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Synthesis and cyclic voltammetry of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids

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Abstract

The chemical co-precipitation route was opted for the synthesis of chromium ferrite (CrFe_2O_4) nanoparticles and the pristine multi-walled carbon nanotubes (MWCNTs) were used for the preparation of desired $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15,$ and 20 wt% nanohybrids using the ultra-sonication method. Toluene was used for the first time as dispersive medium for the preparation of these nanohybrids. The crystalline structure, morphology, vibrational modes, and electrochemical performance of these nanohybrids were characterized by using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry. The structural properties of pristine MWCNTs, CrFe_2O_4 nanoparticles, and $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids are evaluated by XRD and Raman spectroscopy. The SEM images presented the attachment of CrFe_2O_4 nanoparticles on the surface of MWCNTs. The specific capacitance was decreased with increasing number of cycles, while it was observed to be increased with increasing MWCNTs content. From EIS, the decrease in charge transfer resistance was observed with the increased loadings of MWCNTs, which showed the enhanced electrochemical behavior of these nanohybrids. Therefore, the significant improvement in electrochemical properties showed that these nanohybrids can be promising candidates for energy storage devices like lithium-ion (Li-ion) batteries.

1 Introduction

In recent times, researchers are focusing on the production of high-energy storage devices that got maximum power deliverance and bearability. The subsequent generations need maximum energy, high power, smart range, and ecologically friendly storage devices for various applications [1–4]. Li-ion batteries presently signify its importance in portable

electronics market as rechargeable batteries or large-scale electrical grids that require high power densities and higher energy [5–7]. The electrochemical performance of a material can be constrained with electrolyte, current collector, electrode material, and the separator [8]. Transition metal oxides (TMOs) bear high theoretical capacity in contrast to conventional graphite, resulting in great interest as storage devices [9, 10]. The iron-based materials have been widely used in various applications like catalyst medical, magnetic resonance imaging, and energy storage devices [11–17]. The diverse morphology of ferrites-based materials revealed high electrochemical properties [18]. Ferrite nanoparticles can be produced in sponge-like shapes by numerous routes like co-precipitation, sonochemical, hydrothermal, sol-gel, solvothermal method, and nanocasting [19–21]. Poor cyclic performance is the main challenge in using iron-based materials, which is the point of interest to be investigated. The pseudo behavior of charge storage for hydroxides, selenides, metal oxides, sulfides, and conductive polymers takes place due to fast reversible surface faradic reactions at electrolyte interface [22–25]. Diverse studies have been made to investigate the formation of composites along with conductive materials like MWCNTs, single-walled carbon nanotubes (SWCNTs), carbon nanoplatelets, reduced

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graphene, graphene oxide, and carbon nanofibers [26–33]. The Cr-based ferrite nanoparticles exhibit high theoretical capacity, eco-friendly, high abundance, large volume variation, and poor electronic conductivity [34–36]. The electrochemical performance of bare α - Fe_2O_3 nanoparticles was significantly improved with the addition of MWCNTs. The α - Fe_2O_3 /MWCNTs revealed high specific initial discharge capacity and preserved a stable discharge capacity with minimum capacity degradation [37]. The metal oxides are observed to have outstanding capacitance but low electrical conductivity and electrochemical stability that restrict their device applications [38]. The MWCNT-based NiFe_2O_4 nanohybrids were fabricated and high specific capacity, excellent rate capability, better cyclic performance by giving 97% columbic efficiency were found [39]. The tungsten (Ti)-decorated titania nanotubes, Au/ TiO_2 - WO_3 nanocomposites, Ti-based copper (Cu) nanotubes composites, and manganese- or cobalt-based TiO_2 nanocomposites were produced for the study of electrochemical properties [40, 41]. The MnFe_2O_4 nanoparticles showed remarkable specific capacitance at 5 mVs^{-1} and 25% retention was observed at 100 mVs^{-1} [42]. The MnFe_2O_4 /graphene electrode materials showed sphere-like morphology and have notable electrochemical stability and better specific capacitance [43]. The CuFe_2O_4 /rGO composites were synthesized using the thermo-chemical reaction method to examine the effects of rGOs on the structural, dielectric properties, and battery performance of CuFe_2O_4 nanoparticles. The CuFe_2O_4 /rGO composites showed remarkably enhanced electrochemical properties with the addition of rGOs [44]. The ZnFe_2O_4 nanoparticles got higher theoretical capacity, but slow Li-ions diffusion and poor electrical conductivity restrict the rate capabilities for fast charge/discharge [45, 46]. The carbon was proved to be an inactive substance to alleviate the active constituent. The porous carbon, graphene, and carbon nanotube-based composites with metal oxide nanoparticles dispersed in carbon matrix were investigated and it is an efficient approach to avoid aggregation of nanoparticles by chemical bonding [47–50]. In the present study, the CrFe_2O_4 /(MWCNTs)_x; x=0, 5, 10, 15, and 20 wt% nanohybrids were synthesized by ultra-sonication-assisted route. The CrFe_2O_4 nanoparticles and MWCNTs were dispersed for the first time using toluene, a dispersive medium, for these nanohybrids. The electrochemical response of these nanohybrids was estimated by cyclic voltammetry and electrochemical impedance spectroscopy at room temperature.

