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C Indira Priyadharsini, P M Anbarasan, V Aroulmoji, V Siva. Synthesize, Characterization and Electrochemical Investigations of Cobalt Oxide Nanoparticles to Supercapacitor Application. AEGAEUM JOURNAL, 2020. <hal-03093575>

HAL Id: hal-03093575

<https://hal.science/hal-03093575v1>

Submitted on 15 Jan 2021

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Synthesize, Characterization and Electrochemical Investigations of Cobalt Oxide Nanoparticles to Supercapacitor Application

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ABSTRACT

This article describes the synthesis and characterization of Cobalt Oxide (Co₃O₄) nanoparticles prepared via the hydrothermal method to examine the behavior of supercapacitor performance. The phase structure and purity of the synthesized nanoparticles were confirmed by XRD and the crystallite size was calculated as 13.76 nm using Scherrer's formula. The structure and morphology of the synthesized samples were characterized by FT-IR, X-ray diffraction (XRD), transmission electron microscopy (TEM), Field Emission Scanning Electron Microscopy (FE-SEM). The electrochemical performance was analyzed using galvanostatic charge and discharge studies (GCD), Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The FTIR and XRD results indicated that the synthesized samples were highly pure well-crystallized cubic phase. FE-SEM result reveals the synthesized nanoparticles have micro-nano rock-like structure and the SAED pattern confirms the nature of polycrystalline. The electrochemical performance has been examined through CV, GCD, and impedance analysis. The greatest specific capacitance (SCs) value is achieved to be 698.4 F g⁻¹ on 1mA/cm² current density which maintains good cyclic stability after 500 cycles.

Keywords: Hydrothermal, Specific Capacitance, Cyclic stability, HRTEM, SAED.

1. INTRODUCTION

Globally, the steady increase of 5% energy per year has gained its attention in the need of most urgent alternative sources of clean and green renewable energy and has become a top

priority challenge of both developed and also the developing countries. In the current circumstances, the most essential thing is to develop energy storage devices to replace the highly utilized fossil fuels for safer and greener energy production. Additionally, it is important to generate continuous power supply for electronic equipment, portable devices, and electricity for the development of high-performance energy storage devices [1]. In this situation, supercapacitors are of great interest in the scientific community because of their high power density, exclusive charge storage mechanism, fast recharge capacity, safety, and also long life cycle duration [2,3]. Depending upon the process of charge storage, the supercapacitors are separated by two categories, one is EDLCs and the other is pseudocapacitors (faradaic). Nowadays, researchers are actively interested in developing the pseudocapacitive materials, for instance, the use of various metal oxides and the accomplishing polymers to gain high particular capacitance for the high energy supercapacitors. Amongst the various metal oxides, transition metal oxides that contain distinctive characteristics of Faradic capacitor, Co_3O_4 is often utilized oxides due to its significance for a multiplicity of scientific technologies and rich natural resources of Co element. Moreover, Cobalt oxide behaves like a semiconductor (p-type) with a regular spinel structure. The Cobalt oxide has been prepared through many simple steps, low cost, and environment-friendly means, and may be used in many different functional applications, including sensors [4], supercapacitors [5], and batteries [6]. As an electrode substance of supercapacitors, Co_3O_4 has been prepared by various techniques namely hydrothermal, a microwave method, solvothermal, a sol-gel method, and chemical bath deposition [7–9]. In this, the hydrothermal method is green and less expensive. The preparation of Co_3O_4 nanoparticles in the course of the hydrothermal method normally requires reducing agents. The morphology and porous substances have a lot of impact on capacitance and charge storage adequacy. The integration and advancement of all parts of supercapacitor including electrode materials, electrolyte, current collector, and separator are important to the general performance of the supercapacitor [10]. Many researchers studied and reported that this material has been used as the best electrode due to its high SCs and large operating potential window. In particular, Kalyanjyoti Deori et al [11] successfully prepared Co_3O_4 hexagonal platelet particles which showed a capacitance value of 476 F g^{-1} measured at 0.5 Ag^{-1} of current density. Gao et al.[5] synthesized aligned Co_3O_4 nanowire arrays by hydrothermal process and achieved the SCs of $\sim 746 \text{ Fg}^{-1}$. Gwang-Su Jang et al [12] synthesized cobalt oxide (Co_3O_4) nanorods through the hydrothermal method achieved the SCs of $\sim 226.3 \text{ Fg}^{-1}$ on the scan rate of $\sim 10 \text{ mV s}^{-1}$. At 0.5 Ag^{-1} of current density, the high SCs of 330 Fg^{-1} were obtained by Jiang et al [13] through cobalt oxide nanostructures that were synthesized through the solvothermal method. Zhen et al [14] prepared

