

Research Papers

Microwave-assisted fabrication of high-performance supercapacitors based on electrodes composed of cobalt oxide decorated with reduced graphene oxide and carbon dots

Sevda Yetiman^a, Hilal Peçenek^a, Fatma Kılıç Dokan^{b,*}, M. Serdar Onses^{a,c,f}, Erkan Yılmaz^{a,d}, Ertugrul Sahmetlioglu^{a,e,**}

^a ERNAM-Erciyes University Nanotechnology Application and Research Center, Kayseri 38039, Turkey

^b Department of Chemistry and Chemical Processing Technologies, Mustafa Çıkrıkcıoğlu Vocational School, Kayseri University, Kayseri, Turkey

^c Department of Materials Science and Engineering, Faculty of Engineering, Erciyes University, Kayseri 38039, Turkey

^d Technology Research and Application Center (TAUM), Erciyes University, Kayseri 38039, Turkey

^e Department of Basic Sciences of Engineering, Kayseri University, Kayseri 38039, Turkey

^f UNAM-Institute of Materials Science and Nanotechnology, Bilkent University, Ankara 06800, Turkey

ARTICLE INFO

Keywords:

Carbon dots

Electrochemical studies

Metal oxide

Microwave irradiation

ABSTRACT

This study presents microwave-assisted preparation of cobalt oxide (Co_3O_4) based nanocomposite electrodes doped with carbon dots and reduced graphene oxide. The calcination of the precursors at 400°C for 2 h results in nanocomposites. A three-electrode cell in 2M KOH solution is used for the electrochemical measurements. The carbon dot containing electrodes enables the highest specific capacitance of 936 Fg^{-1} at 0.5 Ag^{-1} current density. Specific capacitances of pure Co_3O_4 , and $\text{Co}_3\text{O}_4/\text{RGO}$ electrodes are 448 Fg^{-1} and 482 Fg^{-1} at 0.5 Ag^{-1} , with good rate capability even at 10 Ag^{-1} , respectively. The cyclic stability of the electrodes is reasonably high and the electrodes retain 93%, 87%, and 88% of their initial capacitance after 10,000 cycles for Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$, and $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$, respectively. The optimized $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ electrodes were used to fabricate a symmetric supercapacitor that exhibits high specific capacitance (126 Fg^{-1} 0.25 Ag^{-1}) and long cycle life (%81 retention after 10,000 cycles). The fabricated supercapacitor has energy density of 17.5 Wh kg^{-1} and power density of 2522 W kg^{-1} . The outstanding results demonstrate the promise of carbon dots doped transition metal oxides-based nanoparticles as promising electrodes for supercapacitor applications.

1. Introduction

In reply to the requirements of modern society and consistent environmental concerns, it is necessary to have modern, reasonably priced yet eco-friendly energy conversion and storage systems. The high energy capacity and long-term endurance are important aspects of the energy storage systems. Batteries, electrochemical supercapacitors (ESCs), and fuel cells are the most approved types of electrochemical energy storage/conversion systems developed for this purpose [1–10]. Supercapacitors (SCs), in particular, have received a great deal of attention in recent years due to their high power densities, long cycle lifetimes, and fast charge-discharge rates [11–18]. When having almost unlimited

lifetime and recharged ability in seconds, low energy densities (electrical energy storage per volume) of SCs raise the problem that these devices are either enlarged in size to become useable or frequently need to be recharged [19]. Consequently, boosting the energy density of SCs without reducing the power density is a big dilemma.

When all physical actions and chemical reactions occurring at the electrode/electrolyte interface taken into account, the electrode materials play vital roles in SCs. Mesoporous transition metal oxides such as SnO_2 , RuO_2 , In_2O_3 , NiO , MnO_2 , and Co_3O_4 are the mostly investigated electrode materials due to, large specific surface areas, proper pore size distribution, controllable size and shape, high capacitance, good redox performance, high power density, and long charge-discharge cycling

* Corresponding author at: Department of Chemistry and Chemical Processing Technologies, Mustafa Çıkrıkcıoğlu Vocational School, Kayseri University, Kayseri, Turkey.

** Corresponding author at: ERNAM-Erciyes University Nanotechnology Application and Research Center, Kayseri 38039, Turkey.

E-mail addresses: fatmakilic@kayseri.edu.tr (F.K. Dokan), sahmetlioglu@erciyes.edu.tr (E. Sahmetlioglu).

<https://doi.org/10.1016/j.est.2022.104103>

Received 5 December 2021; Received in revised form 20 January 2022; Accepted 25 January 2022

Available online 7 February 2022

2352-152X/© 2022 Elsevier Ltd. All rights reserved.

[20–23]. Among these materials, Co_3O_4 with ultrahigh theoretical capacity (3560 Fg^{-1}) and long cycling life has elicited extensive interest as redox-active electrodes for SCs [24–26].

Carbon-based materials such as activated carbon (AC), graphene, graphene oxide (GO), reduced graphene oxide (RGO), carbon nanotubes (CNTs), and carbon dots (CDs) are indispensable for studies aiming to achieve high efficiency [27,28]. Especially, graphene-doped metal oxide cathode electrode studies intensively increased since graphene was discovered in 2004 [29–32]. Many research focuses on this excellent material as large patches of graphene provide an appropriate platform and large surface area (a theoretical value of $2630 \text{ m}^2 \text{ g}^{-1}$) for integration of metal oxides [33]. The addition of graphene improves the performance of the electrodes by providing better structural stability due to having a high electron transport rate, electrical and thermal conductivity, and electrolyte contact area [34,35].

CDs possess stunning properties such as low cost, simple synthetic procedures, good chemical stability, immense surface defects, good accessibility for ions and mass, which make them interesting in energy-oriented applications. CDs contain hydrophilic surface functional groups such as $-\text{COOH}$, $-\text{COOR}$, and $-\text{OH}$ and provide a convenient interface for the interaction between electrolyte and electrodes (especially in water-based electrolyte). The doping of CDs improves the specific capacities and cycle stabilities of the electrode materials [36,37]. However, numerous interfaces among the small size of CDs cause high internal resistance, and agglomeration of the small particles decreases the accessible specific surface area (SSA) of the CDs. Therefore, CDs are rarely used alone as SCs electrode materials [38,39]. However, via a suitable combination with transition metal oxides/ sulfides or conductive polymers they can become sufficient for SCs applications [40].

The synthesis method is also one of the influential parameters that affect the results. Up to date, there has been a few studies on microwave-assisted method that has many benefits such as rapidness, phase purity, narrow particle size distribution [41,42]. Park et al. examined Co_3O_4 -graphene nano composites and reported the maximum specific capacitance of 305 Fg^{-1} at the scan rate of 10 mVs^{-1} and retention was 72% after 1000 continuous cycles [43]. Cui et al. analyzed microwave treated Co_3O_4 nanomaterial and could achieve maximum specific capacitance of 456 Fg^{-1} [44]. Vijayakumar and co-workers synthesized microwave treated Co_3O_4 and the reported maximum specific capacitance was 519 Fg^{-1} at 0.5 mA/cm^2 . They observed only about 1.3% degradation in specific capacitance after 1000 cycles [45]. As far as we know there is no prior study focusing on Co_3O_4 decorated with reduced graphene oxide and CDs prepared by microwave-assisted methods. Responding to this gap of knowledge, within the scope of this study we prepared three different types of electrodes (Co_3O_4 , $\text{Co}_3\text{O}_4\text{@RGO}$, and $\text{Co}_3\text{O}_4\text{@RGO@CDs}$) using that advantageable system. Consequentially, CDs doping enhanced the electrochemical properties almost two times (936 Fg^{-1}) with a good rate and cyclic capacity retention (88% after 10,000 cycles). Moreover, the SSC device formed by two identical $\text{Co}_3\text{O}_4\text{@RGO@CDs}$ electrodes (same mass and specific capacity) succeeded to obtain a high specific capacitance of 126 Fg^{-1} at the current density of 0.25 Ag^{-1} with long cycle life (81% retention after 10,000 cycles). The persuasive results prove the usage of carbon dots doped transition metal oxides-based nanoparticles as hope-inspiring electrodes for supercapacitor applications.

2. Experimental section

Materials: Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), potassium hydroxide (KOH), urea ($\text{CO}(\text{NH}_2)_2$), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), dimethyl sulfoxide (DMSO) were obtained from Merck (GERMANY). Polyvinylidene fluoride (PVDF) and n-methyl-2-pyrrolidone (NMP) were purchased from Sigma Aldrich, (USA). Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was also obtained from Horosan Kimya (TURKEY). All chemical reagents and solvents for synthesis and analysis were used without further purification and deionized water (DI) ($18.2 \text{ M}\Omega \text{ cm}$ resistivity) was used

throughout the study.

2.1. Synthesis of carbon dots (CDs)

CDs were synthesized according to the procedure reported by Zhai et al. with some modification [46]. $1.5 \text{ g C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and $3 \text{ g CO}(\text{NH}_2)_2$ were added into 10 mL DI water and stirred until forming a transparent solution. Subsequently, the solution was subjected to 700 W of microwave irradiation for 5 min using a microwave oven. To remove impurities, the dark brown solid was re-dissolved in DMSO and centrifuged several times at speed of $10,000 \text{ rpm}$ for 10 min . The obtained CDs were 8 nm in diameter with green emission under 450 nm light. In Fig. S1†, the size distribution histogram of CDs measured by dynamic light scattering (DLS) measurement and green emission color photograph can be seen.

2.2. Synthesis of Co_3O_4

The synthesis of Co_3O_4 was done by facile microwave irradiation route with some modification reported elsewhere [14]. In a typical water/stock solution route, 3 mmol of $\text{H}_2\text{C}_2\text{O}_4$ was dissolved in 10 mL of DMSO to form a homogeneous solution under continuous magnetic stirring (300 rpm). After $\text{H}_2\text{C}_2\text{O}_4$ has dissolved completely 3 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added to the solution and ultrasonicated for one hour. Subsequently, 10 mL of DI was added dropwise until a pinky color was observed.

2.3. Synthesis of $\text{Co}_3\text{O}_4\text{@RGO}$

The synthesis of GO was done by the modified Hummer method using natural graphite powder [47]. The above-described procedure was similar. 25 mg of GO was dissolved in 10 mL of DI and ultrasonicated for one hour before adding dropwise to the $\text{H}_2\text{C}_2\text{O}_4/\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ homogeneous solution until a dark brown color appeared.

2.4. Synthesis of $\text{Co}_3\text{O}_4\text{@RGO@CDs}$

Fig. 1. presents the schematic illustration of the experimental process. $4 \text{ wt\%}$ (100 mg) CDs were dissolved in 10 mL of DMSO solution and mixed with $\text{H}_2\text{C}_2\text{O}_4/\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ homogeneous solution. GO was dissolved in 10 mL of deionized water in another beaker and added dropwise to this solution until a dark green color was observed.