2 Experimental

2.1 Material synthesis

The chemical co-precipitation route was adopted for the synthesis of CrFe_2O_4 nanoparticles. For this, 0.1 molarity solution of chromium nitrate $\{\{\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}\}\}$ and 0.2

molarity solution of iron nitrate $\{\{\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}\}\}$ were used and they were homogeneously mixed by continuous stirring. The mixture was heated at 90°C and a solution of 0.3 molarity sodium hydroxide (NaOH), which was previously heated to 80°C , was added dropwise to the mixture and stirred for 50 min at 90°C . The solution was then cooled to room temperature and washed several times with double-distilled water to achieve pH 7. The resultant solution was dried at 100°C using microwave oven for 12 h followed by annealing at 500°C for 4 h to get spinel phase CrFe_2O_4 nanoparticles. The product was ground in mortar and pestle to eliminate agglomeration. For the preparation of CrFe_2O_4 /(MWCNTs)_x; x=0, 5, 10, 15, and 20 wt% nanohybrids, pre-acquired MWCNTs and CrFe_2O_4 nanoparticles were separately taken in 50 ml of toluene. For uniform dispersion, these were sonicated for 2 hrs at room temperature and then the CrFe_2O_4 nanoparticles were added into MWCNTs solutions. The mixture was again sonicated using ultra-bath sonicator for 6 hrs and, then, the solution was dried at 100°C in a microwave oven. The dried product was annealed at 350°C for 2 h and it was further homogenized using mechanical mixing to avoid any agglomeration to acquire CrFe_2O_4 /(MWCNTs)_x; x=0, 5, 10, 15, and 20 wt% nanohybrids.

2.2 Characterization techniques

Powder X-rays Diffraction (XRD) with the use of $\text{CuK}\alpha$ (1.5405 \AA) radiation was employed to investigate the phase formation and crystallinity of CrFe_2O_4 nanoparticles, MWCNTs, and CrFe_2O_4 /(MWCNTs)_x nanohybrids. Raman spectroscopy was monitored using Laser Confocal micro-Raman spectrometer with the aid of Renishaw Via-Reflex, equipped with 3 lasers having different wavelengths with resolution of 2 cm^{-1} . The morphology of CrFe_2O_4 nanoparticles, MWCNTs, and CrFe_2O_4 /(MWCNTs)_x nanohybrids was checked by SEM with the help of an JEOL-JSM 6390. An FTIR spectrometer Perkin Elmer was used to carry out FTIR spectroscopy of these nanohybrids in the range of 390 – 1800 cm^{-1} with the aid of KBr pellet technique.

2.3 Electrochemical measurements

The electrochemical measurements of CrFe_2O_4 /(MWCNTs)_x; x=0, 5, 10, 15, and 20 wt% nanohybrids were carried out using coin-type cells with Li-foil as both the reference and counter electrode at room temperature. The working electrodes were prepared with the active material, conductive materials (acetylene black), and a polyvinylidene fluoride (PVDF) binder in weight ratio of 8:1:1. About 3 mg electrode materials were coated on a round copper with a diameter of 1 cm. The electrolyte was 1 M LiPF_6 in a mixture of 50 vol% ethylene carbonate (EC) and 50 vol% dimethyl carbonate (DMC). A celgard 2325 microporous

membrane was used as a separator. The CR2025 coin-type cells were assembled in argon-filled glove box with the concentration of moisture and oxygen below 1.0 ppm. The cyclic voltammetry (CV) measurements of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15,$ and 20 wt% nanohybrids were performed on an electrochemical workstation (AMETEK, VMC-4) in the voltage range of 0–3.0 V and a scan rate of 0.1 mVs^{-1} . The electrochemical impedance spectroscopy (EIS) of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ electrodes was tested in a frequency range from 0.01 Hz to 100 KHz.

3 Results and discussion

3.1 Structural investigations

XRD technique was used to explore phase formation and crystal structure of pristine MWCNTs and $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids. The XRD spectra of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15,$ and 20 wt% nanohybrids are shown in Fig. 1. The peaks at $30.2^\circ, 35.6^\circ, 37.5^\circ, 43.6^\circ, 53.7^\circ, 57.2^\circ, 62.6^\circ,$ and 64.9° correspond to (220), (311), (222), (400), (422), (511), (440), and (433) planes established in the cubic FCC crystal structure for CrFe_2O_4 nanoparticles. The XRD pattern of pristine MWCNTs is given in the inset of Fig. 1, which shows two peaks at 25.2° and 42.4° corresponding to (002) and (100) planes, respectively. In Fig. 1, the characteristic peak for MWCNTs was obtained at 25.2° with (002) plane that corresponds to their graphitic reflection. The most intense peak at 35.6° attributed to the (311) plane of CrFe_2O_4 phase verifies the crystallinity of this component [51]. No additional peaks were observed in the samples and it confirms the absence of impurities in these nanohybrids. This described the entire attachment

