3O_4nanocrystals [27]. The fabricated transparent pseudocapacitor exhibited a capacitance of 177 F/g (6.03 mF/cm^2) at a scan rate of 1 mV/s, as well as long cycling stability with 100% retention after 20,000 cycles. However, there are still some problems associated with the Co_3O_4 based electrode, such as poor electrical conductivity which decreases the rate capability of adevice [16].

Therefore, in the present work an attempt has been made to get the advantages of both the EDLC and the pseudocapacitor. Graphene nanosheets have been mixed to $Co_3O_4$and a hybrid electrode of Co_3O_4/graphene nanosheets has been developed by a simple solution based approach. Co_3O_4 has been chosen because of its simple preparation, excellent electrochemical behaviour in alkaline as well as organic electrolyte. The morphology, structures, and dimension of Co_3O_4 can be easily controlled by adjusting the process parameters [28,29]. Graphene with 2D structure may provide structural stability and electron transfer [5,6] to Co_3O_4 and hence can improve the capacitance of the device. Co_3O_4 nanoparticles can be tightly attached on the surface of graphene nanosheets.

2. Experimental details

2.1. Synthesis of Co_3O_4 nanoparticles and graphene nanocomposite

Graphene and Co_3O_4 nanoparticles were used to make nanocomposite. The chemicals, cobalt nitrate and ammonium oxalate were used to synthesize Co_3O_4. Co_3O_4 nanoparticles were prepared by solution based approach and the details can be found in the literature [30–35]. The composition of these powders were 4:1 mass ratio that is 20% graphene was added to 80% Co_3O_4 to make the nanocomposite electrode. **Fig. 1** shows the systematic procedure to prepare Co_3O_4–graphene nanocomposite electrode. Initially, Co_3O_4 nanoparticles were dispersed in DI water (20 ml) with polyvinyl alcohol (PVA) which is used as binder between graphene sheets and Co_3O_4 nanoparticles. The solution was kept on a hot plate at 60 °C under magnetic stirring. The graphene nanosheets were then added to the Co_3O_4 solution. This prepared slurry of Co_3O_4 and graphene was deposited on two stainless steel substrates of size 0.5 cm × 0.5 cm each by drop-casting approach (**Fig. 1**). The synthesized electrodes were annealed at a 100 °C for 1 h. The crystal structure of the nanocomposite electrode was studied by X-ray diffraction (XRD) with CuKα radiations. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed in order to study the surface morphology of the electrode. Further, Raman spectroscopy (Horiba, HR 8000, Argon laser 514.5 nm) was also used to study the present phases in the electrode.

2.2. Electrochemical measurements

The cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements were performed for electrochemical measurements of the Co_3O_4 and graphene nanocomposite. All electrochemical measurements were performed in a two-electrode symmetric cell configuration. A tea-bag cloth soaked in 1 M KOH was placed between the electrodes. CV and GCD measurements were carried out using a biologic Potentiostat SP-300 instrument. The CV measurements were performed at different scan rates of 10, 20, 50, and 100 mV/s. The voltage window was fixed in the potential range of −0.5 to +0.5 V. Charging/discharging curves were obtained in the same voltage window and at different currents. Electrochemical impedance spectroscopy (EIS) was also employed to study the electrochemical properties of the electrode in details.

3. Results and discussion

XRD pattern of the prepared nanocomposite is illustrated in **Fig. 2** (a). The XRD pattern showed the peaks at position of 2θ = 19.02°, 27°, 31.3°, 36.87°, 38.62°, 44.85°, 55.73, 59.35° and 65.24°. All peaks, except one at ~27°, belong to the cubic phase structure of Co_3O_4. The obtained spectrum match with the JCPDS card No: 073–1701 file with lattice constant a= 8.08 Å. In addition to the peaks of Co_3O_4, a different peak at ∼27° corresponds to the interplanar stacking of the graphene sheets. No other peaks are seen in the XRD spectrum. Therefore, XRD confirms the formation of nanocomposite consisting of Co_3O_4 and highly conducting graphene nanosheets.

