



Enhancement of electrochemical properties of porous rGO by controlled growth CoFe₂O₄ nanoparticles

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Received: 12 May 2023

Accepted: 31 July 2023

Published online:
23 August 2023

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ABSTRACT

A study area in supercapacitor research is the design and manufacturing of composite electrode materials that combine the advantages of various materials. The rGO/CoFe₂O₄ composite material is produced by growing cobalt ferrite particles on the surface of rGO using a simple and highly efficient thermal reduction technique. The results show that the electrochemical properties of rGO are significantly improved by the incorporation of cobalt ferrite. rGO sheets are used as supporting frameworks for the CoFe₂O₄ nanoparticles, while the CoFe₂O₄ particles provide more active sites for redox reactions. The prepared rGO/CoFe₂O₄ show excellent electrochemical properties, with a high specific capacitance of 283 F/g at a current density of 0.1 A/g and a specific capacitance retention of 90.5% after 1000 cycles. The attractive performances exhibited by rGO/CoFe₂O₄ composites make them potential electrode materials for supercapacitors in future.

1 Introduction

Reduced graphene oxide (rGO) is a rapidly rising two-dimensional carbon material with the fascinating electronic, thermal, optical, magnetic, and chemical properties [1, 2]. Because of the outstanding properties, rGO finds prominent applications in the electronic devices, such as supercapacitor [3], battery [4], solar cell [5], and sensors [6]. In addition, other essential applications are printed electronics, conductive coatings [7], energy storage [8], etc.

Despite the fact that rGO has a lot of advantages, it still has limitations due to its intrinsic capacitance and comparatively slow charge–discharge rate. The charge–

discharge rate as well as the specific capacitance for the rGO electrode can be increased by combining rGO with electrode materials that work on the pseudo-capacitance principle. The transition metal oxide is a typical pseudo-capacitive supercapacitor electrode material which can be used to modify rGO material.

The transition metal oxides commonly used to modify rGO include RuO₂ [9], MnO₂, and Co₃O₄ [10, 11]. However, single metal oxides have certain limitations, such as weak mechanical strength and short life cycle [12]. In recent years, multi-metal oxides such as ZnCo₂O₄, NiCo₂O₄, and CoFe₂O₄ have been widely used in order to modify carbon-based electrode materials, including rGO [13–15].

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CoFe₂O₄ is one of the most well-known multi-metal oxides due to its high electrochemical activity and numerous active sites that are advantageous to redox processes. Numerous researchers are therefore interested in this oxide in an effort to modify carbon-based electrode materials and, in particular, to enhance capacitance performance [16].

Utilizing salts as precursors to bring metal ions to the surface of porous materials is an established technique for the fabrication of composites based on porous materials and metals. Chemical and thermal reduction can then be used to obtain composite materials with a variety of unique characteristics [13, 17, 18].

The RuO₂/rGO nanocomposite material was fabricated by Kim et al. by the in situ and microwave method [19]. Zhao et al. also successfully fabricated RuO₂/rGO composite materials by solution precipitation. The authors used NH₃ solution to adjust the pH of RuCl₃ and GO salts. GO was reduced to rGO by the microwave method [18]. Gao et al. dissolved Co(NO₃)₂ and Zn(CH₃COO)₂ salts into the GO dispersion. Urea is used to adjust the pH of the solution. The mixture was hydrothermally heated at 120 °C for 5 h to obtain ZnCo₂O₄/rGO material [13]. CoSe₂ oxides were coated on nickel foam by hydrothermal method for 8 h. The CoSe-Se@Ni foam electrodes exhibited a specific capacitance of 1750.81 F.g⁻¹ at 1 A.g⁻¹ [20]. The CoFe₂O₄/rGO hydrogel material fabricated by Zheng et al. by the hydrothermal method has a specific capacitance of 356 F/g at a density of 0.5 A/g [21].

In this study, the rGO/CoFe₂O₄ aerogel was synthesized using a co-precipitation method in an aqueous solution, followed by ice template and heat reduction. This approach is simple, immediate, and enables the reduction of the material to graphene while simultaneously incorporating CoFe₂O₄ nanoparticles. The obtained materials are used to fabricate the supercapacitor electrodes, which have excellent electrochemical properties.