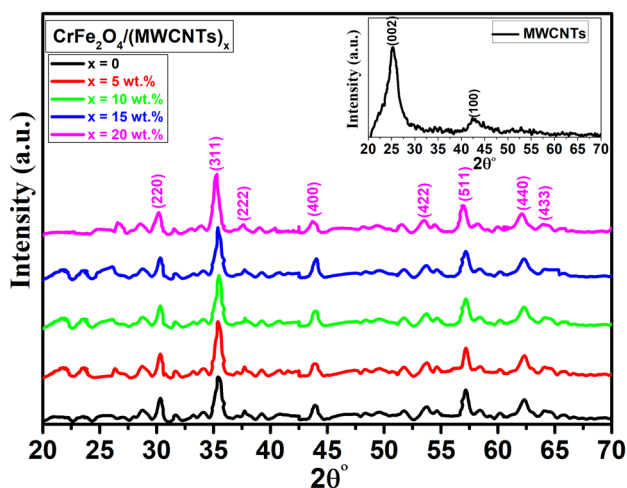


Fig. 1 XRD patterns of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15$ & 20 wt% nanohybrids and in the set the XRD pattern of pristine MWCNT

of CrFe_2O_4 nanoparticles on MWCNTs, thus demonstrating uniform dispersion. The Debye-Scherrer formula was used to compute the crystallite size of CrFe_2O_4 nanoparticles using the intense peak of (311) plane and the value of 30 nm was found. The peak broadening with increasing the MWCNTs content indicates the adsorption of CrFe_2O_4 on MWCNTs and crystallite size decrease.

Raman spectroscopic investigations were carried out at room temperature to examine the disordered structures of the synthesized material. Raman spectra of $\text{CrFe}_2\text{O}_4/\text{MWCNTs}$ nanohybrid is given in Fig. 2 a, which is further split into spectrum of CrFe_2O_4 nanoparticles (Fig. 2b) and MWCNTs (Fig. 2c). The Raman spectrum in Fig. 2a recognized three different spectral intervals below 700 cm^{-1} , which are owed to stretching vibrational modes of CrFe_2O_4 nanoparticles. The Raman intensity peaks around 473 and 685 cm^{-1} can be assigned to the characteristic peaks of the CrFe_2O_4 nanoparticles that are involved in symmetric stretching of oxygen atoms to metal ions in tetrahedral voids, frequently experienced in crystalline spinel nanostructures. The peak appeared at 336 cm^{-1} is assigned to E_g vibration mode and the peak appeared at 578 cm^{-1} is due to T_{2g} vibration mode. The Raman spectrum of $\text{CrFe}_2\text{O}_4/\text{MWCNTs}$ nanohybrid shows prominent peaks in between 1200 and 1600 cm^{-1} range. The two peaks appeared at 1345 cm^{-1} and 1606 cm^{-1} , as shown in Fig. 2b, are basically assigned to the D and G bands that correspond to induced disorder of graphitic carbonaceous materials and the C-C stretching, respectively [31, 52]. Essentially, the intensity of bands indicates contribution of sp^2 -hybridized carbon on nanoparticles' surface. It was reported in previous studies that carbon-coated LiFePO_4 gave very low D: G band intensity, which corresponded to enlarged electronic conductivity of the carbonaceous material owing to increased $sp^2:sp^3$ ratio in terms of carbon coordination, that results in enhanced electrochemical performance of composite electrodes [31, 53, 54]. Therefore, it is evident from Raman investigations of CrFe_2O_4 nanoparticles that the synthesized nanostructure is spinel as already established from the XRD analysis.

3.2 Scanning electron microscopy (SEM)

The SEM images of pristine MWCNTs and $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 10,$ and 20 wt% nanohybrids are given in Fig. 3a–d, respectively. The diameter of MWCNTs was estimated to be 30–35 nm, while CrFe_2O_4 nanoparticles were observed to be 32 nm in size, and that was further verified by using histogram and was found in good agreement with estimated crystallite size. Some agglomerations were also observed in SEM images that show nanoparticles coalescence due to diffusion of atoms. The SEM images of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=10$ and 20 wt% nanohybrids showed that large number of nanoparticles is still embedded

Fig. 2 Raman spectra of **a** $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids, **b** CrFe_2O_4 nanoparticles, and **c** MWCNTs, respectively