Finally, all of the precipitates were exposed to 700 W of microwave irradiation for 3 min using a household microwave oven. After cooling to room temperature, water and ethanol were used to remove impurities. The obtained particles were vacuum dried at 85°C for 12 h and calcinated at 400°C for 2 h at a rate of $1^\circ \text{C min}^{-1}$, in flowing air to obtain the pure Co_3O_4 , $\text{Co}_3\text{O}_4\text{@RGO}$, and $\text{Co}_3\text{O}_4\text{@RGO@CDs}$ structures. During this time with the effect of applied high energy, GO turned into RGO.

2.5. Structural characterization

The structure and morphology of Co_3O_4 , $\text{Co}_3\text{O}_4\text{@RGO}$, and $\text{Co}_3\text{O}_4\text{@RGO@CDs}$ were analyzed by field emission scanning electron microscope (FE-SEM, Gemini 550) and scanning transmission electron microscope (STEM, Gemini 550). The crystallographic structures of the particles were clarified by employing Bruker AXS D8 X-ray powder diffractometer with simple cubic lattice and $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$), and the scan range (2θ) was from 5° to 90° . Raman spectra of the nanoparticles were measured by WITec alpha 300 M dispersive Raman spectrometer consisting of He-Ne laser system (Excitation of wavelength is 532 nm). The pore size distribution, total pore volume and the specific surface area (SSA) were analyzed by the Brunauer-Emmett-Teller (BET), and (Barrett-Joyner-Halenda) BJH methods. X-ray photoelectron spectroscopy (XPS) was applied using thermo scientific K-Alpha

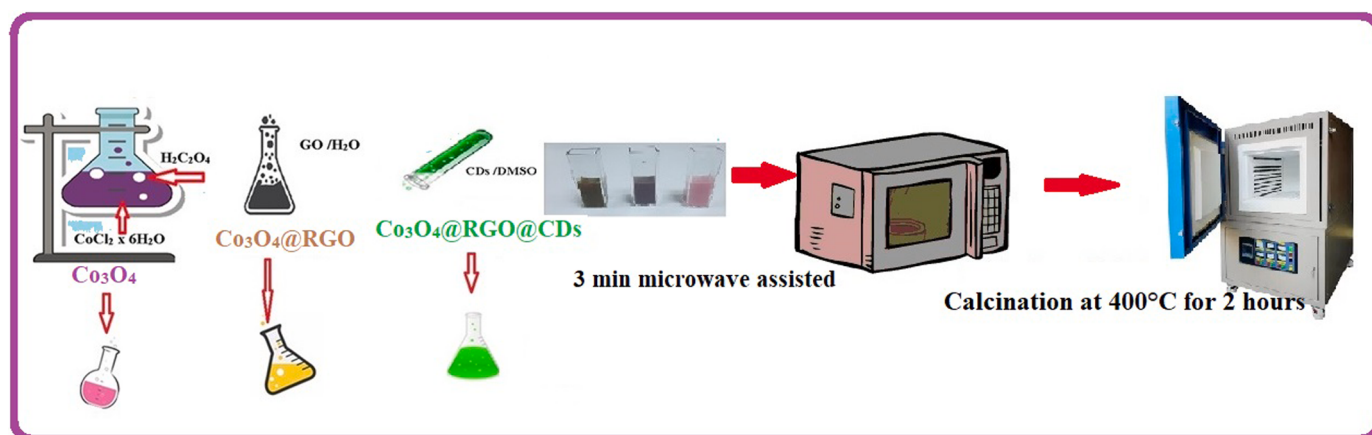


Fig. 1. The synthesis steps of Co_3O_4 , $\text{Co}_3\text{O}_4@\text{RGO}$ and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$.

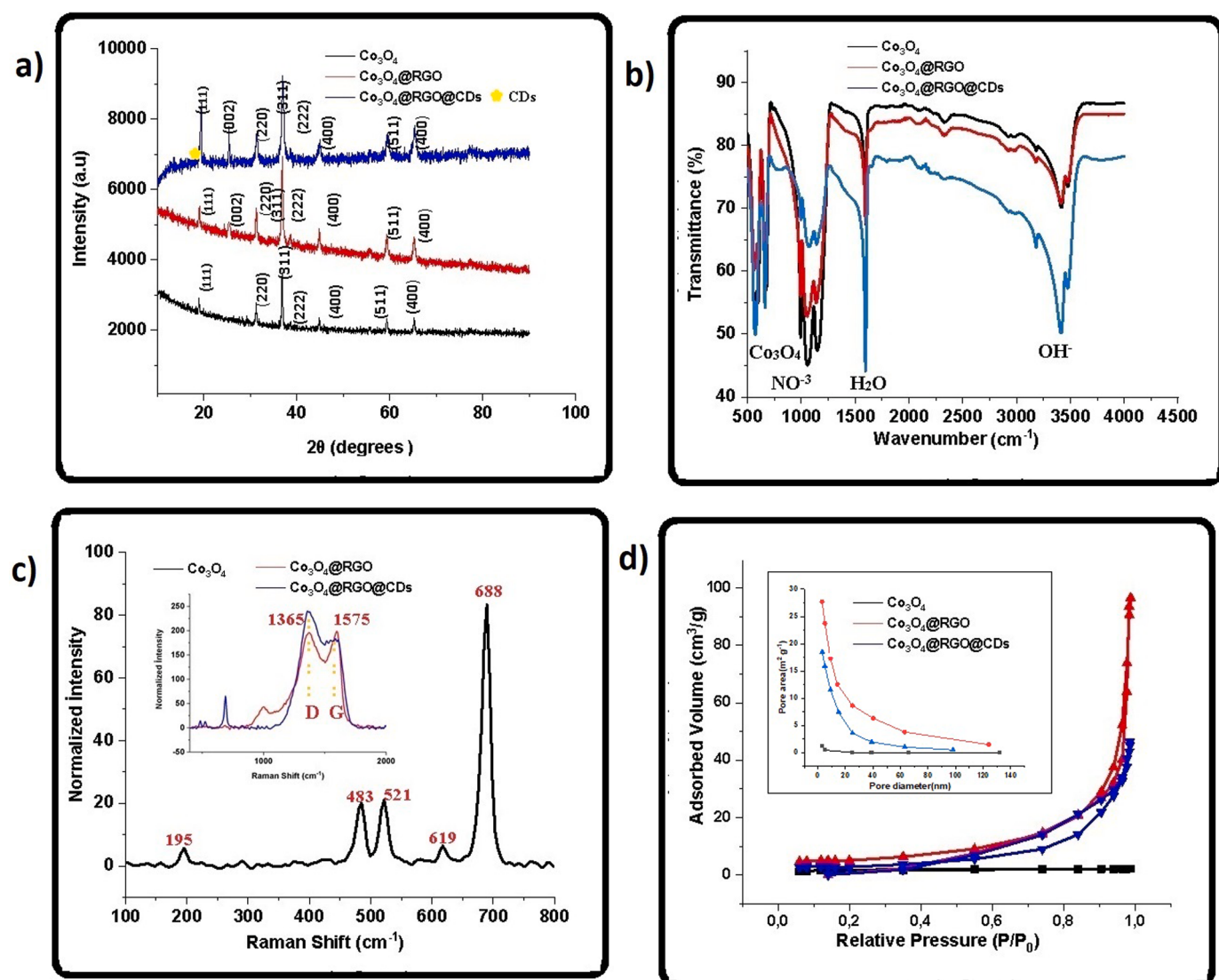


Fig. 2. (a) XRD patterns of Co_3O_4 (black line), $\text{Co}_3\text{O}_4@\text{RGO}$ (red line), and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$ (blue line), (b) FTIR spectra of Co_3O_4 (black line), $\text{Co}_3\text{O}_4@\text{RGO}$ (red line), and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$ (blue line), (c) Raman spectrum of Co_3O_4 , inside $\text{Co}_3\text{O}_4@\text{RGO}$, and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$. (d) N_2 adsorption-desorption isotherms of Co_3O_4 (black line), $\text{Co}_3\text{O}_4@\text{RGO}$ (red line), and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$ (blue line). Inside shows the pore size distribution for the patterns.

X-Ray photoelectron spectrometer (spot size=400 μm).

2.6. Electrochemical characterization

The working electrodes were fabricated by mixing the electroactive materials (Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$, and $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ (85 wt%), acetylene black (10 wt%), and PVDF (5 wt%), several drops of NMP solvent and ultrasonicated for 3 h to form a homogeneous slurry. Then this slurry was dropped onto a nickel foam ($1\text{ cm} \times 1\text{ cm}$) and vacuum dried at 85°C for 12 h. Approximately 1.0 mg of active material was used as the loading material.

The electrochemical measurements were performed in a three-electrode configuration with Pt foil ($1 \times 1\text{ cm}^2$) as the counter electrode and silver /silver chloride (Ag/AgCl) as the reference electrode. Cyclic voltammetry (CV) tests were analyzed between -0.05 and 0.55 V (vs. Ag/AgCl) at different scan rates of 5–100 mV s^{-1} . The galvanostatic charge-discharge (GCD) analysis was performed in the potential range of -0.05–0.410 V (vs. Ag/AgCl) and specific current densities in the range of 1–20 A g^{-1} . It was not possible to reach CV curves positive potential window 0.55 V from GCD, appropriate maximum positive potential range was chosen as 0.410 V. The long-term GCD tests were done in the potential range of -0.05–0.410 V (vs. Ag/AgCl) at a current density of 10 A g^{-1} .

Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 0.01 to 100 kHz at open-circuit potential with an AC perturbation of 5 mV.

The optimized two similar $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ electrodes were fabricated to test the performance of symmetric capacitors for practice implementation. All electrochemical measurements and assessments were performed in 2M KOH aqueous electrolyte with Gamry Reference 3000 instrument.

3. Results and discussion

3.1. Structural and morphological studies

The crystalline structure of the prepared Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$, and $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ were analyzed by using X-ray diffraction. In Fig. 2a. (black line), the peaks at 2 theta values of 19.3, 31.2, 36.5, 44.7, 55.4, 59.1, 65.2 refer to the (111), (220), (311), (400), (511), (440) and (533) planes of Co_3O_4 , respectively. This result confirmed as prepared Co_3O_4 has a cubic crystal structure (JCPDS 42-1467) [45]. In Fig. 2a (red line), the peak at 24.7 is the characteristic peak of the (002) plane of RGO, and in Fig. 2a (blue line) the weak peak around 19.5 belongs to CDs [48,49].

FTIR spectra of the samples are shown in Fig. 2b. The bands seen at 564 cm^{-1} and 660 cm^{-1} correspond to the characteristic vibrational modes of Co-O in Co_3O_4 [48]. The band detected at 1100 cm^{-1} owes to stretching vibrations of NO_3^- ions [45]. The band corresponding to molecular water was detected at 1595 cm^{-1} and the broad peaks in all the samples at around $3100\text{--}3400\text{ cm}^{-1}$ can be assigned to the symmetric stretching vibrations of surface adsorbed water molecules. Due to RGO and CDs ratios are low Co_3O_4 peaks seem to be dominant.