2 Experimental

2.1 Chemicals

Graphite powder, Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, and KMnO₄ were supplied by Aladdin Chemical Co. H₂SO₄ 98%, H₃PO₄ 85%, HCl, H₂O₂ 30%, and

NH₄OH 25% were commercially available from Fisher Scientific.

2.2 Preparation of rGO/CoFe₂O₄ composite

GO dispersion was produced by advanced Hummer method [22]. Firstly, 2.0-g graphite powder was added to 100-ml acid solution having 9:1 (volume/volume ratio) of concentrated H₂SO₄ and H₃PO₄ has been prepared and kept in an ice bath. Then, 6.0-g KMnO₄ was gradually added while stirring. The addition rate of KMnO₄ was carried out carefully to avoid sudden increase of temperature. After that, the reaction mixture is heated and stirred for 8 h at 50 °C. As the reaction extended, the mixture turned out to be paste. Finally, the distilled water is added into the mixture for stopping this reaction. To ensure the completion of reaction with KMnO₄, the suspension was further treated with 30% H₂O₂ solution. The resulted mixture was washed with HCl and H₂O, respectively, followed by filtration and drying, and thus GO sheets were obtained.

Accurately weigh the masses of Co(NO₃)₂ and Fe(NO₃)₃ compounds based on the molar ratio of Co(NO₃)₂:Fe(NO₃)₃ = 1:2 and dissolve in 50 mL of the GO dispersion. The mixture was stirred for 1 h. Adjust pH to 12 using an ammonia solution. The mixture is centrifuged and then washed with distilled water until neutral. A magnetic stirrer and ultrasound were used to redistribute the produced in 50 mL of distilled water. The mixture is poured into the containers, cooled to - 40 degrees Celsius for two hours, and then freeze-dried for twenty-four hours. rGO/CoFe₂O₄ composite was produced by calcining the mixture in a N₂ gas atmosphere at 500 °C. Samples of materials with symbols rGO/CoFe₂O₄-x, where x is the concentration of Co(NO₃)₂ salt used (mmol/L), were obtained depending on the molar concentration of the salt. The synthetic route of rGO/CoFe₂O₄ composite is shown in Fig. 1.

When 50 mL of the GO mixture was replaced with 50 mL of distilled water, the aforementioned procedure was repeated in order to obtain CoFe₂O₄ powder.

2.3 Characterization

A Bruker D8-Advance (Germany) X-ray diffractometer with CuK radiation in the angle range 2θ from 10 to 70° was used to determine the crystal

structure of rGO/CoFe₂O₄. Using a Tri-Star 3000 at 77 K and at a degassing temperature of 200 C for 5 h, the specific surface area and porosity distribution of materials were examined.

The morphologies and structural properties of the prepared materials were characterized by field emission scanning electron microscopy (FESEM; HITACHI S-4800) and high-resolution transmission electron microscopy (HRTEM; JEM 2100). The crystal structure of the obtained samples was determined on an X-ray diffractometer (XRD, Bruker Advance 8). The graphitization degree was determined by Laser Micro-Raman spectrometer (Raman Microscope - DXR3, Thermo Scientific).

2.4 Supercapacitor electrode preparation and electrochemical measurements

Two-electrode setups were employed to measure the electrochemical properties of the prepared sample. The nickel foil was pretreated with absolute ethanol and dried at 80 °C for 3 h. The rGO/CoFe₂O₄ composites were coated on the nickel foil with a size ϕ 8 mm. An aqueous solution of 6-M KOH was used as the electrolyte. Electrodes made by the method mentioned above were immersed into the electrolyte. Then, two electrodes were assembled in a cell lock.

The electrochemical performances of rGO/CoFe₂O₄ electrodes were investigated by Cyclic Voltammetry (CV), Galvanostatic Charging–Discharging (GCD), and Electrochemical Impedance Spectroscopy (EIS) measurements, which were carried out by Autolab PGSTAT309n (Metrohm, Switzerland). The

specific capacitance (C_s) of the electrodes materials and energy density of supercapacitor (E) were calculated viz., Eq. (1) and Eq. (2), respectively [23].

$$C_s = \frac{2I\Delta t}{m\Delta V}, \quad (1)$$

where I , Δt , ΔV , and m represent current, discharging time, potential window, and the mass of the active material on electrode, respectively.

$$E = \frac{1}{4}C \times \Delta V^2 \quad (2)$$

Where E is the energy density (Wh/kg).