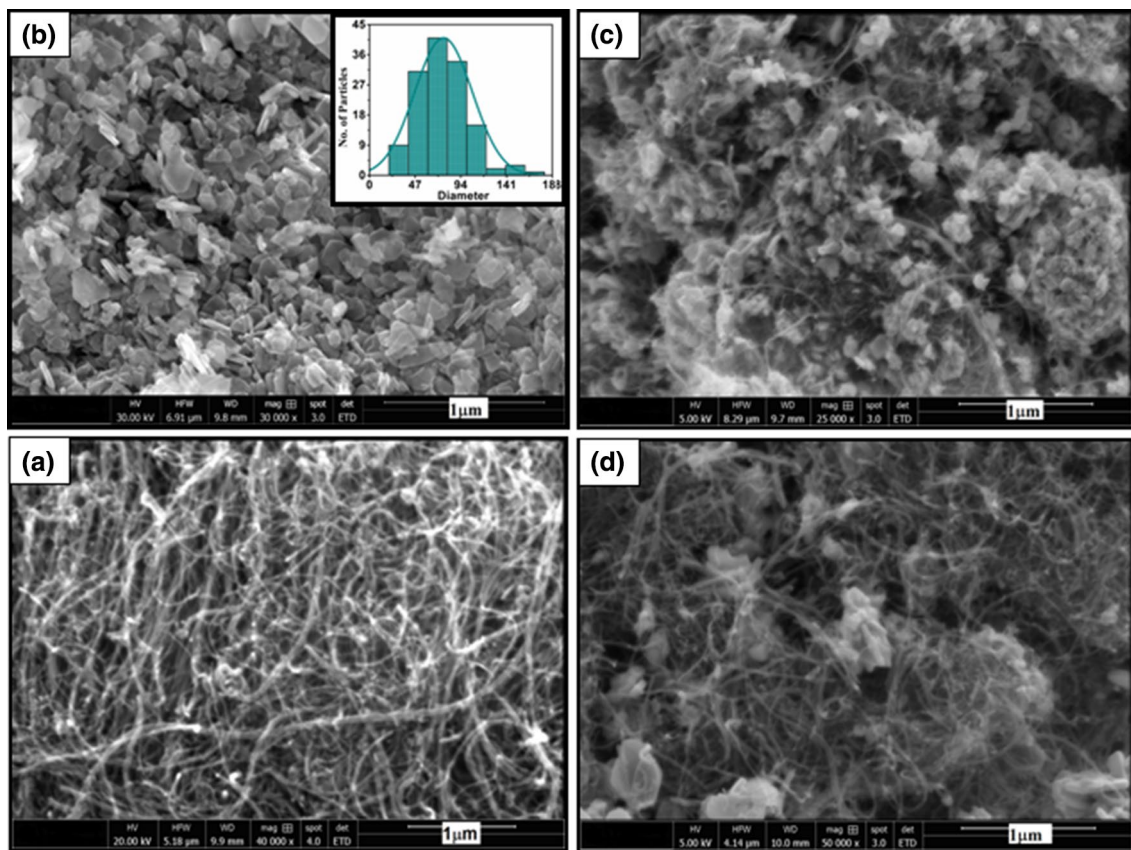
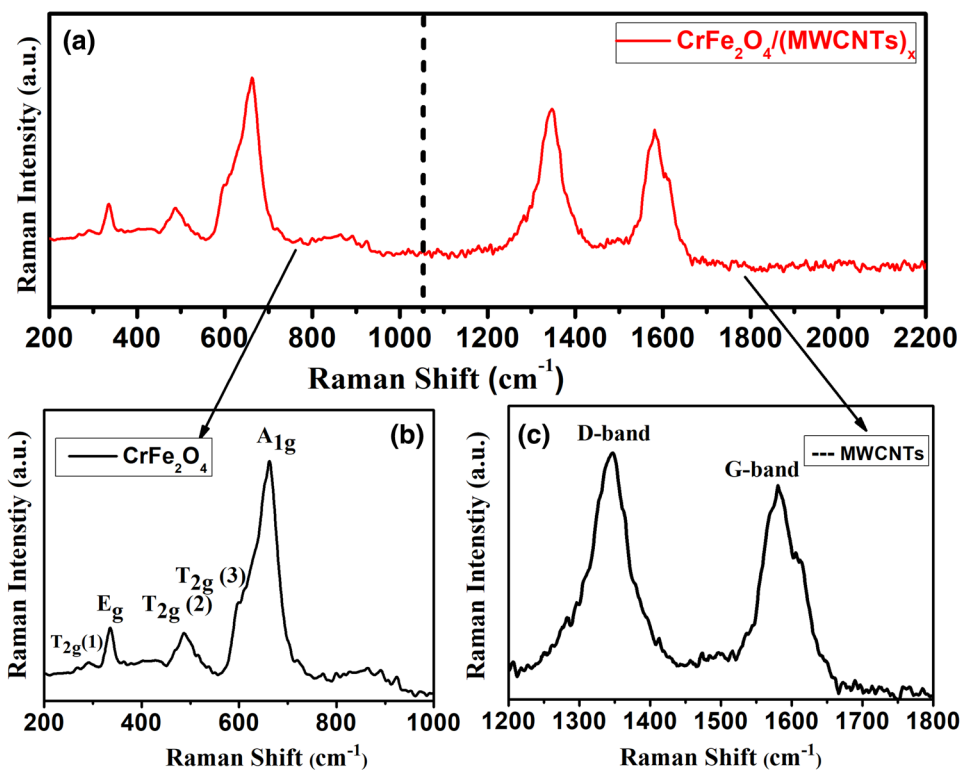


Fig. 3 **a** SEM image of pristine MWCNTs and **b–d** SEM images of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids with $x = 0, 10,$ and 20 wt%, respectively.