Co₃O₄ nanoparticles based electrode for pseudo-supercapacitor which shows maximum SCs of ~304 Fg⁻¹.

Realizing the importance of Co₃O₄ nanomaterials, the present work was carried out on the synthesis of Co₃O₄ nanoparticles (NPs) through the hydrothermal method. The synthesized nanoparticles were applied as an electrode material to fabricate the high-performance pseudo supercapacitors. The crystalline and the structural characterizations exhibit a good crystal quality of the synthesized Co₃O₄ NPs. The fabricated pseudo-supercapacitor based on Co₃O₄ NPs-electrode shows a high capacitance of ~898.4 Fg⁻¹.

2. EXPERIMENTAL

2.1 Preparation of the Co₃O₄

The Co₃O₄ NPs were synthesized via a simple hydrothermal route. The required stoichiometric proportion of Co (NO₃).6H₂O and CO (NH₂)₂ was mixed in 60 ml double distilled water. After magnetic stirring, the liquid was loaded into a 60 ml autoclave sealed and kept in hot air oven maintained for 12 hrs at the temperature of 120 °C. Furthermore, the product is washed quite a lot of times by distilled water, and heated at 60 °C overnight. The final sample is further heated upto 400 °C for 4 hrs.

2.2 Characterization of the Co₃O₄

The structure and also phase of Co₃O₄ nanoparticles were examined by X-ray diffraction (XRD) (Bruker AXS D8 Advance). The average crystallites size calculated using Debye Scherrer equation i.e., $[d = 0.9\lambda / \beta \cos \theta]$, where β according to the full width at half maximum of the diffraction peak (FWHM), $K = 0.89$, θ is the Bragg diffraction angle and λ is the X-ray wavelength corresponding to the Cu K α radiation. The morphology of the synthesized samples was viewed by Field Emission Scanning Electron Microscopy (FESEM) (CAREL ZEISS) analysis. The High Resolution Transmission Electron Microscopy (HRTEM) images with (Selected Area Diffraction Pattern (SAED) patterns were recorded using a Jeol/JEM 2100 Transmission electron microscope. The electrochemical properties of the Co₃O₄ were taken out (electrochemical workstation of CHI660E) by Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD) and electrochemical impedance spectroscopy (EIS) tests which were conducted using three-electrode systems in 3M KOH electrolyte solution at room temperature.

2.3 Electrode preparation and Electrochemical Performance Measurement

Electrochemical output tests were worked out by a tri-electrode device on an electrochemical workstation. The Co₃O₄ layered on nickel foam was used directly in 3 mol / L

KOH solution as a working electrode. The working electrode was manufactured by the combination of active material, activated carbon, and PVDF in NMP solvent in the respectively mixed ratio (80:10:10) until homogenous slurry was achieved. Then, the final slurry was covered on nickel foam and dried in an oven for 10 h at 80°C. The Ag/AgCl and platinum wire electrode were applied as a reference and counter electrodes respectively. CV was taken out in the potential window from -0.1 to 0.5V at various scan rates (10 mV/s, 20 mV/s, 25 mV/s, 50 mV/s, and 75 mV/s). GCD measurements were carried out with the potential range from -0.1 to 0.5V at specific current densities ranging from 1mA cm⁻² to 10 mA cm⁻². The Electrochemical Impedance Spectroscopy test was performed within the frequency rate level from 1Hz to 100 kHz.