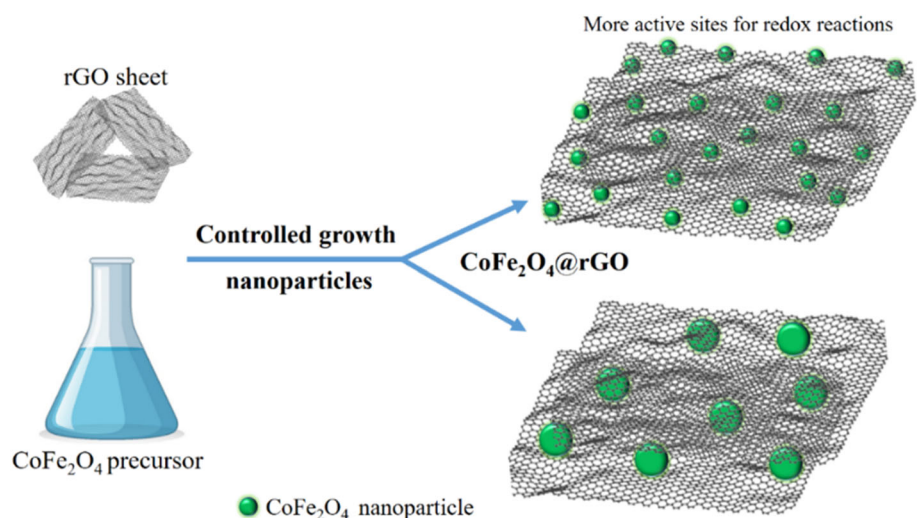
3 Results and discussion

The hydroxide compounds of Co²⁺ and Fe³⁺ were precipitated on the surface of the rGO sheets in the basic environment. The concentration of the precursor salts employed directly affects the density and size of CoFe₂O₄ particles. rGO sheets are used as supporting frameworks for the CoFe₂O₄ nanoparticles, while the CoFe₂O₄ particles work as fillers to improve delamination efficiency and reduce rGO fragment aggregation. rGO serves as a conducting substrate to maintain the continuous diffusion of ions, while CoFe₂O₄ particles provide more active sites for redox reactions.

The results of X-ray diffraction (XRD) and Raman spectra are used to illustrate the properties of the phase composition of rGO/CoFe₂O₄ composites.

The XRD pattern of materials are shown in Fig. 2a. Only two distinctive peaks at $2\theta = 25.6$ and 42.9° ,

Fig. 1 Schematic for preparing the rGO/CoFe₂O₄ composite material



respectively, that are typical of high-graphite carbon materials (002) and (101) are visible in the XRD pattern of the rGO aerogel sample [24, 25]. Peaks typical for face-centered cubic CoFe_2O_4 crystals can be seen as (220, 311, 400, 422, 511, and 440) as well as the peaks intensity usual for rGO also dramatically reducing as the CoFe_2O_4 concentration rose in samples rGO/ CoFe_2O_4 -3 and rGO/ CoFe_2O_4 -4 [25].

The characteristic peaks at 1355 and 1590 cm^{-1} for the D and G bands of rGO may still be seen in the Raman spectra of rGO/ CoFe_2O_4 samples (Fig. 2b) [22]. As the concentration of CoFe_2O_4 increased, the intensities of these two peaks are significantly reduced. The results of CoFe_2O_4 nanoparticles was produced with a cation distribution of $[\text{Fe}_{0.69}\text{Co}_{0.31}](\text{Co}_{0.69}\text{Fe}_{1.31})\text{O}_4$, as seen by the characteristic peaks for CoFe_2O_4 nanoparticles at positions 207, 307, 473, and 693 cm^{-1} [26].

Surface morphology of the rGO/ CoFe_2O_4 samples was studied using TEM and SEM techniques. The results of SEM imaging demonstrate that the research successfully manufactured rGO and CoFe_2O_4 materials. The appearance of CoFe_2O_4 particles on the surface of rGO flakes is shown in Fig. 3. CoFe_2O_4 particle placement is fairly consistent. The CoFe_2O_4 particles with a size of about 10–20 nm are evenly distributed on the surface of the rGO sheet in the rGO/ CoFe_2O_4 -2 and rGO/ CoFe_2O_4 -3 samples. With particles that are about 50 nm in size, the rGO/ CoFe_2O_4 -4 sample seems to have larger ones. When the amount of $\text{Co}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ salts employed in the fabrication process steadily rises, it

can be seen that CoFe_2O_4 nanoparticles tend to grow in size and lose homogeneity. The aggregation of oxide particles during precipitation and heat treatment is what causes the above phenomena.