The Raman spectra of the samples can be seen in Fig. 2c. The peaks observed at 195, 493, 521, 619, and 688 belong to the pure Co_3O_4 calculated at 400°C for 2 h. The inset of Fig. 2c. shows the Raman spectrum of the composite materials. The peaks at 1365 cm^{-1} and 1575 cm^{-1} were referred to as sp^3 (D band) and sp^2 (G band) hybridization carbon atoms, respectively. As it is seen in the Raman spectrum, D band intensity is more than the intensity of G band and ID/IG ratio gives the disorder measurement in the samples. The obtained results are consistent with results in the literature [50] indicating the formation of RGO.

To analyze the porosity of Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$, and $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$, N_2 adsorption-desorption isotherms were evaluated. The isotherm for Co_3O_4 shows a very small adsorbed amount of N_2 gas, indicating a nonporous characteristic. Compared with the isotherms for Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$ and $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ show a more adsorbed

amount of N_2 gas, probably due to the existence of micropores. RGO doped material owes the largest SSA $17.52\text{ m}^2\text{g}^{-1}$. SSA of pure Co_3O_4 , and $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ are $5.53\text{ m}^2\text{g}^{-1}$, and $10.15\text{ m}^2\text{g}^{-1}$, respectively. The average pore size value of Co_3O_4 increased with the addition of RGO so BET results and pore sizes of $\text{Co}_3\text{O}_4/\text{RGO}$ are higher than pure Co_3O_4 (Fig. 2d). Although, CDs addition decreased the porous nature of $\text{Co}_3\text{O}_4/\text{RGO}$, considered to the incorporation of CDs particles in between the pores or the layers of RGO. STEM images of the particles (Fig. 4 b–f) also verify this hypothesis the formation of RGO. The pore size distribution of the patterns is also shown in Fig. 2d (inside). The measured average pore sizes of Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$, $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ are 45 nm, 53.2 nm and 48.2 nm, respectively.

The chemical configuration/ chemical character on the surface was characterized by XPS as depicted in Fig. 3(a–d) Fig. 3a. shows the survey spectrum of $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ comprising Carbon (C), Nitrogen (N), Oxygen (O), and Cobalt (Co) elements. Fig. 3b. shows the high resolution spectrum (HRS) of Co 2p presents 2 prologue spin-orbit peaks of 2p $3/2$ (786.32 eV), 2p $1/2$ at (796.1 eV) and two more satellite peaks. Furthermore, in Fig. 3c. the HRS of carbon peaks are depicted. Four distinct peaks belonging to C-C/C=N, C-N/C=N, C-O, C=O with the binding energy values 285.1, 286.2, 287.6 and 288.2 eV are seen, respectively. HRS of N presented in Fig. 3d. as N1s in which, 3 distinct peaks corresponding to pyridinic-N, graphitic-N, and pyrrolic-N with the binding energies of 403.1 eV, 398.2 eV, 397.2 eV, respectively. In Fig S2[†] HRS of O1s in which the peaks owes to C-O, C-O-H, C-O-H with binding energies of 532.3 eV, 534 eV and 534.8 eV is shown, respectively. These validations affirmed the construction of $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ [51].

The morphology of the samples was studied using FESEM and STEM techniques. Fig. 4(a–e) show the FESEM images and Fig. 4(b–f) display STEM images of Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$, and $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$, respectively. The high energy applied during microwave irradiation caused the particles to become uniform and homogenous. FESEM and STEM images show the uniform distribution of nanoparticles. As microwave irradiation reduced the GO and decreased the lateral size of the GO, the layers were also distorted. Therefore, the layered structure of the RGO can not be observed.

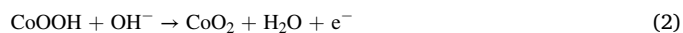
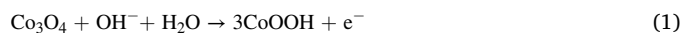
3.2. Electrochemical studies

3.2.1. Cyclic voltammetry studies

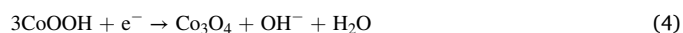
The cyclic voltammograms of the electrode $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ at 20, 50 and 100 mV s^{-1} in the potential range of -0.05–0.55 V (vs. Ag/AgCl) using 2.0M KOH as the electrolyte are presented in Fig. 5a. Well observed redox peaks verifying the Faradic nature of the material can be clearly seen from CV curves. The cyclic voltammograms of Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$, and the comparison of the three electrodes are presented in Fig. S3 a,b)[†] and Fig. 6a. While anodic and cathodic peaks were more distinct for Co_3O_4 with RGO and CDs addition these peaks shifted [52, 53].

The equation of the redox process belongs to Co_3O_4 in alkaline electrolyte is shown as follows:

Anodic scan:



Cathodic scan:



The specific capacitance $C(\text{Fg}^{-1})$, the energy density (E, Wh kg^{-1}), and the power density (P, W kg^{-1}) were reckoned according to the following equations:

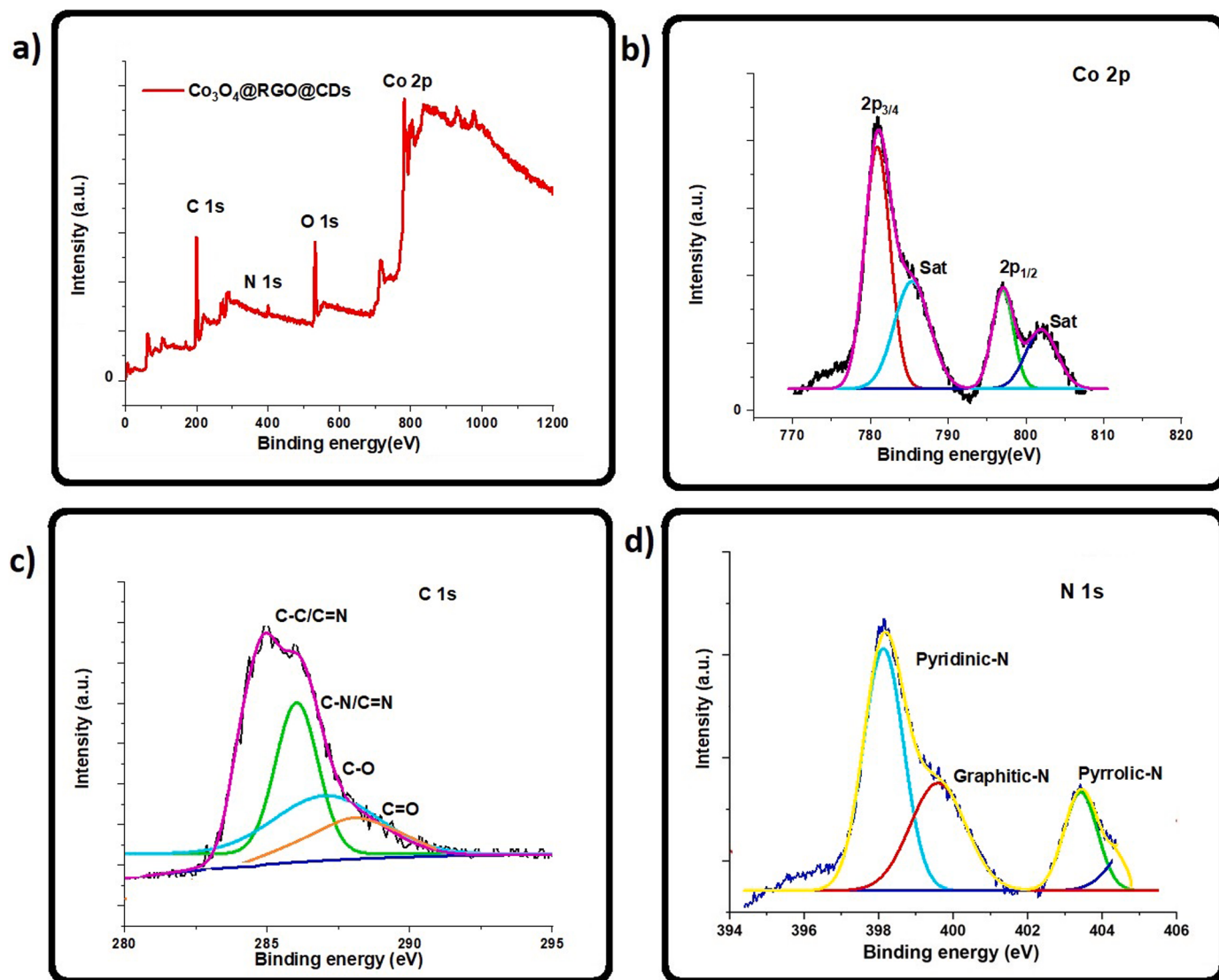


Fig. 3. XPS analysis of $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$ nanocomposite. (a) survey spectrum, (b) high resolution spectrum of Co 2p, (c) high resolution spectrum of C1s, and (d) high resolution spectrum of N1s.

$$C_s = \frac{\int I(V) dV}{v \times m \times \Delta V} \quad (5)$$

$$E = (C \times \Delta V^2) / 7.2 \quad (6)$$

$$P = E / \Delta t \quad (7)$$

where $\int I(V) dV$ is the area surrounded by the CV curves, v (mV s^{-1}) is the scan rate, m (g) is the mass of the active material and ΔV (V) is the applied potential window. E (Wh kg^{-1}) and P (W kg^{-1}) also represent the energy density and power density (P , W kg^{-1}), respectively.

Based on the above Eq. (5), the specific capacitance values of the samples at various scan rates were calculated. As shown in Table 1, CDs doped sample $\text{Co}_3\text{O}_4 @\text{RGO}@\text{CDs}$ possesses the highest specific capacitance value 773 F g^{-1} at the scanning rate of 1 mVs^{-1} and specific capacitance of $\text{Co}_3\text{O}_4@\text{RGO}$ and Co_3O_4 at the same scan rates are 315 F g^{-1} and 216 F g^{-1} , respectively. Pure Co_3O_4 has the lowest value since this result can be obviously deduced from CV curves which visibly increased by the incorporation of RGO and CDs. The enhanced current value in the CV loops of $\text{Co}_3\text{O}_4@\text{RGO}$ and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$ electrodes signifies the higher level of charge storage.

In Fig. 5b, and in Fig. S3 c,d)[†] the linearity between anodic/cathodic

peak current density and scan rate led by surface redox reactions can be seen [52,54–57]. R^2 shows the consistence between experimental data to linear fit. As a result of polarization, the increase in scan rate causes the anodic peaks to shift towards the larger potential range and the cathodic peaks to shift towards the lower potential range. While the OH^- ions just intercalate with the outer surface of the electrode at high scan rates, the OH^- ions interact both of the inner and the outer surface of the electrode at lower scan rates. Although the current density increased with the scan rate, Co_3O_4 , $\text{Co}_3\text{O}_4@\text{RGO}$ and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$ still had noticeable redox peaks, which confirmed good charge/discharge reversibility [45,52].