3. RESULT AND DISCUSSIONS

3.1 The Structure of Co₃O₄.

Figure 1(a) reveals the XRD diffraction pattern of prepared Co₃O₄. All the mentioned peaks can be referred to pure cubic phase structure of Co₃O₄ specimens (JCPDS number 43-1003) no other peaks were identified in the powder XRD pattern of Co₃O₄. The peaks at 19°, 31.2°, 36.8°, 38.5°, 44.8°, 55.6°, 59.3°, and 65.2° attributed to (111), (220), (311), (222), (400), (422), (511) & (440) indicating the presence of crystalline Co₃O₄ [14]. The crystallites size of synthesized Co₃O₄ was calculated by Scherrer formula ($d = K\lambda/\beta \cos\theta$), for the corresponding main diffraction peak, where K is the constant value of 0.9, λ is the wavelength related of Cu K α radiation, β is the FWHM of the maximum diffraction peak and θ is the Bragg angles. The crystallite size of the Co₃O₄ nanoparticles calculated is about 13.76 nm for the Co₃O₄. The lattice parameter value of Co₃O₄ is calculated as $a = 7.959$ and was comparable to JCPDS ($a = 8.084$). There is a small negligible value difference with the original value depending upon the material's crystalline nature and also the ionic radius.

3.2 FT-IR spectral studies of Co₃O₄

The FT-IR spectra results of pure Co₃O₄ nanoparticles ranging from 4000 to 400 cm⁻¹, is shown in Figure 1(b). There is no noticeable absorption peaks related to symmetric vibration of -OH groups and O-H vibration from H₂O. However, the Co₃O₄ nanoparticles have a peak on 667 cm⁻¹ and 574 cm⁻¹ which is assigned to the Co-O band of stretching vibration mode [15,16]. This confirms the strong structure of pure Co₃O₄ nanoparticles. The weak bands that appear at 1070 cm⁻¹ are attributed to stretching vibration $\nu(\text{C}=\text{O})$.

3.3 Morphological studies of Co₃O₄

Co₃O₄ nanoparticles have huge authority on electrochemical properties. The FESEM image of Co₃O₄ nanoparticles with various scanning range and magnifications is shown in Figure

2. From that, it can be analyzed that Co_3O_4 nanoparticles have quasi cubic shapes with a broad distribution of the particle size. And also it exhibits nano rocks like structure. The HRTEM analysis of the Co_3O_4 nanoparticles with various magnifications shown in Figure 3 (a-d) and further confirms the morphology and the analogous SAED pattern reveals the polycrystalline character of Co_3O_4 nanoparticles through it having more bright spots. The SAED pattern (inset Figure 3d) represents the (111) and (311), planes of the cubic structure of Co_3O_4 nanoparticles that is an accurate agreement with the XRD results. Further, HRTEM images (Figure 3d) also make known that the rocks are aggregated nanoparticles that are well-interconnected to form stable nano rocks. The interplanar spacing of Co_3O_4 nano rocks is found to be 0.27 nm for Co_3O_4 which suited well with the plane of (220).

3.4 Supercapacitor performance studies

Cyclic Voltammetry was firstly tested by the electrode system of three, where Ag as the reference and the counter-electrode as platinum. Figure 4(a) reveals the CV curve of Co_3O_4 nanoparticles at the various scan rates of 10,20,25,50 and 75 mV/s in a potential ranges from -0.1-0.50 V. From the CV curve, very clear and sharp redox peaks were appeared and it shows the nature of pseudocapacitance. Because redox reactions are mainly dependent on the insertion-disinsertion of protons as of the electrolyte at decreasing scan rates, the distribution of ions from the electrolyte knows how to enter into nearly all the effective holes of the electrode [2]. The shape of curves has diverted from an ultimate rectangular shape that indicates the pseudocapacitive action of cobalt oxides [17]. The faradaic reactions can be explained by the below equations [18]

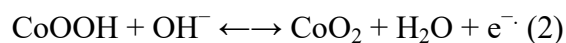
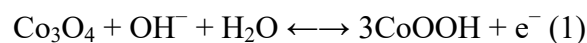