Further investigation for the structure properties of the $Co_3O_4$and graphene composite electrode was carried out by Raman spectroscopy. **Fig. 2(b)** depicts the obtained Raman spectrum of the nanocomposite electrode, which has all the expected characteristics, Raman peaks of pure phase Co_3O_4 and multilayer graphene nanosheets. The peaks which are between 400 and 700 cm^{-1} are attributed to the crystalline structure of Co_3O_4. Among them D and G-bands are also observed which suggests the presence of graphene nanosheets in the composite [36,37]. Hence, Raman analysis also indicates the formation of Co_3O_4/graphene nanocomposite based electrode.

Fig. 3(**a)-(c)** shows the SEM micrographs of prepared sample of Co_3O_4/graphene nanocomposite. The micrographs are recorded at different magnifications and at different places. Here in these micrograph images it can be noticed that there are two types of microstructure namely sheets and particles. From the magnified SEM images, it is visible that the creases and crinkles are formed due to the 2D structure of graphene nanosheets [28]. Graphene nanosheets with 2D structure are also expected to offer larger surface to volume ratio for electrolyte ions [28]. It is also visible that the graphene sheets and Co_3O_4 are independently present and formed the nanocomposite. The higher surface to volume ratio would increase the electrochemical properties of the nanocomposite electrode [3]. In **Fig. 3(a)** it is visible that the Co_3O_4 is densely present and mechanically attached to the graphene sheet. The role of graphene sheet is to improve the electrical conductivity of the electrode and ions mobility over the electrode surface [38,39]. A large numbers of void can also be seen on the electrodes, which is beneficially for large power density of a supercapacitor.

The adhering property of Co_3O_4 with graphene sheets was confirmed with TEM (**Fig. 3(d)**). For TEM, the sample was removed from the current collector and placed on a Cu grid. The graphene sheets and Co_3O_4 nanoparticles can be seen in the TEM image (**Fig. 3(d)**). The nanoparticles are found to be adhered with the graphene sheets. No separate graphene sheets or nanoparticles are observed, which indicates that the nanoparticles remain attached to the graphene sheets and making good electrical contact for supercapacitor application. Crystallinity of the Co_3O_4 particle can be confirmed in HRTEM image (**Fig. 3(e)**). The lattice fringes belong to the plane (220) (0.285 nm) of Co_3O_4.

Electrochemical properties of the synthesized Co_3O_4/graphene nanocomposite electrode were determined in two electrode configuration by CV and GCD. **Fig. 4 (a)** depicts the CV curve recorded in the voltage window of −0.5 to +0.5 at different scan rates.