3.2.2. Chronopotentiometry

The charge-discharge properties and cyclic stability of $\text{Co}_3\text{O}_4@\text{RGO}$ and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$ were tested at different current densities in a potential window of -0.05 – 0.41 V (vs. Ag/AgCl) in 2M KOH aqueous electrolytes. The nonlinearity on charge-discharge curves verifies the pseudocapacitance nature of Co_3O_4 [25,54,57,58].

The specific capacitance of all electrodes reached the highest value at the lowest current densities. As known at low current density electrode contact with the more electroactive surface of OH^- ions while high current density causes diffusion with OH^- ions and that situation reduces

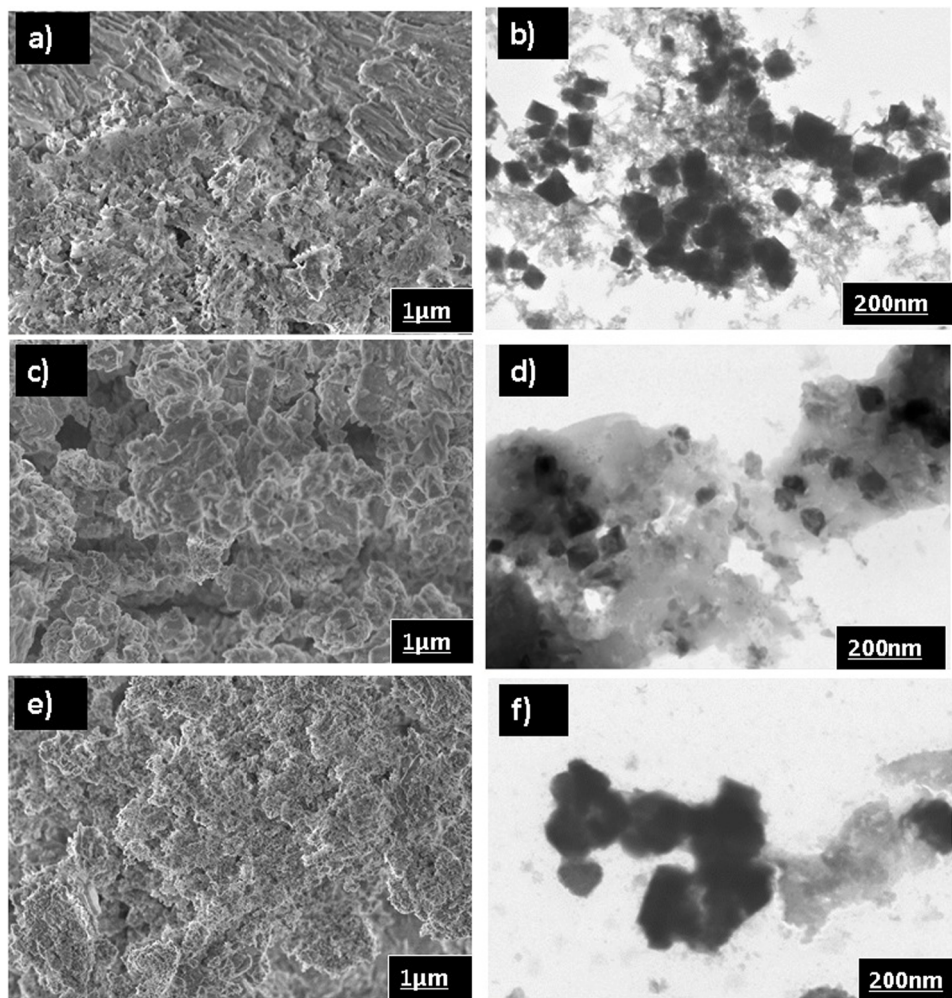


Fig. 4. FESEM and STEM images of the electrode materials (a,b) Co_3O_4 , (c,d) $\text{Co}_3\text{O}_4@\text{RGO}$ and (e,f) $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$.

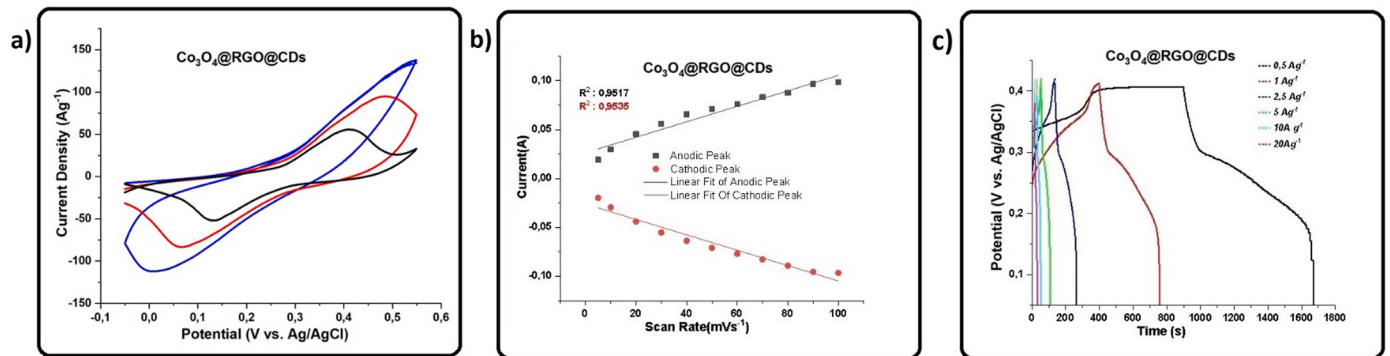


Fig. 5. (a) Cycling voltammograms, (b) Anodic and cathodic peaks current variation with scan rates and (c) Charge-discharge curves of $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$.

the specific capacitance [59].

The discharge curves of the electrodes at different current densities were presented in Figs. 5c. and S3 e,f). While Co_3O_4 could reach maximum discharge time of 419 s, $\text{Co}_3\text{O}_4@\text{RGO}$ and $\text{Co}_3\text{O}_4@\text{RGO}@\text{CDs}$ could reach 441 s and 777 s, respectively. Due to RGO and Co_3O_4 synergistic effect, RGO doped material had higher capacitance than pure Co_3O_4 . However, there was not much increase on specific capacitance since RGO morphology was disordered. Moreover, as the clearly seen from Fig. 6b. CDs doped electrode had the largest charge-discharge time with an increased potential window, owing to the fast-moving ability of

CDs [60]. The pseudocapacitive structure of Co_3O_4 caused the charging time of some electrodes to become more than discharging time. Therefore, observation of regular triangular shapes could not be possible on some GCD curves.

The specific capacitance results of the electrodes calculated from the charge-discharge curve by using the following equation was demonstrated in Fig. 6a.

$$C = \frac{I \Delta t}{m \Delta V} \quad (6a)$$

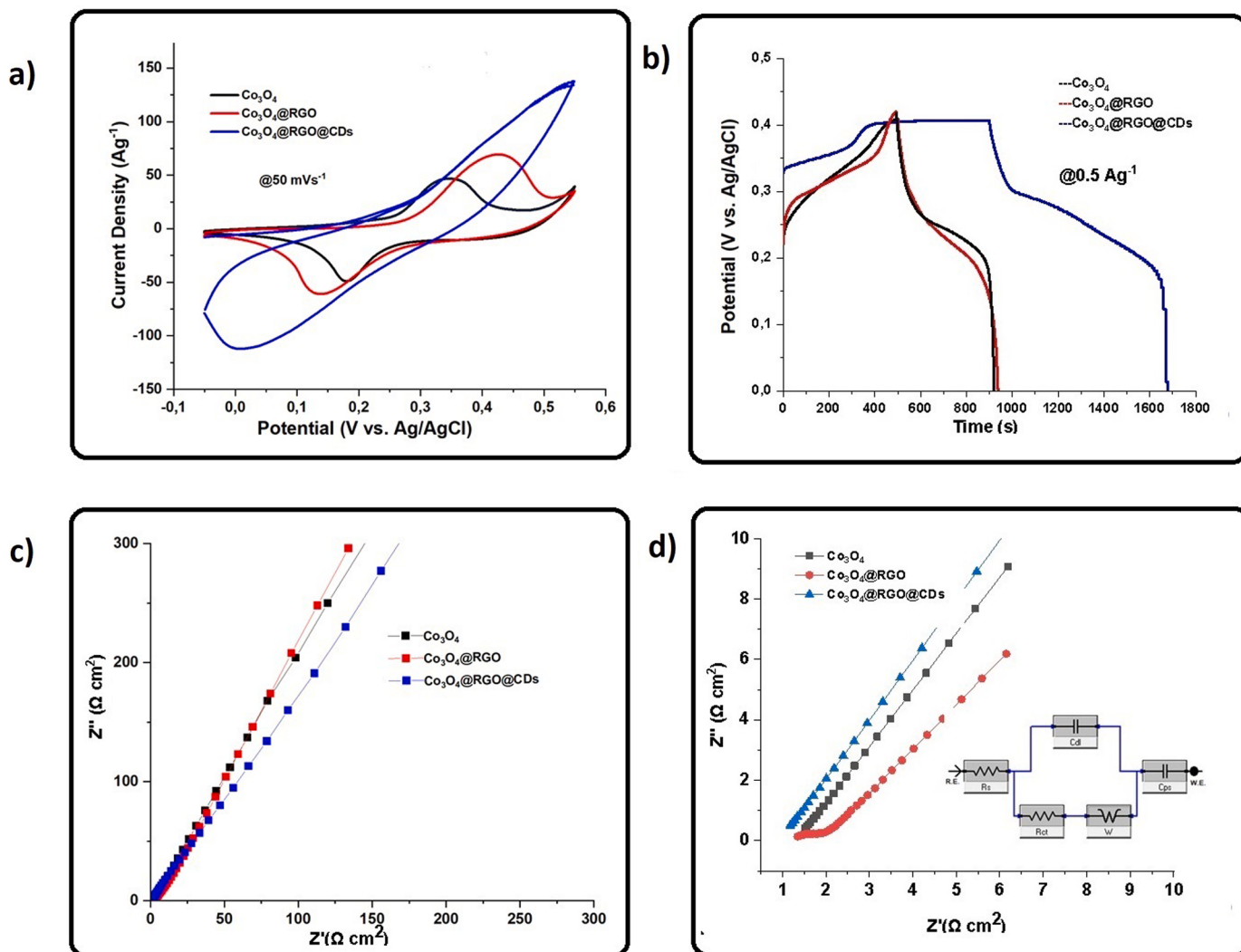


Fig. 6. (a) Comparison of cycling voltammograms, and charge –discharge curves (b) of Co_3O_4 , $\text{Co}_3\text{O}_4@\text{RGO}$, $\text{Co}_3\text{O}_4@\text{RGO@CDs}$ electrodes. Electrochemical impedance spectra (EIS) of Co_3O_4 , $\text{Co}_3\text{O}_4@\text{RGO}$, $\text{Co}_3\text{O}_4@\text{RGO@CDs}$ electrodes (c) at low frequency range in 2M KOH solution, and (d) at high frequency range (Inside corresponding equivalent circuit for modeling the measured impedance spectroscopy).