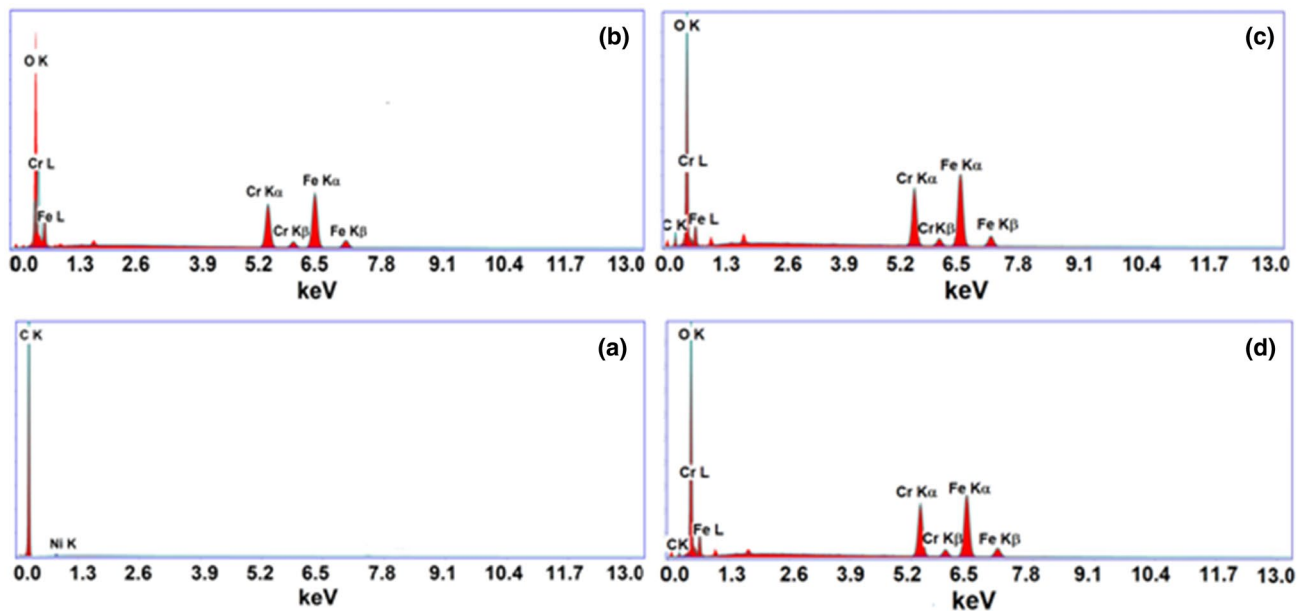


Fig. 4 a EDX spectrum of pristine MWCNTs and b–d EDX spectra of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids with $x = 0, 10,$ and 20 wt%, respectively

on MWCNTs owing to π – π interactions that signify the high efficiency of dispersion route.

3.3 Energy dispersive X-rays spectroscopy (EDX)

EDX is an analytical technique employed to study the elemental and chemical composition of a sample, which signifies that each element has distinct electronic structure leasing a unique set of peaks at its emission bands [55]. The EDX spectra of pristine MWCNTs and $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 10,$ and 20 wt% nanohybrids are shown in Fig. 4a–d. The element contents in these nanohybrids were experimentally estimated and they are listed in Table 1. It is evident from EDX spectra that there are no foreign elements observed, excepting the constituent components of Cr, Fe, O, and C in these nanohybrids.

3.4 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15,$ and 20 wt% nanohybrids are shown in Fig. 5. The strong absorption modes at $398, 503,$ and 566 cm^{-1} of CrFe_2O_4 nanoparticles are basically representative for tetrahedral (A) and octahedral (B) sites. The metal-oxygen-elongated vibrational modes at A and B sites are basically attributed to these absorption modes. In FTIR spectra, the establishment of these two sublattices vibrational modes acknowledge single-phase spinel structure configuration [56–59]. A slight shift in vibrational modes was noticed with increasing contents of MWCNTs and it indicates the subsistence of

Table 1 Compositional analysis of pristine MWCNTs and $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 10,$ and 20 wt% nanohybrids.