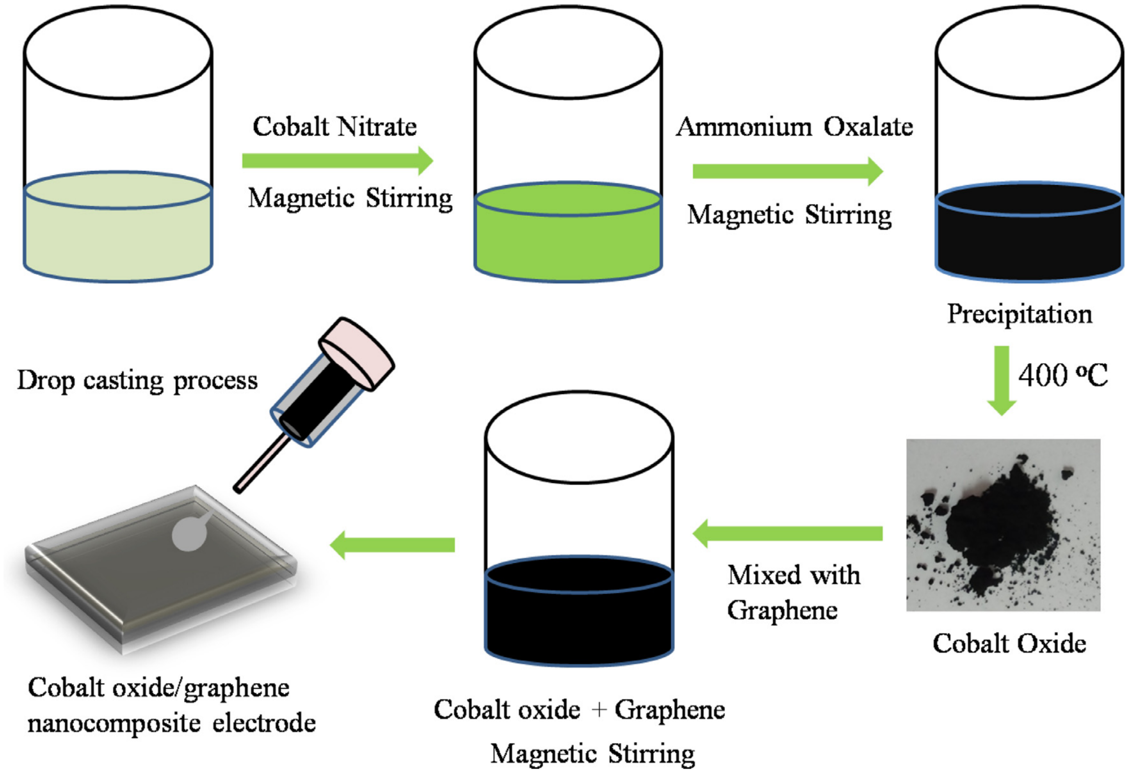

Fig. 1. systematic procedure to prepare cobalt oxide–graphene nanocomposite electrode.

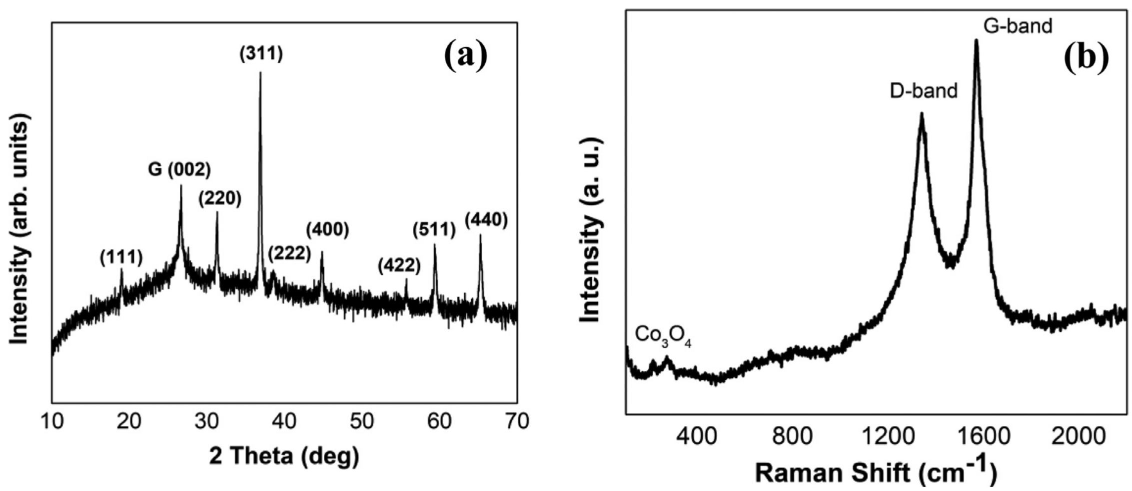

Fig. 2. (**a**) XRD spectrum of Co_3O_4 /graphene nanocomposite electrode and (**b**) Raman spectrum obtained from the nanocomposite.

This measurement gives the specific capacitance value of particular electrode at different voltage and scan rate. In this method of characterization, the voltage is changed on the device at a constant rate and the resulted current is recorded. An ideal capacitor exhibited a rectangular shaped CV curve [40–42]. In our case, a little distortion in the CV curve is observed for the Co_3O_4/graphene nanocomposite. It is basically due to the pseudocapacitive nature of Co_3O_4 [40–44]. The redox behaviour seen in the CV curve clears the presence of pseudocapacitive behaviour thus confirms the contribution of Co_3O_4 to the overall capacitance. The charge-storage mechanism of the Co_3O_4/graphene nanocomposite electrode in KOH solution is as follows [45].

$$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^- \ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The resulted CV has two signatures, electric double layer capacitance from the graphene and pseudocapacitance from the Co_3O_4. Further, the scan rate was increased in order to check the stable performance from the composite electrode (**Fig. 4**(**a**)). There is an increased in CV current with the increase in scan rate. The capacitive current is proportional to the scan rate hence highest scanning rate has the highest increase in the current [29–31]. The CV curves could retain the quasi-rectangular shape at all scan rates, suggesting stable electrochemical performance at high charging/discharging rates. But here it is observed that there are little negligible bent in the CV curve because of the series resistance of the device.