Table 1

Specific capacitance variation with different scan rates.

Specific Capacitance (F g^{-1})				
Scan rate (mV s^{-1})	1	20	50	100
Co_3O_4	216	205	185	159
$\text{Co}_3\text{O}_4@\text{RGO}$	315	310	286	211
$\text{Co}_3\text{O}_4@\text{RGO@CDs}$	773	594	437	251

where I (A) is the discharge current, Δt (s) is the discharge time, m (g) mass of the active material, ΔV (V) is the potential window changed during the discharge time. The ratio of discharge current I (A) to mass of the active material m (g) represents the current density $J(\text{Ag}^{-1})$.

The highest specific capacitance of the electrodes are 448 F g^{-1} , 482 F g^{-1} , and 784 F g^{-1} at 0.5 Ag^{-1} , respectively. Although, a distinct decrease of specific capacitance was not observed while current density increased 0.5 Ag^{-1} to 1 Ag^{-1} , especially for Co_3O_4 , and $\text{Co}_3\text{O}_4@\text{RGO}$ decrease with 10 Ag^{-1} and 20 Ag^{-1} was noticeable. As seen from Fig. 6b there was no significant time variation between Co_3O_4 and $\text{Co}_3\text{O}_4@\text{RGO}$ at 0.5 Ag^{-1} . Therefore, the differences between specific capacitances were also not notable. In Fig. 7a the specific capacitance of the materials with various current densities are depicted.

The long-term cyclic stability of the electrodes in 2M KOH was

examined by chronopotentiometry at a current density of 10 A g^{-1} up to 10,000 cycles. In Fig. 7b. the specific capacitance retention of the electrodes is shown. At the first 1000 cycles, the capacitance of Co_3O_4 deteriorates quietly, and after 3000 cycles the retention is 95% of its prime capacitance. The degradations of $\text{Co}_3\text{O}_4@\text{RGO}$, and $\text{Co}_3\text{O}_4@\text{RGO@CDs}$ after 1000 cycles are %3, %1, and the degradations are %6 and %4 after the end of 3000 cycles. At the end of 10,000 cycles the degradation of Co_3O_4 (7%) is less than others indicating Co_3O_4 has better cyclic stability. However, RGO doped $\text{Co}_3\text{O}_4@ \text{RGO}$ has more degradation (13%) than $\text{Co}_3\text{O}_4@\text{RGO@CDs}$ (12%). Comparison of the electrochemical performance of Co_3O_4 , $\text{Co}_3\text{O}_4@\text{RGO}$, and $\text{Co}_3\text{O}_4@\text{RGO@CDs}$ nanocomposites with previously reported values are given in Table 2. Co_3O_4 nanoparticles obtained via microwave method resulted in characteristics that are on par with the materials prepared by other methods.

3.2.3. Electrochemical impedance spectroscopy (EIS)

To further analyze the kinetics of ion and charge transfer performance of the electrode materials, electrochemical impedance spectroscopy (EIS) was used. Fig. 6(c,d) shows the Nyquist plot of the electrodes graphed in the frequency range of 0.01–100 kHz with an amplitude of 5 mV.

The charge transportability is determined by the high-frequency

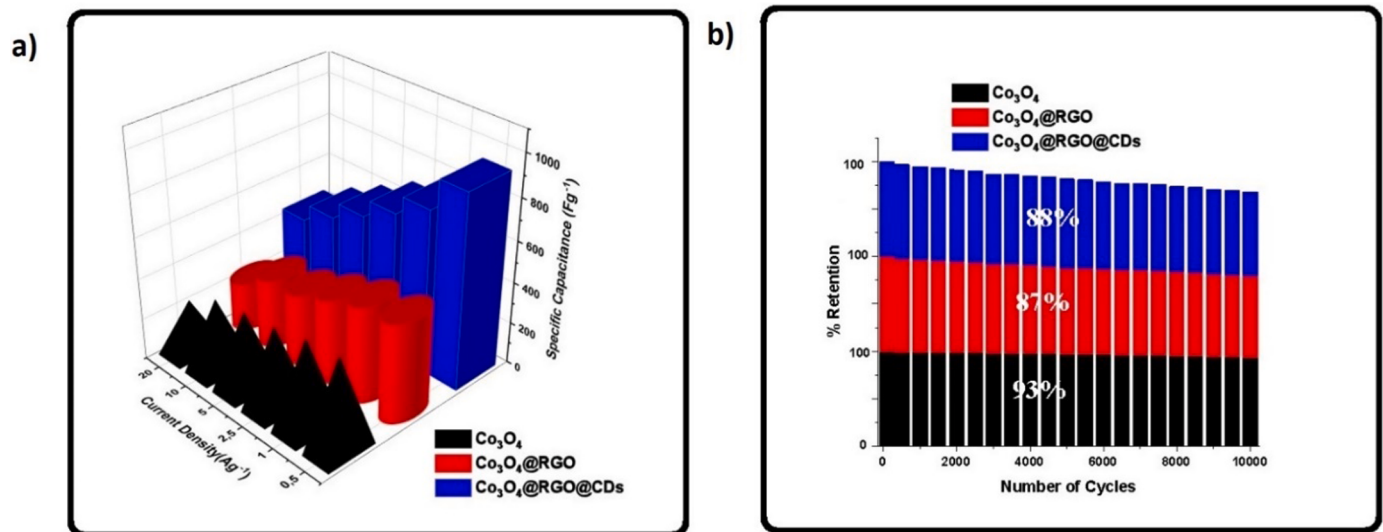


Fig. 7. (a) Variation of specific capacitance of the electrodes as a function of current density, (b) Comparison of cyclic stability performance of the electrodes at 10 A g⁻¹ current density.

Table 2

Comparison on the basis of the three-electrode system.

Structure	Synthesis Method	Electrolyte	Capacitance (F g ⁻¹)	Cycle stability (%)	Refs.
Co ₃ O ₄ Core-shell Microspheres	Hydrothermal	3M KOH	261.1 (0.5 A g ⁻¹)	90.2, 2000 cycles	[61,62]
Co ₃ O ₄ Flower shaped	Hydrothermal	2M KOH	327.3 (0.5 A g ⁻¹)	96, 10,000 cycles	[63]
Co ₃ O ₄ Nanowires	Solution reduction	1M KOH	978 (2 A g ⁻¹)	90, 2000 cycles	[64]
Co ₃ O ₄ Ultra-layered	Hydrothermal	1M KOH	548 (8 A g ⁻¹)	98.5, 2000 cycles	[59]
Co ₃ O ₄ Flower-shaped	Hydrothermal	6M KOH	2005.34 (0.5 A g ⁻¹)	98, 5000 cycles	[65]
Co ₃ O ₄ Honeycomb-like Nanosheets	Hydrothermal	2M KOH	743(1 A g ⁻¹)	97,500 cycles	[66]
Co ₃ O ₄ HollowFluffy Cages	Chemical	2M KOH	948.9 (1 A g ⁻¹)	100, 3500 cycles	[67]
Co ₃ O ₄ Nanosheet	Template	1M KOH	1121 (1 A g ⁻¹)	98.1,6000 cycles	[68]
Co ₃ O ₄ Nanorod	Microwave Irradiation	6M KOH	456(1 A g ⁻¹)	100, 500 cycles	[44]
Co ₃ O ₄ Nanopowder	Microwave Irradiation	2M KOH	519 (0.5 mA/cm ⁻²)	98.7, 1000 cycles	[45]
Co ₃ O ₄ Nano particles	Microwave Irradiation	2M KOH	448 (0.5 A g ⁻¹)	93, 10,000 cycles	This study
Co ₃ O ₄ Nanocubes@ RGO	Solvothermal	1M KOH	278(0.2 mA g ⁻¹)	91.6,2000 cycles	[13]
Co ₃ O ₄ /RGO Nano particles	Hydrothermal	2M KOH	458 (0.5 A g ⁻¹)	95.6,1000 cycles	[69]
Co ₃ O ₄ @RGO Nanosheets	Solvothermal	2M KOH	440.4 (5 A g ⁻¹)	94, 2000 cycles	[70]
Co ₃ O ₄ @RGO Nanosheets	Hydrothermal	6M KOH	894 (1 A g ⁻¹)	95,3000cycles	[71]
Co ₃ O ₄ /RGO Nanoparticles	Hydrothermal	6M KOH	1152 (1 A g ⁻¹)	89,5000 cycles	[72]
Porous Co ₃ O ₄ /RGO	Electrophoretic Deposition	2M KOH	1138.11(1 A g ⁻¹)	80.67,5000 cycles	[73]
Co ₃ O ₄ /RGO nano particles	Microwave Irradiation	2M KOH	482 (0.5 A g ⁻¹)	87, 10,000 cycles	This study
N-CQDs/Co ₃ O ₄	Ultrasonic Treatment	6M KOH	1867 (1 A g ⁻¹)	96, 500 cycles	[51]
Co ₃ O ₄ /RGO/CDs	Microwave Irradiation	2M KOH	936 (0.5 A g ⁻¹)	88,10,000 cycles	This study

region and the low-frequency region is used to identify the ion diffusion resistance. The vertical lines in the low-frequency region express the materials have an ideal capacitance behavior [32]. But, when a 45° angle between that line and the real axis is seen, ion diffusion between electrolyte to electrode interface results in another line called the Warburg line. Fig. 6c. illustrates the low-frequency region of the electrodes and the straight lines indicates Warburg lines (45° angle with real axis) are seen [18,31].

Fig. 6d. shows the high-frequency region (inset shows the equivalent circuit model). The equivalent series resistance (Rs) for the electrode Co₃O₄@RGO (1.27 Ω) was lower than Co₃O₄ (1.568 Ω) and Co₃O₄@RGO@CDs (1.648 Ω). The charge transfer resistance (Rct) of the electrodes Co₃O₄, Co₃O₄@RGO, Co₃O₄@RGO@CDs were 1.035 m Ω, 1.16 m Ω, and 1.566 m Ω, respectively. These results indicate that RGO doped electrode has the lowest electrochemical reaction resistance (Rs) and electron transfer resistance (Rct). Although highly conductive interface between Co₃O₄ and RGO considerably decreased the resistance of Co₃O₄@RGO, CDsts distribution among the pores or layers of RGO might increase the electrical resistance of Co₃O₄@RGO@CDs due to the aggregation of CDs.

3.2.4. Electrochemical performances of a symmetric supercapacitor

To demonstrate the practical utility of the reported materials in applications, we fabricated a symmetric supercapacitor using the Co₃O₄@RGO@CDs composite structure with the highest performance. Two identical electrodes (m: 1 mg) was used to generate a symmetric SC. Fig. 8a. shows the CV profiles of the Co₃O₄@RGO@CDs the hybrid symmetric device at various scans (1000–100–50 mVs⁻¹) within the -0.1–0.9 V potential window. The quasi-rectangular shape without apparent redox peaks of the CV profiles indicates the assembled symmetric supercapacitor device demonstrates an ideal capacitive performance. Moreover, the CV preserved that quasi-rectangular shape even at higher scan rates, such as 500–1000 mVs⁻¹, suggesting the fast charging/discharging features of the device.