Figure 4(b) depicts the GCD behavior of the three-electrode cell of Co_3O_4 on various current densities. Its shape indicates the pseudocapacitive action of Co_3O_4 which is also shown by cyclic voltammetry. For a range of current densities from 1 mA cm^{-2} to 10 mA cm^{-2} , SCs of Co_3O_4 varied from 698.4 F g^{-1} to 269.69 F g^{-1} . Figure 4(c) implies that high specific capacitance value is achieved at low current density is because of quick charge transfer at the edge of the electrolyte and the electrode. Figure 4(d) shows the long time stability graph which investigated at current density 10 mA cm^{-2} . The inset Figure 4(d) shows the GCD cycles. It is clear that the specific capacitance steadily decreased from 269.69 F g^{-1} to 257 F g^{-1} even at 500 cycles.

Figure 5 demonstrates the Co_3O_4 electrode Electrochemical Impedance Spectroscopy. The ionic motion between the electrode and electrolyte surface was observed by EIS within the

frequency range 1Hz to 100 kHz through 5 mV of amplitude. Apparently, the Co_3O_4 electrode charging transfer resistance (R_{ct}) is very small, which indicates that effective electrochemical reaction sites are enough. Additionally, the Co_3O_4 electrode's diffusion resistance is lower, enabling the diffusion of ions in the redox reaction phase.

4. Conclusion

The Co_3O_4 nanoparticles prepared using hydrothermal process. Crystalline structure, phase, and purity of the material were analyzed through the XRD method, and also the average crystallites size was found to be 13.76nm. The results of SEM analysis show that Co_3O_4 particles are agglomerated and look like a nano rock. FTIR spectrum verified the existence of Co and O peak in the Co_3O_4 nanoparticles prepared. The electrochemical measurements suggested that Co_3O_4 nanoparticles coated in nickel foam as a substrate reveal a well specific capacitance of 698.4 F g^{-1} (1 mA cm^{-2}). The overall experimental results show that Co_3O_4 nanoparticles will hopefully be a potential electrode material for high-performance supercapacitors.

Acknowledgments

I would reveal my thank Sophisticated Test and Instrumentation Centre (STIC), Cochin for extending their instrumental technical support of the XRD facility and for recording HRTEM images.

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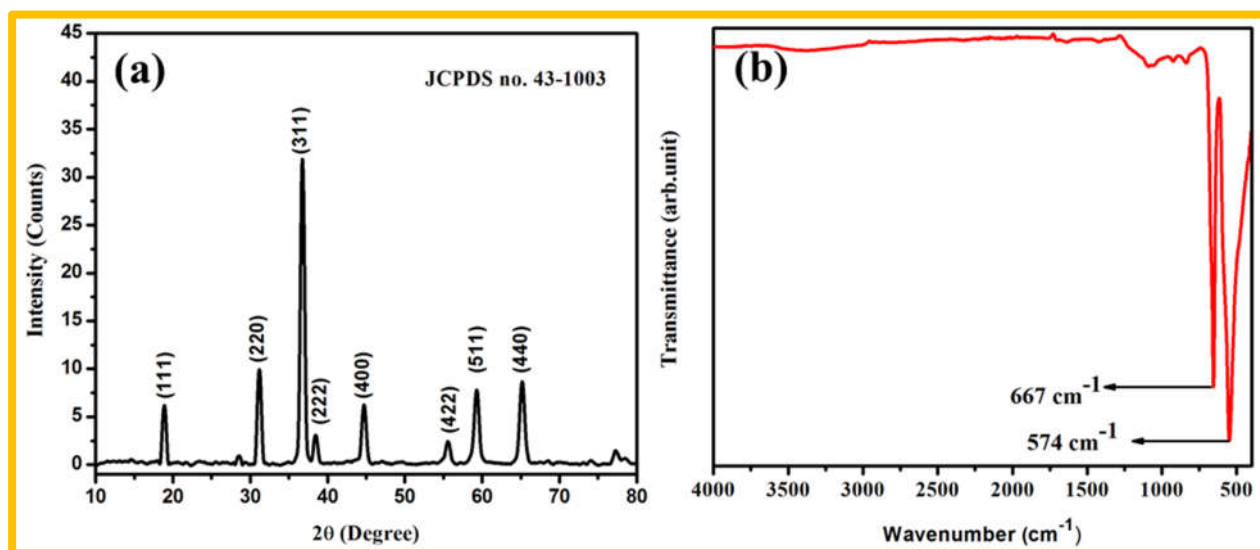