The capacitance of the electrode was determined using the following equation;

$$C = 2I/v.A \quad (3)$$

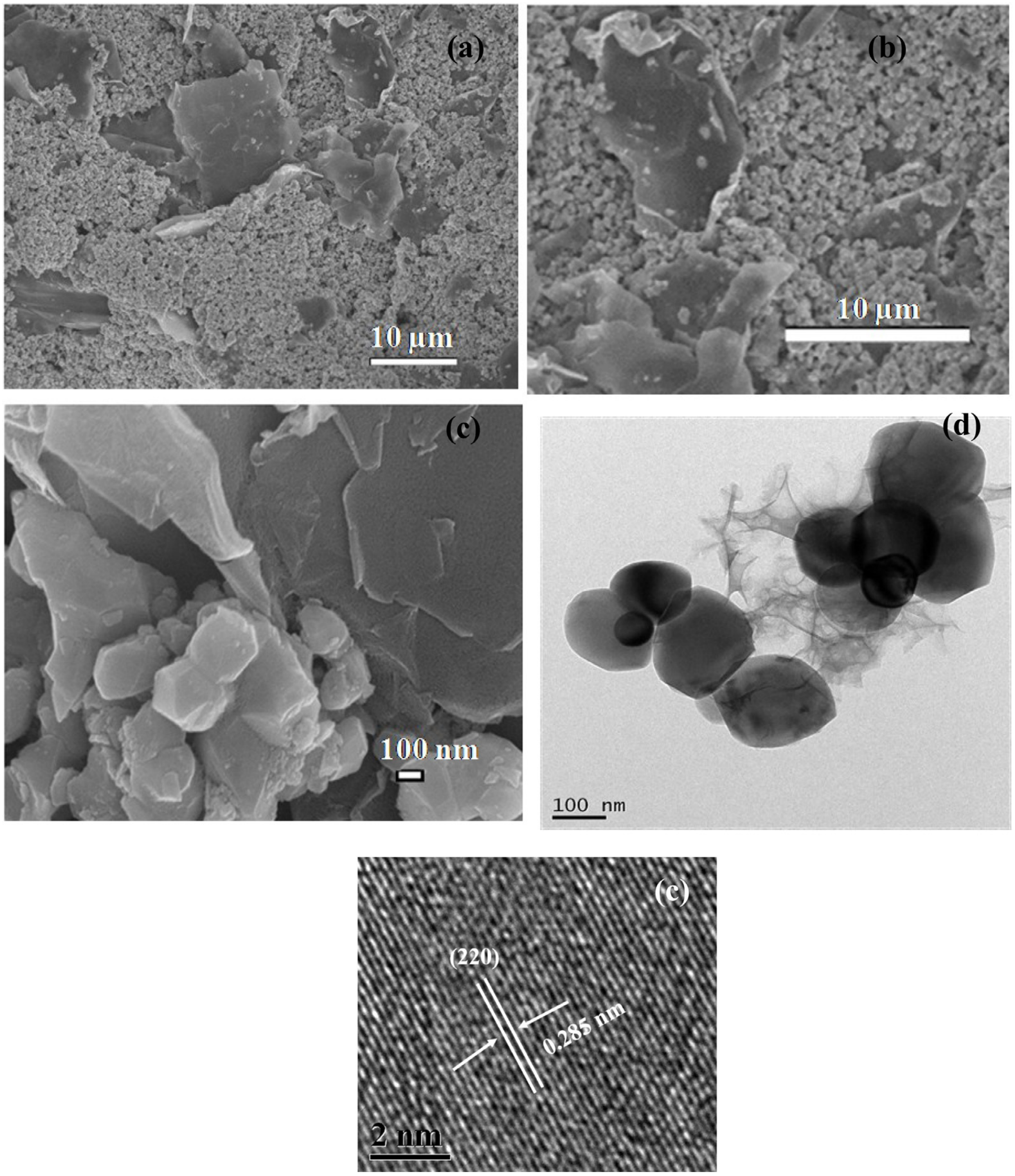

Fig. 3. **(a)-(c)** SEM, **(d)** TEM micrographs of Co_3O_4/ graphene nanocomposite electrode and **(e)** HRTEM image captured on the surface of a Co_3O_4 nanoparticle.