On the surface of the rGO thin sheets, visible CoFe_2O_4 particles can be seen in the TEM image of the rGO/ CoFe_2O_4 -3 material sample (Fig. 4).

Specific surface area and pore distribution are fundamental and essential properties of rGO/ CoFe_2O_4 materials that have a direct impact on their electrochemical properties when used as supercapacitor materials. Figure 5 illustrates the N_2 gas adsorption–desorption isotherm and pore distribution of rGO/ CoFe_2O_4 samples. The N_2 gas adsorption–desorption curve of the rGO sample has the shape typical of materials with macropores, while the rGO/ CoFe_2O_4 samples all have the shape typical of materials with a micropore structure management. The pore distribution diagram also reveals that rGO/ CoFe_2O_4 samples contain almost no pores larger than 30 nanometers. The porosity of the material samples is primarily attributable to apertures ranging in size from 3 to 10 nm.

The results indicate that as the concentration of CoFe_2O_4 increases, the specific surface area of the material tends to decrease, from $162.4\text{ m}^2/\text{g}$ for the rGO sample to only $43.4\text{ m}^2/\text{g}$ for the rGO/ CoFe_2O_4 -4. In addition, the pore volume decreased substantially from 0.23 to $0.06\text{ cm}^3/\text{g}$. Increased concentration and aggregation of CoFe_2O_4 particles can cause the pores on the surface and between the sheets of rGO to become occluded. Nevertheless, the rGO/

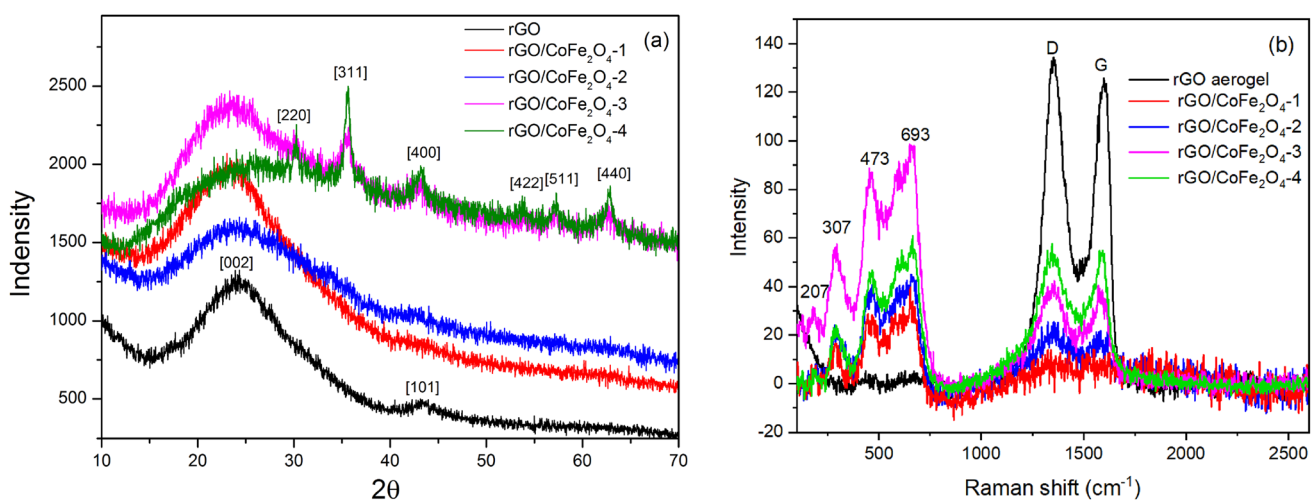


Fig. 2 The XRD pattern **a** and Raman spectroscopy of rGO/ CoFe_2O_4 **b**

Fig. 3 SEM images of CoFe_2O_4 (a), rGO/ CoFe_2O_4 -1 (b), rGO/ CoFe_2O_4 -2 (c), rGO/ CoFe_2O_4 -3 (d), rGO/ CoFe_2O_4 -4 (e), and rGO aerogel (f)