$\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ Nano-hybrids	MWCNTs	0 wt%	10 wt%	20 wt%
Cr (wt%)	–	29.26	19.68	18.1
Fe (wt%)	–	50.02	43.48	43.2
O (wt%)	1.01	20.72	33.58	32.17
C (wt%)	98.99	–	3.26	6.53

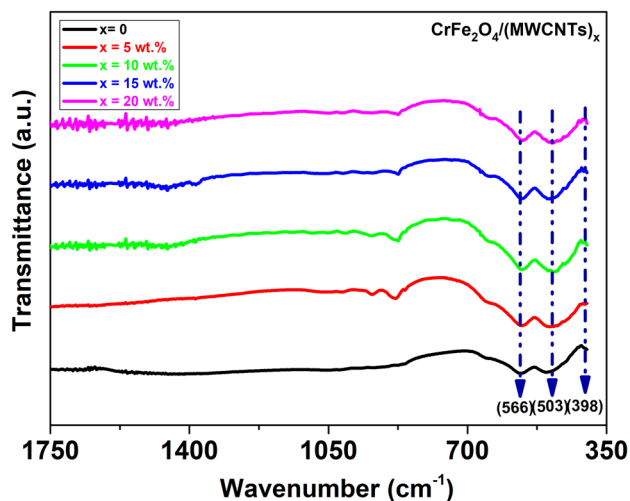


Fig. 5 FTIR spectra of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x = 0, 5, 10, 15,$ and 20 wt% nanohybrids

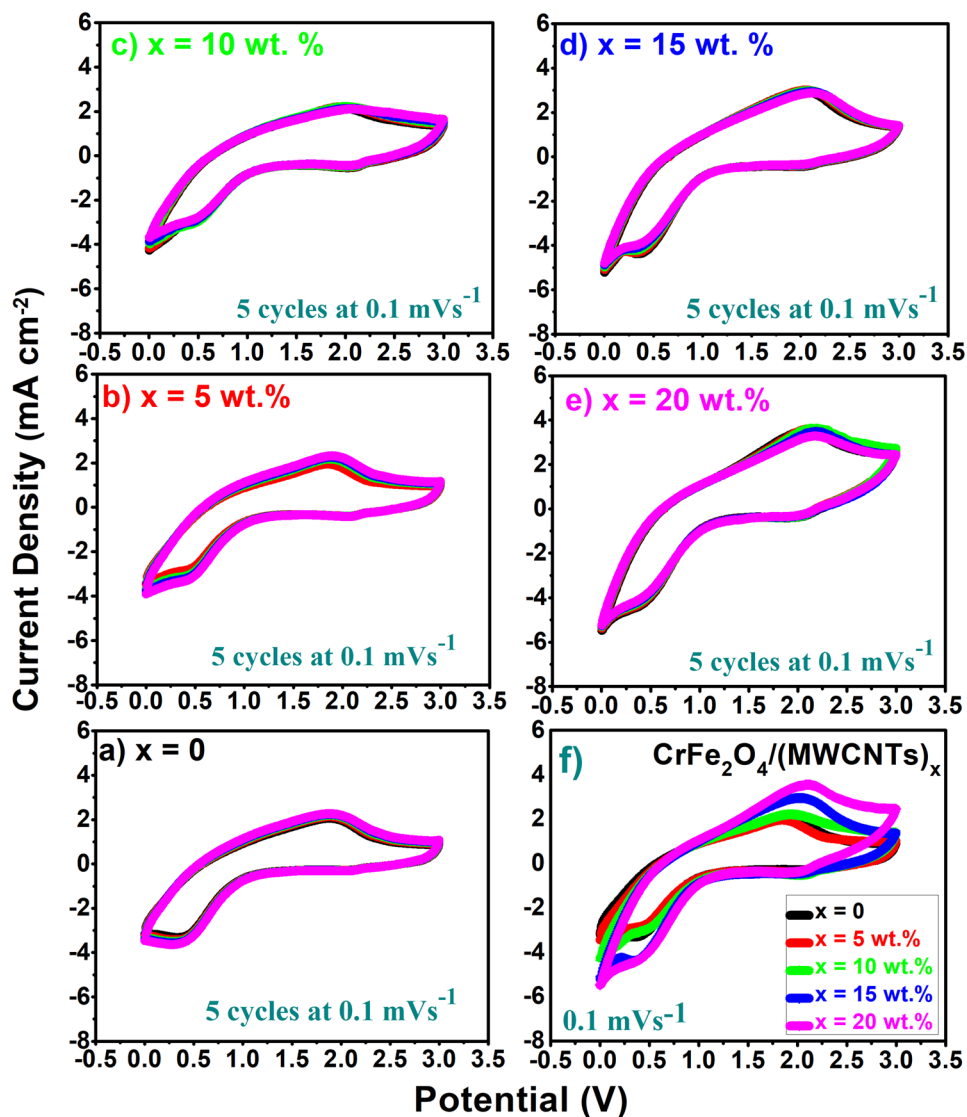
intermolecular forces between CrFe_2O_4 nanoparticles and MWCNTs.