Table 1
Comparison of specific capacitances of Co_3O_4 based electrodes reported in literature and this work.

Electrode	Capacitance	Ref.
Ultrafine Co_3O_4 nanocrystal	177 F/g at 1 mV/s	[27]
Co_3O_4 thin film	74 F/g at 5 mV/s	[52]
Co_3O_4-coated multiwalled carbon nanotube	273 F/g at 0.5 A/g	[53]
Co_3O_4 nanosphere	128 F/g at 10 mV/s	[54]
Activated carbon and cobalt oxide (Co_3O_4) nanocomposite	94 F/g at 1 A/g	[55]
Co_3O_4 and graphene nanocomposite	140 F/g at 20 mV/s	Present work

where, C is the areal capacitance, I is the average of charging and discharging current in the CV, v is the scan rate and A is the area of the electrode.

The composite electrode showed specific capacitance of 28 mF/cm^2 determined at scan rate of 20 mV/s. The areal capacitance is equivalent to 140 F/g, which is comparable to the other electrodes reported in literature [46–56]. The specific capacitance obtained in the present work is compared with the reported values for Co_3O_4 in **Table 1**. The capacitance calculated at different scan rate is depicted in **Fig. 4(b)**. The capacitance decreased to 6.8 mF/cm^2 at scan rate of 100 mV/s. Further, the charge storage capability of the electrode was verified by performing GCD measurement. A constant current was applied and the voltage was monitored. The device was charged and discharged at two currents 20 mA and 32 mA (Fig. 4 (c)). The linear change in the voltage during charging and discharging is typical characteristic of an EDL capacitor. However, there is observed deviation in the shape of charging/discharging curves from a straight line. It could be ascribed to the feature of pseudocapacitance from Co_3O_4. Moreover, the charging/discharging curves at two different currents are able