Figure 1(a). XRD pattern of Co_3O_4 nanoparticles (b) FTIR spectrum of Co_3O_4 nanoparticles

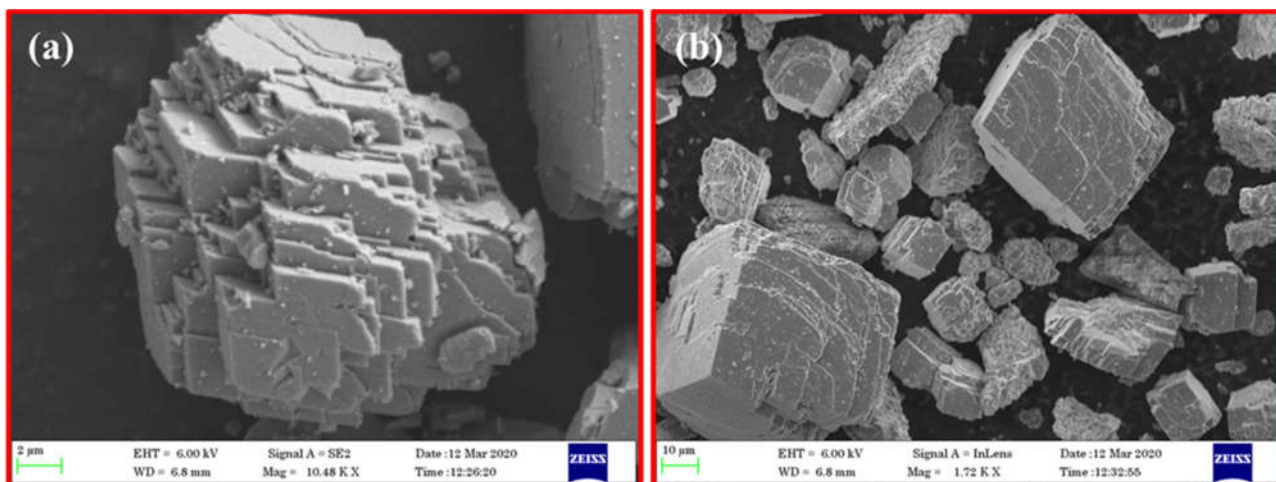


Figure 2 (a, b). SEM images of Co_3O_4 