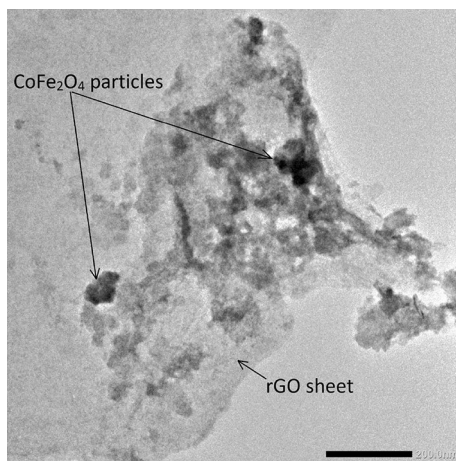
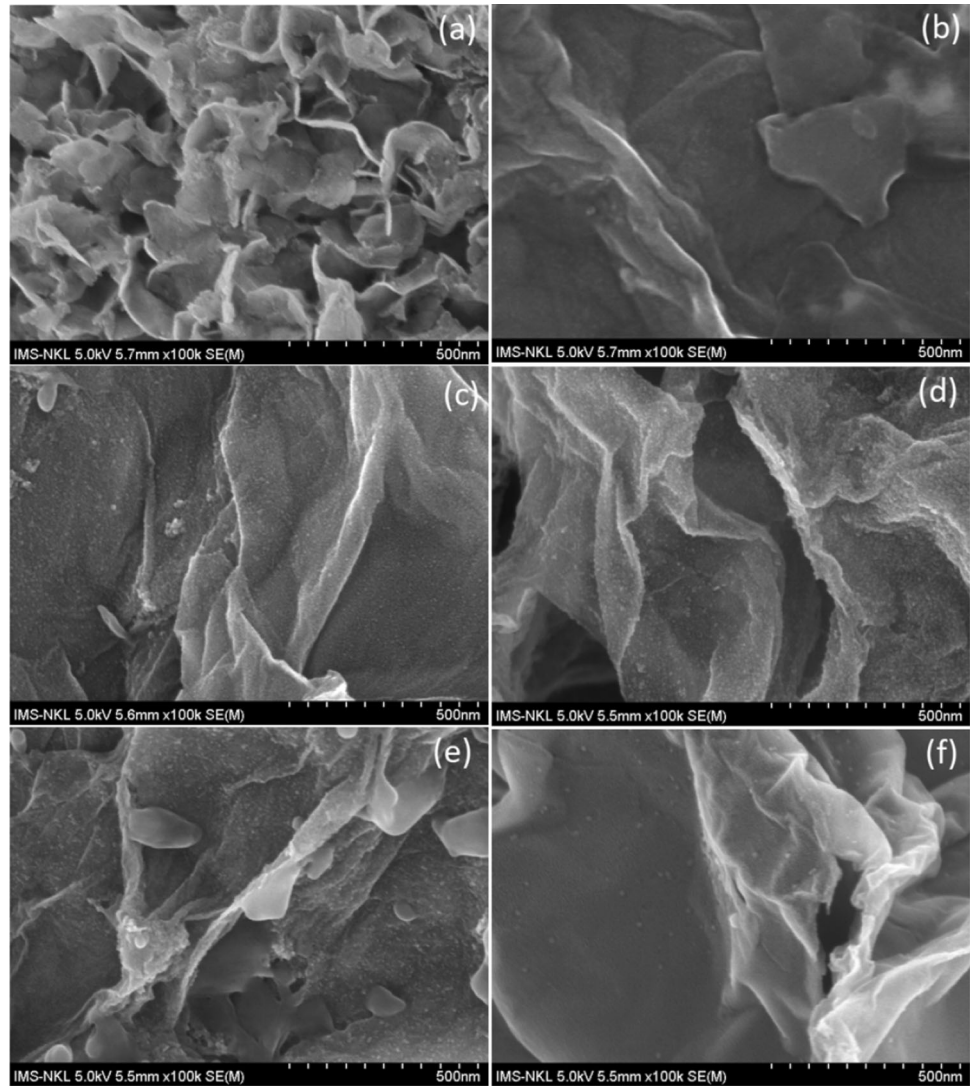


Fig. 4 TEM images of rGO/ CoFe_2O_4 -3

CoFe_2O_4 -3 sample exhibits a greater surface area and pore volume than the other samples. The formation of CoFe_2O_4 particulates to some extent on the surface of GO sheets may be the delamination agent that causes the distance between GO layers to grow. From there, it is clear that selecting the appropriate content allows the application of a quantity of CoFe_2O_4 particles to completely cover the surface of the rGO sheet without having a significant impact on the surface area or porosity of the material.