Following equation was used to obtain equilibration of the mass balance of anode and cathode materials.

$$\frac{M_+}{M_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad (7a)$$

where M , C , ΔV symbolize the mass of the active material, specific capacitance, and potential window for the anode and cathode

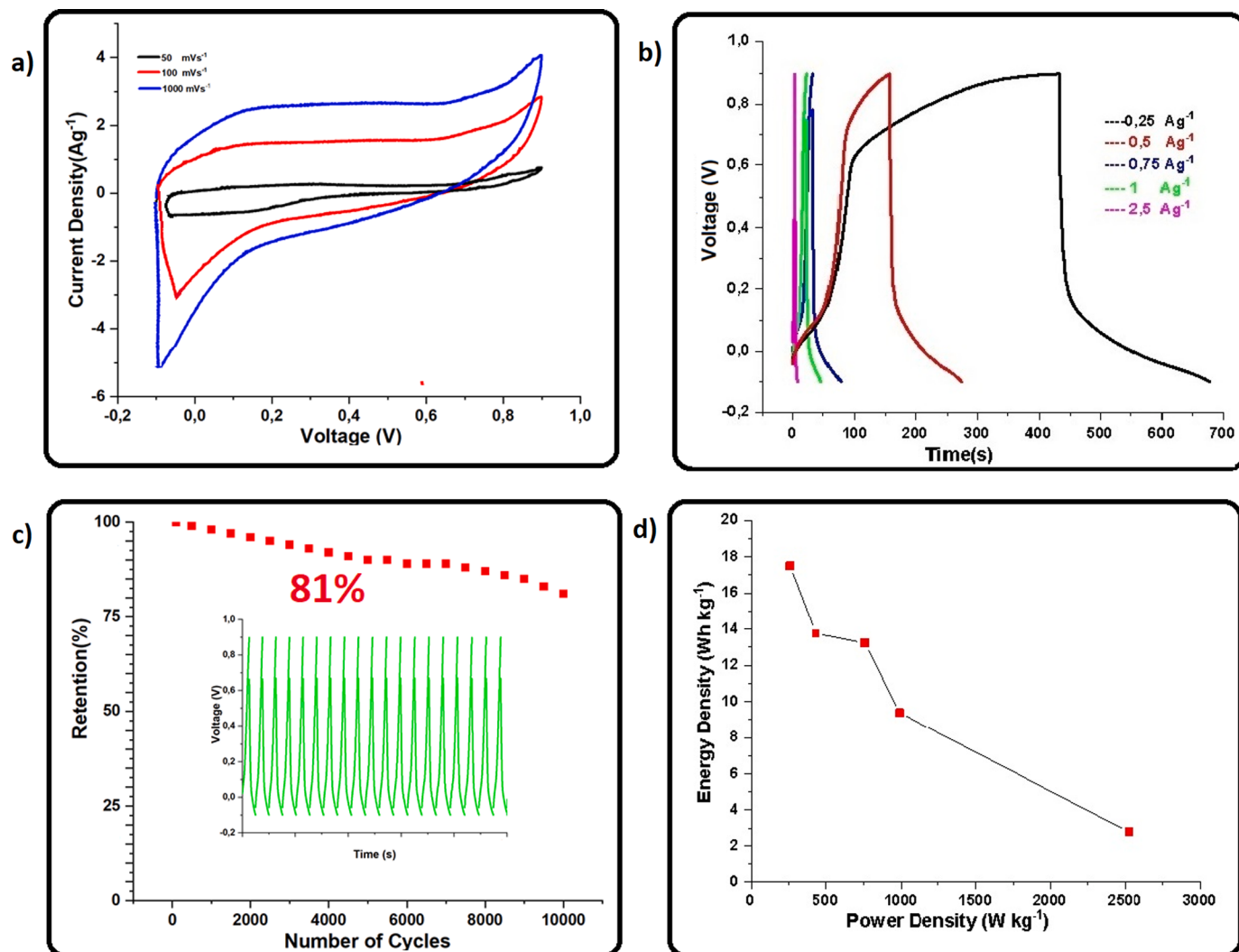


Fig. 8. (a) Cyclic voltammogram of the symmetric supercapacitor at the various scan rate; (b) charge-discharge profile of the symmetric supercapacitor at various current density; (c) cycle stability and capacitance retention of the symmetric supercapacitor current density of 2.5 A g^{-1} and (d) Ragone plot of the symmetric supercapacitor.

electrodes, respectively. Due to similar electrodes were utilized with same mass and specific capacitances, the mass ratio at positive and negative electrodes equals 1 (one).

Fig. 8b. presents the galvanostatic charge-discharge performance of the assembled symmetric supercapacitor at different current densities. Proportionality between time and potential can be seen from the curves indicating quick I-V reaction and exemplary capacitive nature. The calculated maximum and minimum specific capacitances were 126 F g^{-1} at a current density of 0.25 A g^{-1} and 20 F g^{-1} at the current density of 2.5 A g^{-1} . Additionally, the assembled supercapacitor showed a long-term cycling stability at the current density of 2.5 A g^{-1} for 10,000 cycles (Fig. 8c). The capacitance lost 19% of its initial value showing minimal devastation in electrodes due to continuous redox reaction. From Ragone plot Fig. 8d., the specific energy densities ($E_{\text{current density}}$) (Wh kg^{-1}) and power densities ($P_{\text{current density}}$) (W kg^{-1}) were calculated at the different current densities (A g^{-1}) were $E_{0.25}$: 17.5 Wh kg^{-1} - $P_{0.25}$: 256 W kg^{-1} ; $E_{0.5}$: 13.76 Wh kg^{-1} - $P_{0.5}$: 430 W kg^{-1} ; $E_{0.75}$: 13.24 Wh kg^{-1} - $P_{0.75}$: 758 W kg^{-1} ; E_1 : 9.38 Wh kg^{-1} - P_1 : 990 W kg^{-1} , and $E_{2.5}$: 2.8 Wh kg^{-1} - $P_{2.5}$: 2522 W kg^{-1} , respectively for the symmetric supercapacitor in which the results are compatible with the literature.

4. Conclusion

To summarize, this research focused on effects of CDs and reduced graphene oxide effects on cobalt oxide (Co_3O_4) based nanocomposites for supercapacitor applications. The active materials of the electrodes were obtained in a short duration of 5 min using a microwave-assisted route. Electrodes doped with CDs possessed the maximum specific capacitance as 936 F g^{-1} at 0.5 A g^{-1} current density and 784 F g^{-1} at 1 mVs^{-1} scan rate. Specific capacitances of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{RGO}$ electrodes were also obtained as 448 F g^{-1} and 482 F g^{-1} at 0.5 A g^{-1} , respectively. Degradation of the electrodes was examined for 10,000 cycles and results were reported as 7%, 13%, and 12% for Co_3O_4 , $\text{Co}_3\text{O}_4/\text{RGO}$, and $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$, respectively. The symmetric supercapacitor was assembled by using two identical $\text{Co}_3\text{O}_4/\text{RGO}/\text{CDs}$ electrodes. High specific capacitance (126 F g^{-1} 0.25 A g^{-1}) and long cycle life (%81 retention after 10,000 cycles) were observed. Moreover, the highest energy density and power density were 17.5 Wh kg^{-1} and 2522 W kg^{-1} , respectively. Our approach has shown the promise of microwave-assisted preparation of CDs doped metal oxide electrodes for high-performance supercapacitors.

Author statement

Dear Editor,

This study has not been previously published elsewhere. As authors, we accept all necessary responsibilities.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Research Fund of the Erciyes University (Project Number FBG-2020-9715).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.est.2022.104103](https://doi.org/10.1016/j.est.2022.104103).