nanoparticles with various magnifications

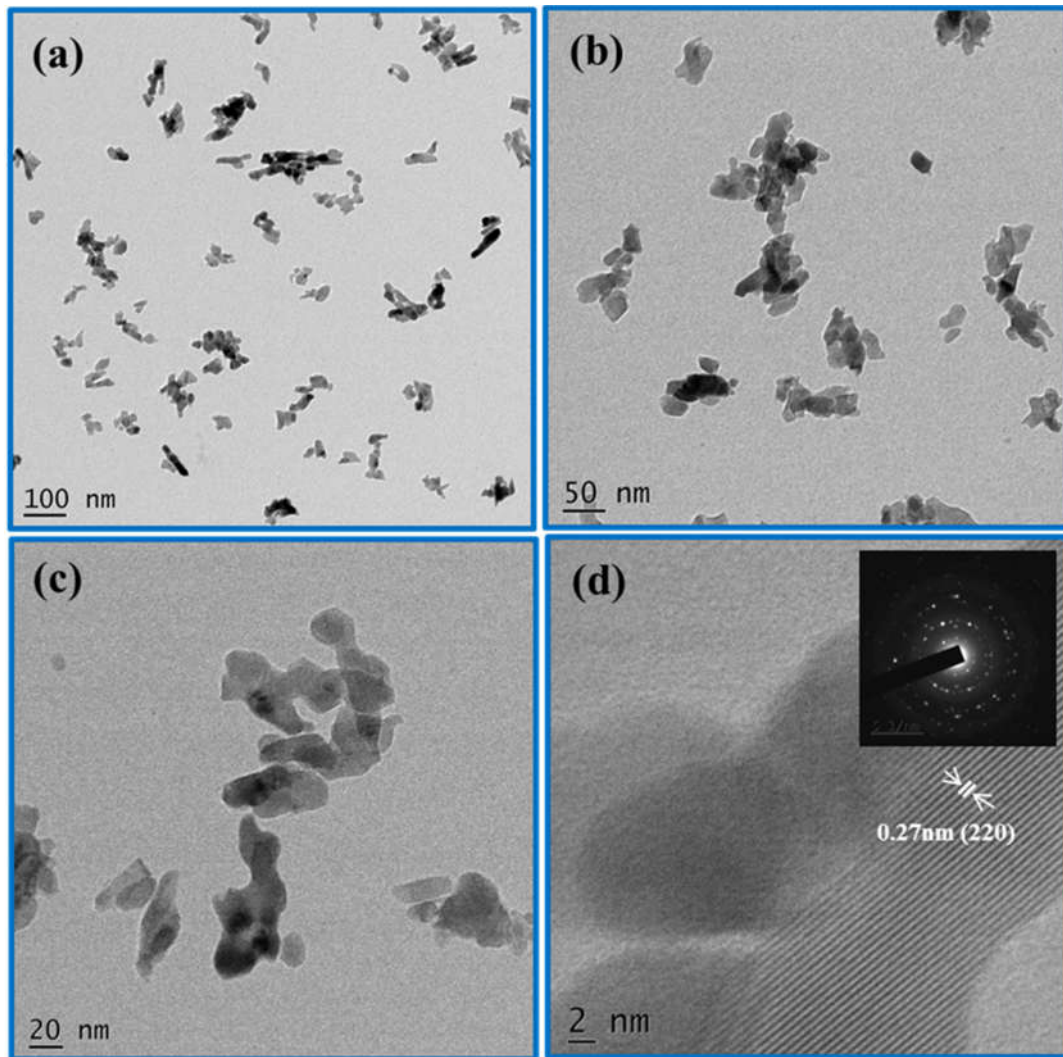


Figure 3 (a,-d). HRTEM images of Co_3O_4 nanoparticles with various magnifications