Figure 6a shows the CV curves of prepared samples at scan rate of 20 mV/s. According to the results, the CV curve of highly symmetrical rGO/ CoFe_2O_4 samples indicates that the reversibility of the electrochemical process is quite excellent. It can be identified that the mechanism of energy storage and release is mainly based on the adsorption and

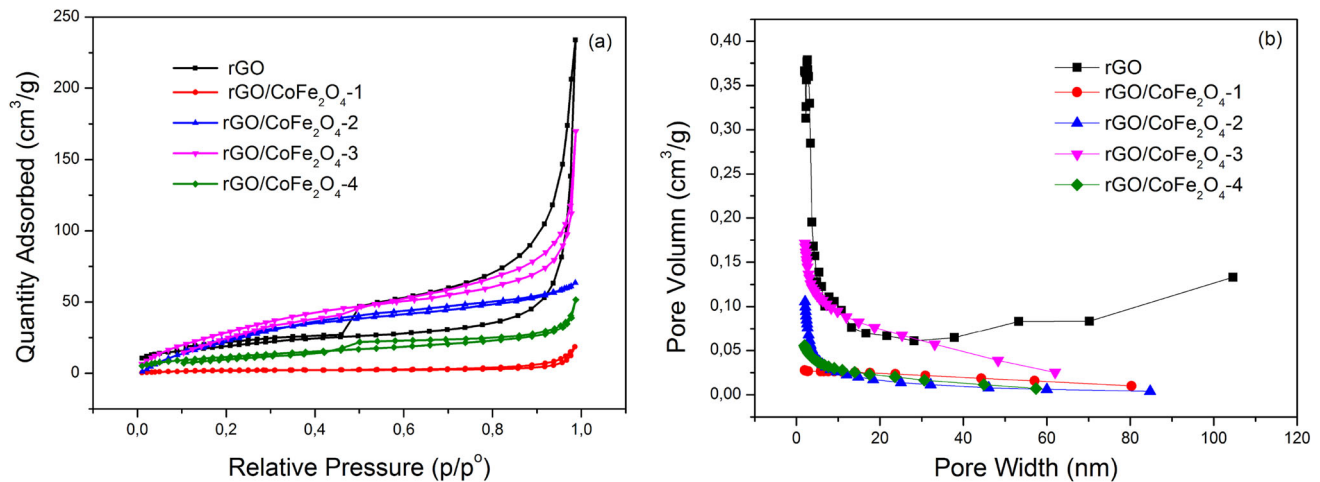


Fig. 5 N₂ adsorption–desorption isotherm (a) and pore volume distribution (b) of rGO/CoFe₂O₄

desorption processes on the surface of the material. The rGO/CoFe₂O₄-3 sample has the largest area of the CV curve, and the area representing the pseudo-capacitance characteristic is more evident compared to other samples. Figure 6b shows the CV curves of rGO/CoFe₂O₄-3 at different scan rates varying from 5 to 100 mV/s. The obvious increase of current with scan rate indicates a good rate capability for rGO/CoFe₂O₄ electrodes at high scan rate.

Figure 6c displays the findings of GCD curves of various rGO/CoFe₂O₄ at 0.2 A/g of scan rate. It is obvious that the charge curves are asymmetric to the corresponding discharge counterparts in the whole potential region. It can prove the pseudo-capacitor behavior of prepared materials. According to the charge/discharge curves, rGO and rGO/CoFe₂O₄-1, rGO/CoFe₂O₄-2, rGO/CoFe₂O₄-3, rGO/CoFe₂O₄-4, and CoFe₂O₄ samples have specific capacitances of 88, 120, 141, 265, 136, and 70 F/g, respectively.

Figure 6d shows GCD curves of prepared electrodes at different current densities varying from 0.1 to 1 A/g. It is clear that the material, even at high scanning speeds and current densities, maintains a decent scanning potential curve shape and a significant specific capacitance. At current densities of 0.1, 0.2, 0.3, 0.5, and 1.0 A/g, the rGO/CoFe₂O₄-3 electrode has specific capacitances of 283, 265, 253, 242, and 232 F/g, respectively. The specific capacitance remains at 82% compared to the 0.1-A/g current density when the current density reaches 1.0 A/g. This demonstrates the good performance of the produced material for a variety of discharge current densities.