References

- [1] M. Vangari, T. Pryor, L. Jiang, Supercapacitors: review of materials and fabrication methods, *J. Energy Eng.* 139 (2013) 72–79, [https://doi.org/10.1061/\(asce\)ey.1943-7897.0000102](https://doi.org/10.1061/(asce)ey.1943-7897.0000102).
- [2] S. Satpathy, S. Das, B.K. Bhattacharyya, How and where to use super-capacitors effectively, an integration of review of past and new characterization works on super-capacitors, *J. Energy Storage* 27 (2020), 101044, <https://doi.org/10.1016/j.est.2019.101044>.
- [3] T.M.I. Mahlia, T.J. Saktisadhan, A. Jannifar, M.H. Hasan, H.S.C. Matseelar, A review of available methods and development on energy storage; technology update, *Renew. Sustain. Energy Rev.* 33 (2014) 532–545, <https://doi.org/10.1016/j.rser.2014.01.068>.
- [4] H.J. Qiu, L. Liu, Y.P. Mu, H.J. Zhang, Y. Wang, Designed synthesis of cobalt-oxide-based nanomaterials for superior electrochemical energy storage devices, *Nano Res.* 8 (2015) 321–339, <https://doi.org/10.1007/s12274-014-0589-6>.
- [5] Y. Zou, X. Zhang, J. Liang, C. Xiang, H. Chu, H. Zhang, F. Xu, L. Sun, Encapsulation of hollow Cu₂O nanocubes with Co₃O₄ on porous carbon for energy-storage devices, *J. Mater. Sci. Technol.* 55 (2020) 182–189, <https://doi.org/10.1016/j.jmst.2020.02.014>.
- [6] Y. Liu, C. Xiang, H. Chu, S. Qiu, J. McLeod, Z. She, F. Xu, L. Sun, Y. Zou, Binary Co–Ni oxide nanoparticle-loaded hierarchical graphitic porous carbon for high-performance supercapacitors, *J. Mater. Sci. Technol.* 37 (2020) 135–142, <https://doi.org/10.1016/j.jmst.2019.08.015>.
- [7] C. Xiang, Q. Wang, Y. Zou, P. Huang, H. Chu, S. Qiu, F. Xu, L. Sun, Simple synthesis of graphene-doped flower-like cobalt-nickel-tungsten-boron oxides with self-oxidation for high-performance supercapacitors, *J. Mater. Chem. A* 5 (2017) 9907–9916, <https://doi.org/10.1039/c7ta00234c>.
- [8] H. Jiang, C. Zhou, X. Yan, J. Miao, M. You, Y. Zhu, Y. Li, W. Zhou, X. Cheng, Effects of various electrolytes on the electrochemistry performance of Mn₃O₄/carbon cloth to ultra-flexible all-solid-state asymmetric supercapacitor, *J. Energy Storage* 32 (2020), <https://doi.org/10.1016/j.est.2020.101898>.
- [9] L. Zhang, P. Cai, Z. Wei, T. Liu, J. Yu, A.A. Al-Ghamdi, S. Wageh, Synthesis of reduced graphene oxide supported nickel-cobalt-layered double hydroxide nanosheets for supercapacitors, *J. Colloid Interface Sci.* 588 (2021) 637–645, <https://doi.org/10.1016/j.jcis.2020.11.056>.
- [10] J. Xu, J. Liang, Y. Zou, F. Xu, Q. Chen, C. Xiang, J. Zhang, L. Sun, Layer-by-layer self-assembled GO–MoS₂/Co₃O₄ three-dimensional conducting network for high-performance supercapacitors, *J. Energy Storage* 43 (2021), 103195, <https://doi.org/10.1016/j.est.2021.103195>.
- [11] A. Berrueta, A. Ursua, I.S. Martin, A. Eftekhari, P. Sanchis, Supercapacitors: electrical characteristics, modeling, applications, and future trends, *IEEE Access* 7 (2019) 50869–50896, <https://doi.org/10.1109/ACCESS.2019.2908558>.
- [12] L. Bao, T. Li, S. Chen, C. Peng, L. Li, Q. Xu, Y. Chen, E. Ou, W. Xu, 3D graphene frameworks/Co₃O₄ composites electrode for high-performance supercapacitor and enzymeless glucose detection, *Small* 13 (2017) 1–8, <https://doi.org/10.1002/smll.201602077>.
- [13] A. Numan, N. Duraisamy, F. Saiha Omar, Y.K. Mahipal, K. Ramesh, S. Ramesh, Enhanced electrochemical performance of cobalt oxide nanocube intercalated reduced graphene oxide for supercapacitor application, *RSC Adv.* 6 (2016) 34894–34902, <https://doi.org/10.1039/c6ra00160b>.
- [14] D. Wang, Q. Wang, T. Wang, Morphology-controllable synthesis of cobalt oxalates and their conversion to mesoporous Co₃O₄ nanostructures for application in supercapacitors, *Inorg. Chem.* 50 (2011) 6482–6492, <https://doi.org/10.1021/ic200309t>.
- [15] Y. Yang, C. Yang, K. Tao, Q. Ma, L. Han, Construction of S-doped ZnCo₂O₄ microspindles with enhanced electrochemical performance for supercapacitors, *Vacuum* 181 (2020), <https://doi.org/10.1016/j.vacuum.2020.109740>.
- [16] Y. Li, W. Li, C. Yang, K. Tao, Q. Ma, L. Han, Engineering coordination polymer-derived one-dimensional porous S-doped Co₃O₄ nanorods with rich oxygen vacancies as high-performance electrode materials for hybrid supercapacitors, *Dalton Trans.* 49 (2020) 10421–10430, <https://doi.org/10.1039/d0dt02029j>.
- [17] Y.E. Abu Eldahab, N.H. Saad, A. Zekry, Enhancing the design of battery charging controllers for photovoltaic systems, *Renew. Sustain. Energy Rev.* 58 (2016) 646–655, <https://doi.org/10.1016/j.rser.2015.12.061>.
- [18] Y.E. Abueldeh, N. Saad, A. Abdelnaby Zekry, Enhancing the energy utilization of hybrid renewable energy systems fast charging for electrical vehicle view project, 2020, <https://www.researchgate.net/publication/347628720>.
- [19] M. Khalid, A review on the selected applications of battery-supercapacitor hybrid energy storage systems for microgrids, 2019, [10.3390/en12234559](https://doi.org/10.3390/en12234559).
- [20] J. Jiang, W. Shi, S. Song, Q. Hao, W. Fan, X. Xia, X. Zhang, Q. Wang, C. Liu, D. Yan, Solvothermal synthesis and electrochemical performance in super-capacitors of Co₃O₄/C flower-like nanostructures, *J. Power Sources* 248 (2014) 1281–1289, <https://doi.org/10.1016/j.jpowsour.2013.10.046>.
- [21] S.W. Hasan, Z. Taha, Q. Meng, J. Shen, T. Lyu, J. Zhu, C. Li, Z.Q. Tian, P.K. Shen, Interstitial nanoclusters within graphene sheets for highly conductive, strong and electrochemically active fiber-shaped supercapacitors, *Appl. Mater. Today* 20 (2020), 100768, <https://doi.org/10.1016/j.apmt.2020.100768>.
- [22] S. Wang, P. Ju, Z. Zhu, C. Zhao, Co₃O₄/RGO/Co₃O₄ pseudocomposite grown: *in situ* on a Co foil for high-performance supercapacitors, *RSC Adv.* 6 (2016) 99640–99647, <https://doi.org/10.1039/c6ra17543k>.
- [23] H. Peçenek, S. Yetiman, F.K. Dokan, M.S. Onses, E. Yılmaz, E. Sahmetlioglu, Effects of carbon nanomaterials and MXene addition on the performance of nitrogen doped MnO₂ based supercapacitors, *Ceram. Int.* (2021), 131932, <https://doi.org/10.1016/j.ceramint.2021.11.285>.
- [24] C. Yuan, L. Yang, L. Hou, L. Shen, F. Zhang, D. Li, X. Zhang, Large-scale Co₃O₄ nanoparticles growing on nickel sheets via a one-step strategy and their ultra-highly reversible redox reaction toward supercapacitors, *J. Mater. Chem.* 21 (2011) 18183–18185, <https://doi.org/10.1039/c1jm14173b>.
- [25] X.Y. Liu, Y.Q. Gao, G.W. Yang, A flexible, transparent and super-long-life supercapacitor based on ultrafine Co₃O₄ nanocrystal electrodes, *Nanoscale* 8 (2016) 4227–4235, <https://doi.org/10.1039/c5nr09145d>.
- [26] I. Rabani, R. Zafar, K. Subalakshmi, H.S. Kim, C. Bathula, Y.S. Seo, A facile mechanochemical preparation of Co₃O₄/g-C₃N₄ for application in supercapacitors and degradation of pollutants in water, *J. Hazard. Mater.* 407 (2021), <https://doi.org/10.1016/j.jhazmat.2020.124360>.
- [27] A. Brandt, P. Isken, A. Lex-Balducci, A. Balducci, Adiponitrile-based electrochemical double layer capacitor, *J. Power Sources* 204 (2012) 213–219, <https://doi.org/10.1016/j.jpowsour.2011.12.025>.
- [28] G. Gautham Prasad, N. Shetty, S. Thakur, Rakshitha, K.B. Bommegowda, Supercapacitor technology and its applications: a review, *IOP Conf. Ser. Mater. Sci. Eng.* 561 (2019), <https://doi.org/10.1088/1757-899X/561/1/012105>.
- [29] Q. Ke, J. Wang, Graphene-based materials for supercapacitor electrodes – a review, *J. Materomics* 2 (2016) 37–54, <https://doi.org/10.1016/j.jmat.2016.01.001>.
- [30] H. Wu, D. He, Y. Wang, Facile one-step process synthesized reduced graphene oxide/Mn₃O₄ nanocomposite for a symmetric supercapacitor, *Mater. Lett.* 268 (2020), 127613, <https://doi.org/10.1016/j.matlet.2020.127613>.
- [31] Z. Bo, H. Shuai, S. Mao, H. Yang, J. Qian, J. Chen, J. Yan, K. Cen, Green preparation of reduced graphene oxide for sensing and energy storage applications, *Sci. Rep.* 4 (2014) 1–8, <https://doi.org/10.1038/srep04684>.
- [32] N.A. Devi, S. Nongthombam, S. Sinha, R. Bhujel, S. Rai, W.I. Singh, P. Dasgupta, B. P. Swain, Investigation of chemical bonding and supercapacitive properties of Fe₃O₄-rGO nanocomposites for supercapacitor applications, *Diamond Relat. Mater.* 104 (2020), 107756, <https://doi.org/10.1016/j.diamond.2020.107756>.
- [33] X. Wang, L. Zhi, K. Mu, Transparent, conductive graphene electrodes for dye-sensitized solar cells, *Nano Lett.* 8 (1) (2008) 323–327, <https://doi.org/10.1021/nl072838r>.
- [34] M. Qorbani, T.C. Chou, Y.H. Lee, S. Samireddi, N. Naseri, A. Ganguly, A. Esfandiari, C.H. Wang, L.C. Chen, K.H. Chen, A.Z. Moshfegh, Multi-porous Co₃O₄ nanoflakes @ sponge-like few-layer partially reduced graphene oxide hybrids: towards highly stable asymmetric supercapacitors, *J. Mater. Chem. A* 5 (2017) 12569–12577, <https://doi.org/10.1039/c7ta00694b>.
- [35] C. Zhang, C. Lei, C. Cen, S. Tang, M. Deng, Y. Li, Y. Du, Interface polarization matters: enhancing supercapacitor performance of spinel NiCo₂O₄ nanowires by reduced graphene oxide coating, *Electrochim. Acta* 260 (2018) 814–822, <https://doi.org/10.1016/j.electacta.2017.12.044>.
- [36] M. Naushad, T. Ahamad, M. Ubaidullah, J. Ahmed, A.A. Ghafar, K.M. Al-Sheetan, P. Arunachalam, Nitrogen-doped carbon quantum dots (N-CQDs)/Co₃O₄ nanocomposite for high performance supercapacitor, *J. King Saud Univ. Sci.* 33 (2021), 101252, <https://doi.org/10.1016/j.jksus.2020.101252>.
- [37] S. Sahoo, A.K. Satpati, P.K. Sahoo, P.D. Naik, Incorporation of carbon quantum dots for improvement of supercapacitor performance of nickel sulfide, *ACS Omega* 3 (2018) 17936–17946, <https://doi.org/10.1021/acsomega.8b01238>.
- [38] Y. Zhu, X. Ji, C. Pan, Q. Sun, W. Song, L. Fang, Q. Chen, C.E. Banks, A carbon quantum dot decorated RuO₂ network: outstanding supercapacitances under ultrafast charge and discharge, *Energy Environ. Sci.* 6 (2013) 3665–3675, <https://doi.org/10.1039/c3ee41776j>.
- [39] F.A. Permatasari, M.A. Irham, S.Z. Bisri, F. Iskandar, Carbon-based quantum dots for supercapacitors: recent advances and future challenges, *Nanomaterials* 11 (2021) 1–34, <https://doi.org/10.3390/nano11010091>.