3.5 Cyclic voltammetry (CV)

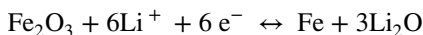
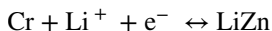
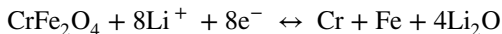
The electrochemical behavior of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids was examined through recording cyclic voltammograms (CV) in voltage range of 0–3.0 V at 0.1 mVs^{-1} scan rate. The CV curves of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15,$ and $20 \text{ wt}\%$ nanohybrids obtained for 5 cycles are given in Fig. 6a–e. In CV curves, the peak that appears in the negative current regime is called cathodic (reduction) peak, while the peak that emerges in the positive current region is termed as an anodic (oxidation) peak. It is evident from the CV curves of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15,$ and $20 \text{ wt}\%$ electrodes that a small peak appeared at 2.3 V in anodic scan ascribed the existence of

side reactions on electrode surfaces. Furthermore, the irreversible decomposition of electrolyte at interfaces caused the formation of a solid electrolyte interphase (SEI). The reduction peak at 0.4 V is attributed to the reduction of CrFe_2O_4 nanoparticles to Cr, Fe, and establishment of Li_2O . In subsequent cycles, the cathodic peak shifts towards low potential, whereas the anodic peak shifted towards higher potential, which suggests the structural and lithium-driven alterations during cathodic and anodic processes [60]. The peak current and area under CV curves did not show any significant diminishing behavior with the increased number of cycles that shows good capacitive conduction and charge storage ability of the working electrodes. The reversible peaks experienced beneath 0.4 V correspond to Li-ion intercalation or de-intercalation processes [45, 61–64]. In the CV curves of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ electrodes, the existence of redox peaks

Fig. 6 The 5 cycles of CV for $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids with **a** $x=0$, **b** $x=5$, **c** $x=10$, **d** $x=15$, and **e** $x=20 \text{ wt}\%$, respectively, and **f** One cycle of CV for $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15,$ and $20 \text{ wt}\%$ nanohybrids.



revealed the pseudo-capacitive conduction of CrFe_2O_4 , which is considerable in entire specific capacitance (C_s) of the electrodes. The redox reactions of CrFe_2O_4 nanoparticles are illustrated below:



For the $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15$, and 20 wt% electrodes, both the oxidation and reduction peaks are positively shifted with increased loadings of MWCNTs as shown in Fig. 6f, that is caused by structural rearrangement of the electrode materials and increased polarization [65]. It is clear from Fig. 6f that the curves show almost similar shaped peaks. However, the integrated peak area and peak currents of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=5, 10, 15$, and 20 wt% electrodes are much higher, as compared to those of bare CrFe_2O_4 , which indicates that the bare electrode has high reactivity and capacity. Moreover, the reduction peak of bare CrFe_2O_4 was found at about 0.40 V, whereas the reduction peaks of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nano hybrids were recorded at a lower potential (i.e.; ~ 0.36 V), which implies that nano hybrids have large irreversible capacity. It was observed that the values of peak-to-peak potential (E_{pp}) increase with increasing contents of MWCNTs in $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ electrodes, as shown in Fig. 7. The area under the CV curves increases linearly with increasing content of MWCNTs, which indicates that maximum electrode active surfaces are accessible with excellent electrical conductivity. The specific capacitance ' C_s ' (F/g) of working electrode was estimated by the following relation [66]:

$$C_s = \frac{\Delta I}{m \times s}$$

where ΔI (A) is the difference of oxidation and reduction peak currents in amperes, m (g) is the loading mass, and s (mVs^{-1}) is the scan rate. The variation in C_s with number of cycles for working electrode of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nano hybrids is shown in Fig. 8. It is obvious that C_s decreases with increasing number of cycles, while it is increased with increasing contents of MWCNTs. This may be due to the passage of maximum number of ions through the electrode, while the interaction between electro-active materials and ions became frail that leads C_s to lower values. It is also evident from Fig. 8 that the values of C_s for synthesized $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nano hybrids are found to be greater with increased loadings of MWCNTs as compared to bare CrFe_2O_4 nanoparticles. Thus, this study can be helpful to estimate the capacitance retention in a material subsequent to certain number of cycles.