The impedance measurement technique enables a deeper comprehension of the electrochemical properties of rGO/CoFe₂O₄ materials. The Nyquist diagram of supercapacitors with rGO, rGO/CoFe₂O₄, and CoFe₂O₄ electrodes makes it simple to compare the resistance properties of different materials. According to Fig. 6e, rGO, rGO/CoFe₂O₄, and CoFe₂O₄ exhibit internal resistances of 0.30, 0.48, and 0.81 ohms, respectively, and charge transfer resistances of 0.60, 0.46, and 0.58 ohms, respectively. The internal resistance and charge transfer resistance of rGO/CoFe₂O₄ materials are significantly reduced by the excellent conductivity of rGO and the rapid charge conversion rate of CoFe₂O₄ by redox reaction.

The excellent electrochemical properties of rGO/CoFe₂O₄ materials are reflected in the long charging life of the supercapacitor electrode. After 1000 cycles of continuous charging, the rGO/CoFe₂O₄ electrode's specific capacitance is still 90.5% of the original (Fig. 6f).

Compared to previous analogous reports on rGO/CoFe₂O₄ composite electrodes, this result was quite favorable (Fig. 7). Therefore, the prepared rGO/CoFe₂O₄ composites exhibit excellent electrochemical performance and can be used as electrode material for supercapacitors.

The Ragone plot (Fig. 7) demonstrates the correlation between energy density and power density at different discharge current densities. A supercapacitor based on the prepared rGO/CoFe₂O₄ composite exhibits a high specific energy density of 29 Wh/kg at a specific power density of 855 W/kg. According to