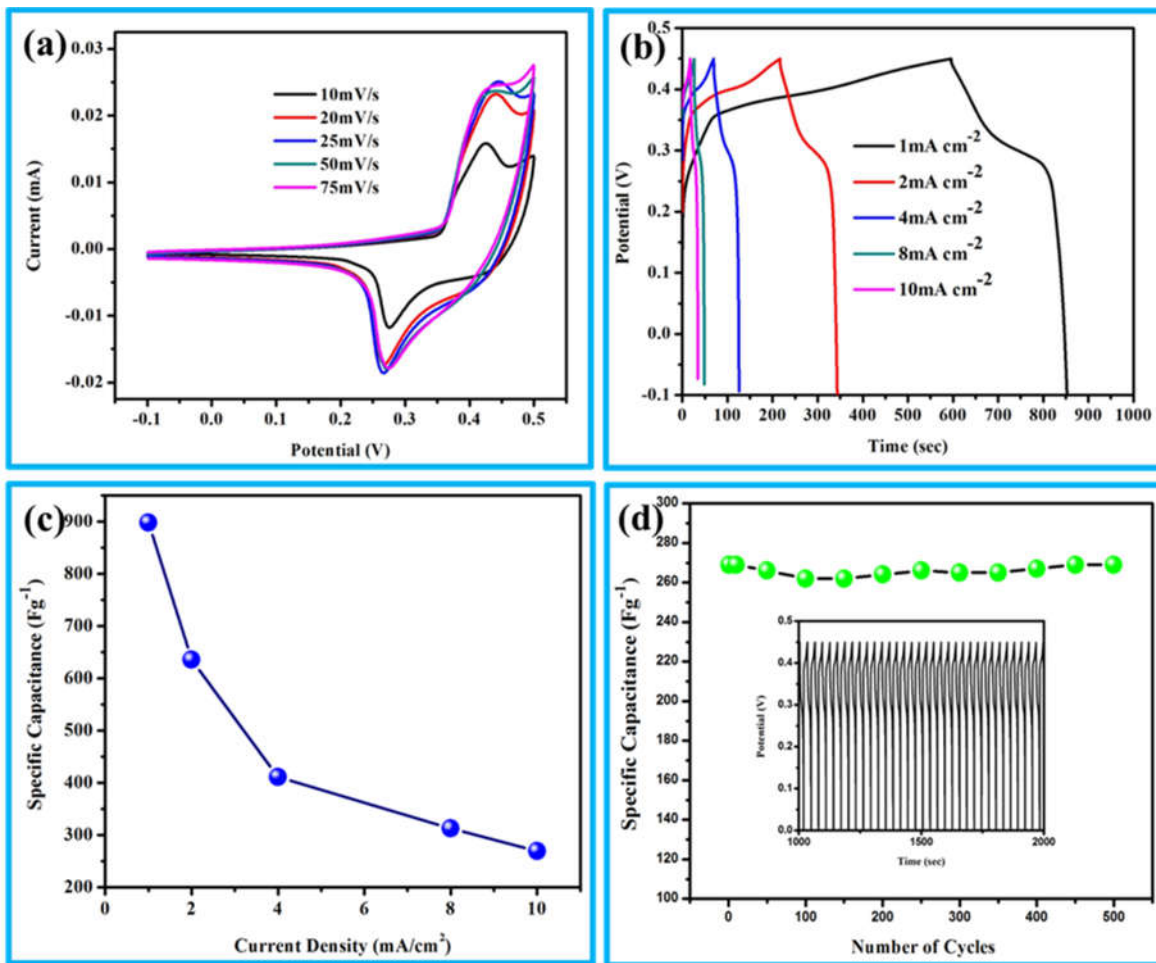


Figure 4 (a). Cyclic voltammogram of Co_3O_4 nanoparticles at different scan rates from 10 mV/s to 75 mV/s (b) GCD profile of Co_3O_4 nanoparticles at different current densities 1-10 mA cm⁻². (c) Variation of specific capacitance vs current density of Co_3O_4 nanoparticles (d) 500 cycle's specific capacitance of Co_3O_4 nanoparticles (current densities 10 mA cm⁻²).

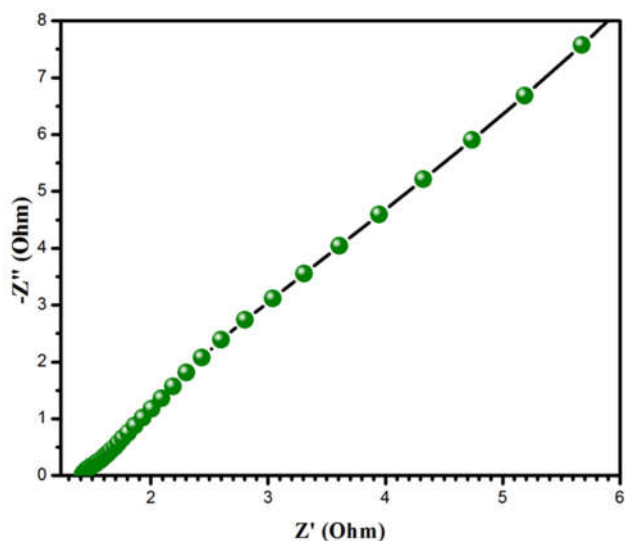


Figure 5. Electrochemical Impedance Spectrum (EIS) of Co_3O_4 nanoparticles.