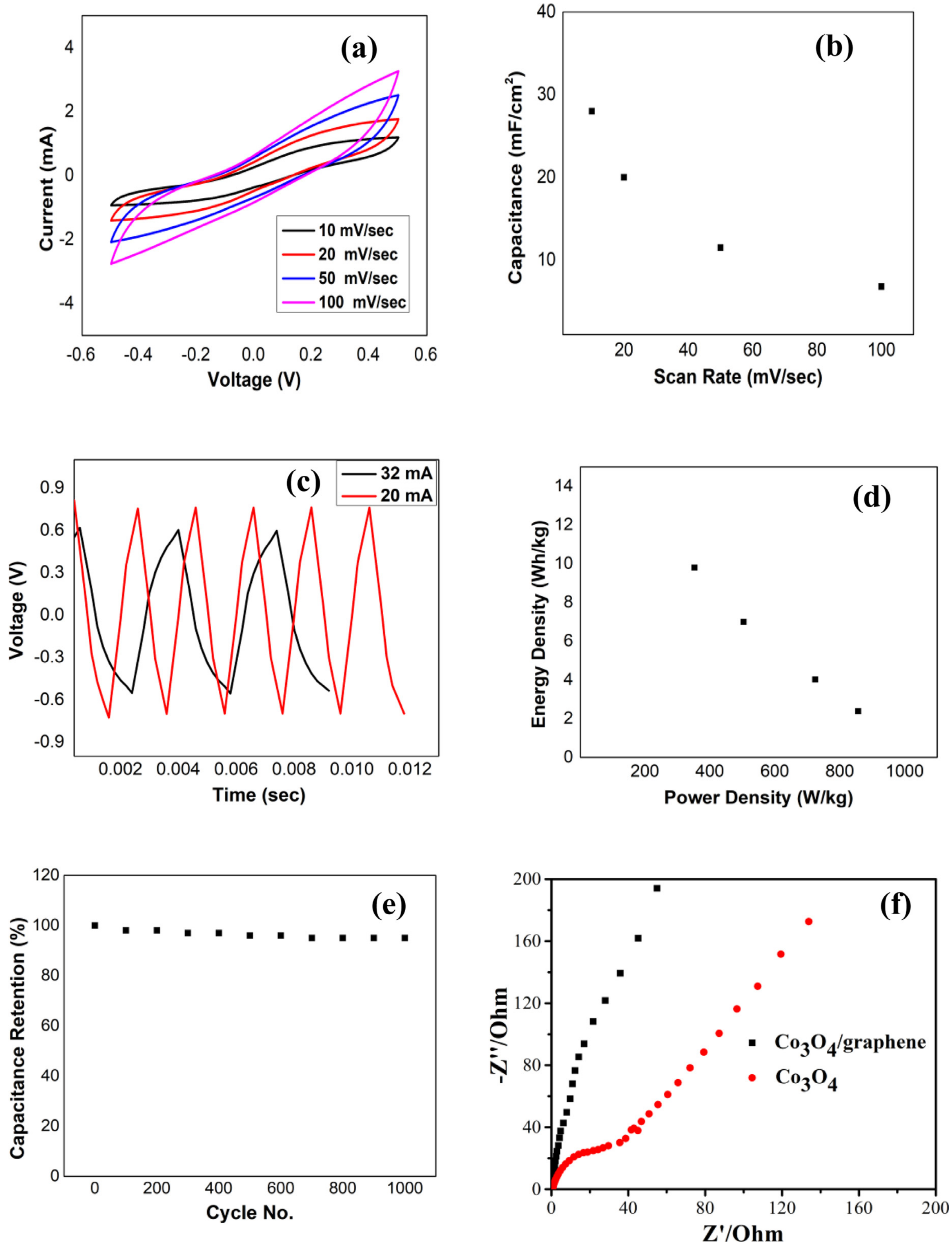

Fig. 4. (**a**) CV curves recorded at different scan rates and (**b**) specific capacitance of nanocomposite based supercapacitor as a function of scan rate. (**c**) GCD curves of the supercapacitor recorded with currents of 20 mA and 32 mA. (**d**) Ragone plot for energy density and power density of the device. (**e**) cycle stability of the device and (**f**) Nyquist plot.

to preserve a similarly symmetric shape, demonstrating high stability of the electrode. Columbic efficiency was also determined to be 97.62%.

Ragone plot which is the relation between energy and power density is presented in Fig. 4(**d**) for Co_3O_4/graphene based supercapacitor. The values of the energy and power density were determined by charging and discharging the supercapacitor at different rates. Energy density was observed in the range of 2.4 to 9.8 Wh/kg and power density from 0.3 to 0.8 kW/kg. The cycle life is an important parameter for any kind of energy storage device.

Therefore, to determine the stability of the electrode, the device was charged and discharged for 1000 cycles. The capacitance retention for every cycle is plotted in **Fig. 4(e)** as a function of cycle number. The electrode can retain the capacitance about 95% after 1000 cycles, indicating its suitability for long-term supercapacitor.

Furthermore, EIS was performed in order to get the idea about change in series and charge transfer resistance after addition of graphene to Co_3O_4. It can be seen in the Nyquist plots (**Fig. 4(f)**) that the charge transfer resistance of the electrode is decreasing with graphene sheets. The series resistance of Co_3O_4 and Co_3O_4/graphene was determined to be 0.64 and 0.17 Ohm, respectively. As compared with Co_3O_4, Co_3O_4/graphene nanocomposite shows lower series resistance, more vertical line and lower charge transfer resistance thus exhibiting better electrochemical performance [56,57].

4. Conclusions

Co_3O_4/graphene nanocomposite has been synthesized by solution based process and tested for supercapacitor application as electrode. The electrochemical properties were evaluated in two electrode system in aqueous electrolyte. The electrode exhibited specific capacitance of 28 mF/cm^2 at scan rate of 20 mV/s. The symmetric supercapacitor can deliver power density in the range of 0.3 - 0.8 kW/kg with energy density of 2.4 to 9.8 Wh/kg. The performance of the device can further be improved by optimizing appropriate concentration of Co_3O_4 and graphene in the nanocomposite. The fabricated device has shown good electrochemical stability with a loss of 5% in capacitance after 1000 cycles. This work suggested that the Co_3O_4/graphene nanocomposite may be a promising electrode in the application of energy storage devices.

Declaration of Competing Interest

The authors declare no conflict of interest.

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