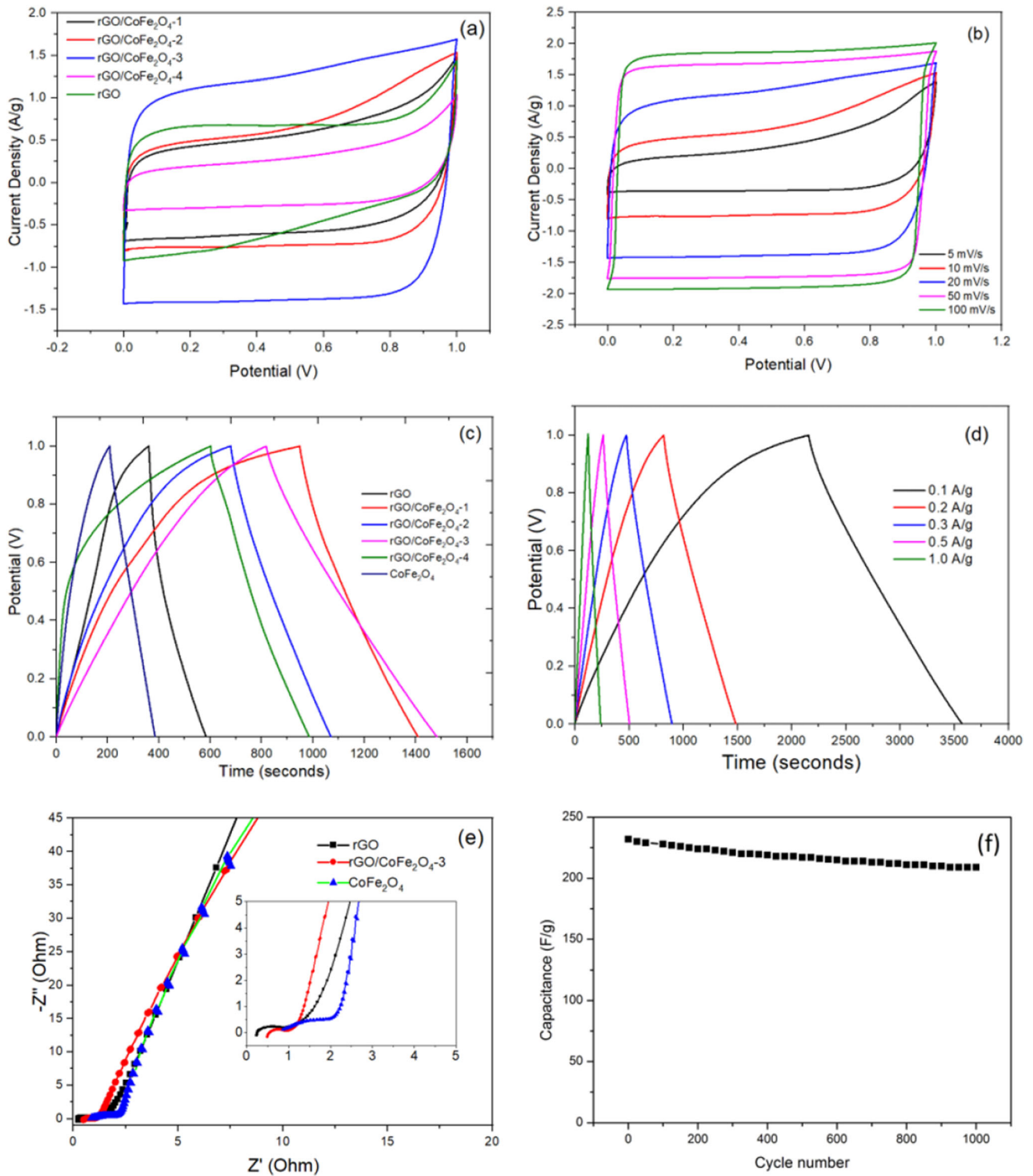


Fig. 6 CV curves of rGO/CoFe₂O₄ at 20 mV/s (a); rGO/CoFe₂O₄-3 at various scan rates (b); GCD curves of rGO/CoFe₂O₄ at 0.2 A/g (c); GCD curves of rGO/CoFe₂O₄-3 at various current densities (d); Nyquist plot (e); and life long (f) of rGO/CoFe₂O₄-3

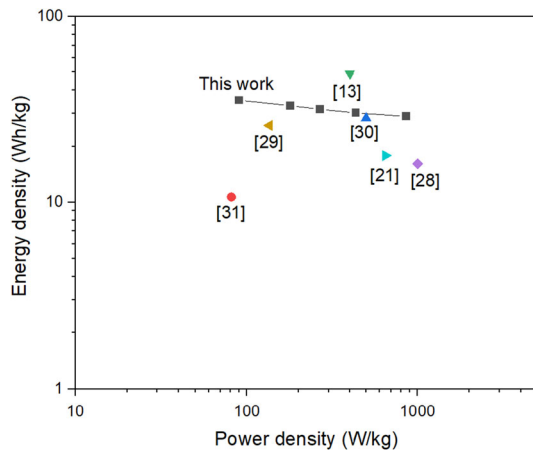


Fig. 7 Ragone plot of the energy density and power density of rGO/CoFe₂O₄ nanocomposite. Comparisons of supercapacitors composed of ZnCo₂O₄-rGO composite [13], CoFe₂O₄/rGO hydrogel [21], rGO/CoFe₂O₄ nanocomposites [27], PEDOT:PSS/rGO [28], rGO/CoFe₂O₄ paper [29], and ZnCo₂O₄ quantum dots/reduced graphene oxide [30]

the Ragone plot, it can be seen that the rGO/CoFe₂O₄ material exhibit excellent electrochemical characteristics compared to similar studies.

4 Conclusion

The rGO/CoFe₂O₄ composite materials were fabricated by a simple thermal reduction process. The rGO/CoFe₂O₄ sample shows porous structure and high specific surface area. CoFe₂O₄ particles of approximately 30 nm in size are distributed on the surface of GO sheets uniformly. The prepared rGO/CoFe₂O₄ showed excellent electrochemical properties, with a high specific capacitance of 283 F/g at a current density of 0.1 A/g and a specific capacitance retention of 90.5% after 1000 cycles. The rGO/CoFe₂O₄ composite material has the potential to be used in the production of high-performance supercapacitor electrodes.

Acknowledgements

The financial support of Science and Technology Development Project (number:788/2021) is gratefully acknowledged.

Author contributions

HVN contributed to material preparation, data interpretation, analysis, and writing and original draft preparation; HTL contributed to data analyzing and writing, reviewing, and editing of the manuscript; THL, TTV, and KTP contributed to discussion and data curation; HTN and TXP contributed to reviewing and editing of the manuscript and supervision. All authors have read and approved the final manuscript.

Funding

This work was supported by Science and Technology Development Project (Grant no.: 788/2021)

Data availability

All the data analyzed are included in this manuscript.

Declarations

Conflict of interest The authors declare no conflict of interest.

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