- [40] C.C. Chang, T.A. Geleta, T. Imae, Effect of carbon dots on supercapacitor performance of carbon nanohorn/conducting polymer composites, *Bull. Chem. Soc. Jpn.* 94 (2021) 454–462, <https://doi.org/10.1246/BCSJ.20200269>.
- [41] I. Bilecka, A. Hintennach, I. Djerdj, P. Novák, M. Niederberger, Efficient microwave-assisted synthesis of LiFePO_4 mesocrystals with high cycling stability, *J. Mater. Chem.* 19 (2009) 5125–5128, <https://doi.org/10.1039/b909545d>.
- [42] S.H. Jung, T. Jin, Y.K. Hwang, J.S. Chang, Microwave effect in the fast synthesis of microporous materials: which stage between nucleation and crystal growth is accelerated by microwave irradiation? *Chem. Eur. J.* 13 (2007) 4410–4417, <https://doi.org/10.1002/chem.200700098>.
- [43] S. Park, S.J. Park, S. Kim, Fabrication and capacitance of Co_3O_4 -graphene nanocomposites electrode prepared by pulse microwave-assisted reduction methods, *Bull. Korean Chem. Soc.* 33 (2012) 4247–4250, <https://doi.org/10.5012/bkcs.2012.33.12.4247>.
- [44] L. Cui, J. Li, X.G. Zhang, Preparation and properties of Co_3O_4 nanorods as supercapacitor material, *J. Appl. Electrochem.* 39 (2009) 1871–1876, <https://doi.org/10.1007/s10800-009-9891-5>.
- [45] S. Vijayakumar, A. Kiruthika Ponnalagi, S. Nagamuthu, G. Muralidharan, Microwave assisted synthesis of Co_3O_4 nanoparticles for high-performance supercapacitors, *Electrochim. Acta* 106 (2013) 500–505, <https://doi.org/10.1016/j.electacta.2013.05.121>.
- [46] Y. Zhai, Y. Wang, D. Li, D. Zhou, P. Jing, D. Shen, S. Qu, Red carbon dots-based phosphors for white light-emitting diodes with color rendering index of 92, *J. Colloid Interface Sci.* 528 (2018) 281–288, <https://doi.org/10.1016/j.jcis.2018.05.101>.
- [47] J. Xu, S. Gai, F. He, N. Niu, P. Gao, Y. Chen, P. Yang, A sandwich-type three-dimensional layered double hydroxide nanosheet array/graphene composite: fabrication and high supercapacitor performance, *J. Mater. Chem. A* 2 (2014) 1022–1031, <https://doi.org/10.1039/c3ta14048b>.
- [48] Z. Chen, Y. Gao, X. Chen, B. Xing, C. Zhang, S. Wang, T. Liu, Y. Liu, Z. Zhang, Nanoarchitected Co_3O_4 /reduced graphene oxide as anode material for lithium-ion batteries with enhanced cycling stability, *Ionics* 25 (2019) 5779–5786, <https://doi.org/10.1007/s11581-019-03134-x>.
- [49] J. Xu, Y. Xue, J. Cao, G. Wang, Y. Li, W. Wang, Z. Chen, Carbon quantum dots/nickel oxide (CQDs/NiO) nanorods with high capacitance for supercapacitors, *RSC Adv.* 6 (2016) 5541–5546, <https://doi.org/10.1039/c5ra24192h>.
- [50] W. Wang, Y. Yuan, J. Yang, L. Meng, H. Tang, Y. Zeng, Z.Z. Ye, J. Lu, Hierarchical core-shell Co_3O_4 /graphene hybrid fibers: potential electrodes for supercapacitors, *J. Mater. Sci.* 53 (2018) 6116–6123, <https://doi.org/10.1007/s10853-017-1971-z>.
- [51] M. Naushad, T. Ahamad, M. Ubaidullah, J. Ahmed, A.A. Ghafar, K.M. Al-Sheetan, P. Arunachalam, Nitrogen-doped carbon quantum dots (N-CQDs)/ Co_3O_4 nanocomposite for high performance supercapacitor, *J. King Saud Univ. Sci.* 33 (2021), 101252, <https://doi.org/10.1016/j.jksus.2020.101252>.
- [52] E. Turaç, M. Ak, E. Sahmetlioglu, M.K. Sener, M.A. Kaya, Synthesis and characterization of poly{2-[3-(1H-pyrrol-2-yl)phenyl]-1H-pyrrole} and its copolymer with EDOT, *Russ. J. Gen. Chem.* 81 (2011) 2510–2516, <https://doi.org/10.1134/S1070363211120164>.
- [53] C. Xiang, M. Li, M. Zhi, A. Manivannan, A Reduced Graphene Oxide/ Co_3O_4 Composite For Supercapacitor Electrode, Elsevier, 2013.
- [54] M.O. Yanik, E.A. Yigit, Y.E. Akansu, E. Sahmetlioglu, Magnetic conductive polymer-graphene nanocomposites based supercapacitors for energy storage, *Energy* 138 (2017) 883–889, <https://doi.org/10.1016/j.energy.2017.07.022>.
- [55] A. Kumbul, E. Gokturk, E. Turac, E. Sahmetlioglu, Enzymatic oxidative polymerization of para-imine functionalized phenol catalyzed by horseradish peroxidase, *Polym. Adv. Technol.* 26 (9) (2015) 1123–1129, <https://doi.org/10.1002/pat.3544>.
- [56] E. Turac, E. Sahmetlioglu, L. Toppare, H. Yuruk, Synthesis, characterization and optoelectrochemical properties of poly(2,5-di(thiophen-2-yl)-1-(4-(thiophen-3-yl)phenyl)-1h-pyrrole-co-edot), *Des. Monomers Polym.* 13 (2010) 261–275, <https://doi.org/10.1163/138577210X12634696333677>.
- [57] A. Kumbul, E. Gokturk, E. Sahmetlioglu, Synthesis, characterization, thermal stability and electrochemical properties of ortho-imine-functionalized oligophenol via enzymatic oxidative polycondensation, *J. Polym. Res.* 23 (2016) 1–11, <https://doi.org/10.1007/s10965-016-0953-1>.
- [58] Q. Liao, N. Li, S. Jin, G. Yang, C. Wang, All-solid-state symmetric supercapacitor based on Co_3O_4 nanoparticles on vertically aligned graphene, *ACS Nano* 9 (2015) 5310–5317, <https://doi.org/10.1021/acsnano.5b00821>.
- [59] S.K. Meher, G.R. Rao, Ultralayered Co_3O_4 for high-performance supercapacitor applications, *J. Phys. Chem. C* 115 (2011) 15646–15654, <https://doi.org/10.1021/jp201200e>.
- [60] M.S. Wu, H.H. Hsieh, Nickel oxide/hydroxide nanoplatelets synthesized by chemical precipitation for electrochemical capacitors, *Electrochim. Acta* 53 (2008) 3427–3435, <https://doi.org/10.1016/j.electacta.2007.12.005>.
- [61] D. Guo, X. Song, F. Li, L. Tan, H. Ma, L. Zhang, Y. Zhao, Oriented synthesis of Co_3O_4 core-shell microspheres for high-performance asymmetric supercapacitor, *Colloids Surf. A* 546 (2018) 1–8, <https://doi.org/10.1016/j.colsurfa.2018.02.072>.
- [62] X. Hu, L. Wei, R. Chen, Q. Wu, J. Li, Reviews and perspectives of Co_3O_4 -based nanomaterials for supercapacitor application, *ChemistrySelect* 5 (2020) 5268–5288, <https://doi.org/10.1002/slct.201904485>.
- [63] K. Ding, X. Zhang, P. Yang, X. Cheng, A precursor-derived morphology-controlled synthesis method for mesoporous Co_3O_4 nanostructures towards supercapacitor application, *CrystEngComm* 18 (2016) 8253–8261, <https://doi.org/10.1039/c6ce01921h>.
- [64] Y. Wang, T. Zhou, K. Jiang, P. Da, Z. Peng, J. Tang, B. Kong, W.B. Cai, Z. Yang, G. Zheng, Reduced mesoporous Co_3O_4 nanowires as efficient water oxidation electrocatalysts and supercapacitor electrodes, *Wiley Online Libr.* 4 (2014), <https://doi.org/10.1002/aenm.201400696>.
- [65] C. Wang, Y. Meng, L. Wang, F. Zhu, Y. Zhang, One step hydrothermal synthesis of flower-shaped Co_3O_4 nanorods on nickel foam as supercapacitor materials and their excellent electrochemical performance, *Chem. Res. Chin. Univ.* 34 (2018) 882–886, <https://doi.org/10.1007/s40242-018-8073-6>.
- [66] W. Jia, J. Li, Z. Lu, Y. Juan, Y. Jiang, Synthesis of honeycomb-like Co_3O_4 nanosheets with excellent supercapacitive performance by morphological controlling derived from the alkaline source ratio, *Materials* 11 (2018), <https://doi.org/10.3390/ma11091560>.
- [67] X. Zhou, X. Shen, Z. Xia, Z. Zhang, J. Li, Y. Ma, Y. Qu, Hollow fluffy Co_3O_4 cages as efficient electroactive materials for supercapacitors and oxygen evolution reaction, *ACS Appl. Mater. Interfaces* 7 (2015) 20322–20331, <https://doi.org/10.1021/acsami.5b05989>.
- [68] Z. Xiao, L. Fan, B. Xu, S. Zhang, W. Kang, Z. Kang, H. Lin, X. Liu, S. Zhang, D. Sun, Green fabrication of ultrathin Co_3O_4 nanosheets from metal-organic framework for robust high-rate supercapacitors, *ACS Appl. Mater. Interfaces* 9 (2017) 41827–41836, <https://doi.org/10.1021/acsami.7b10309>.
- [69] C. Xiang, M. Li, M. Zhi, A. Manivannan, N. Wu, A reduced graphene oxide/ Co_3O_4 composite for supercapacitor electrode, *J. Power Sources* 226 (2013) 65–70, <https://doi.org/10.1016/j.jpowsour.2012.10.064>.
- [70] E. Jokar, A. Irajizad, S. Shahrokhian, Growth control of cobalt oxide nanoparticles on reduced graphene oxide for enhancement of electrochemical capacitance, *Int. J. Hydrog. Energy* 39 (2014) 21068–21075, <https://doi.org/10.1016/j.ijhydene.2014.10.061>.
- [71] F. Du, X. Zuo, Q. Yang, G. Li, Z. Ding, M. Wu, Y. Ma, S. Jin, K. Zhu, Facile hydrothermal reduction synthesis of porous Co_3O_4 nanosheets@RGO nanocomposite and applied as a supercapacitor electrode with enhanced specific capacitance and excellent cycle stability, *Electrochim. Acta* 222 (2016) 976–982, <https://doi.org/10.1016/j.electacta.2016.11.065>.
- [72] X.M. Yue, Z.J. Liu, C.C. Xiao, M. Ye, Z.P. Ge, C. Peng, Z.Y. Gu, J.S. Zhu, S.Q. Zhang, Synthesis of Co_3O_4 /reduced graphene oxide by one step-hydrothermal and calcination method for high-performance supercapacitors, *Ionics* 27 (2021) 339–349, <https://doi.org/10.1007/s11581-020-03797-x>.
- [73] W.L. Jia, J. Li, Z.J. Lu, Y.F. Juan, Y.Q. Jiang, Synthesis of porous Co_3O_4 /Reduced graphene oxide by a two-step method for supercapacitors with excellent electrochemical performance, *J. Alloy. Compd.* 815 (2020), <https://doi.org/10.1016/j.jallcom.2019.152373>.