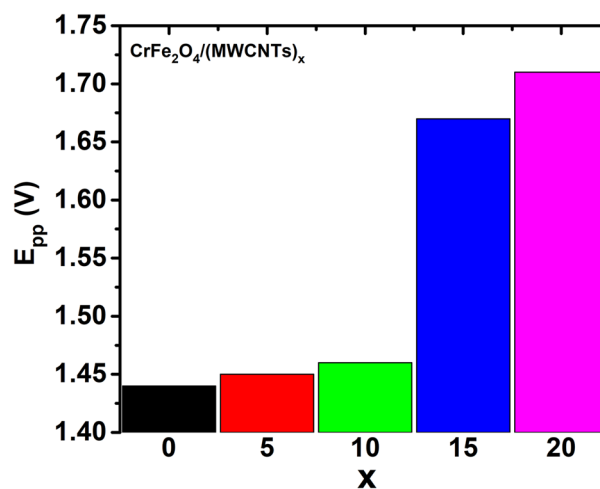


Fig. 7 Variation of E_{pp} versus MWCNTs contents (x) in $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15$, and 20 wt% nano hybrids.

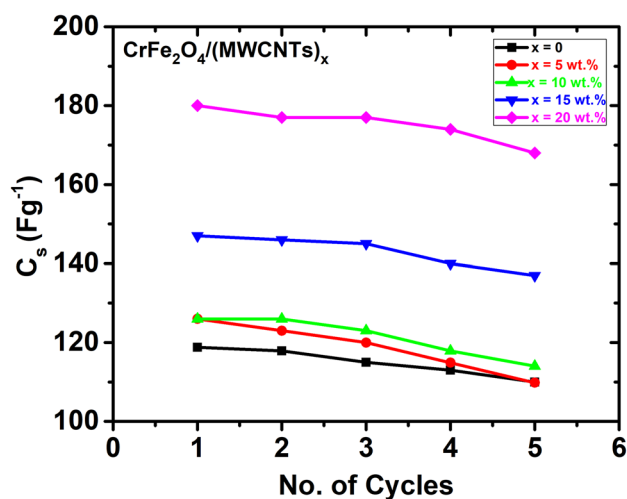


Fig. 8 Variation of C_s versus No. of cycles of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15$, and 20 wt% nano hybrids

3.6 Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) of these synthesized electrodes was conducted to estimate the charge transfer resistance with the aid of Nyquist plots. Generally, in Nyquist plots, the semicircle at high frequency gives charge transfer resistance, while, at low frequency, a straight line appeared that is associated with diverse diffusion-controlled processes that happened at electrode interfaces [67]. Usually, it was noticed that the diameter of semicircle in the Nyquist plots is assigned to the charge transfer resistance (R_{ct}) and it will be higher when the diameter of semicircle is greater. The Nyquist plots of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15$, and 20 wt% electrodes are shown in Fig. 9.

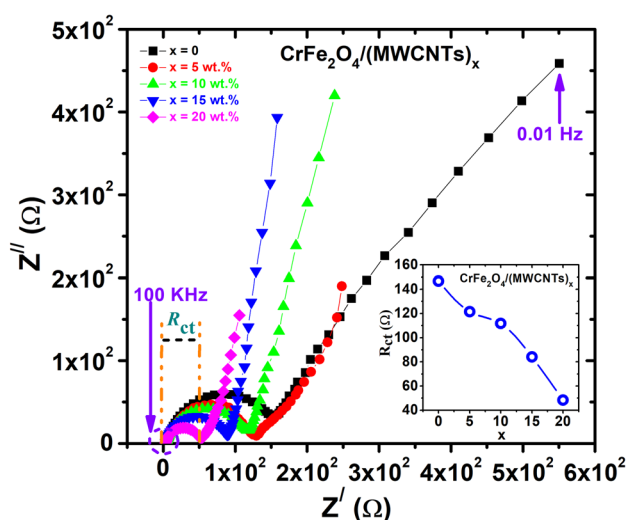


Fig. 9 Nyquist plots of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x = 0, 5, 10, 15,$ and 20 wt% nanohybrids in a frequency range from 0.01 Hz to 100 KHz.

The decrease in semicircle diameter of these electrodes was observed with increased loadings of MWCNTs, and that showed the enhanced electrochemical behavior. The inset of Fig. 9 showed that R_{ct} got high value for bare CrFe_2O_4 electrode that was decreased with increasing contents of MWCNTs. This may be due to good inter-particle electrical contact between nanoparticles and MWCNTs, and thus, the decreased electrical resistivity can be reached. It may also indicate that MWCNTs blocks easy incursion of lithium ions into nanoparticles. Hence, the outcomes exhibit that $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$; $x=0, 5, 10, 15,$ and 20 wt% nanohybrids are useful composites to improve the electrochemical performance of Li-ion batteries.

4 Conclusions

The $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids were successfully synthesized by novel two-step route. First, the bare CrFe_2O_4 nanoparticles were produced by chemical co-precipitation route that were later embedded on the surface of MWCNTs by ultra-sonication-assisted route. The toluene was used as dispersive medium for the first time during synthesis of these nanohybrids. The capacitive performance of these nanohybrids was studied by performing CV experiments and EIS measurements. The CV curves showed that $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids got higher C_s as compared to bare CrFe_2O_4 electrode. Moreover, C_s of $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids was found decreasing with increasing number of cycles that maybe due to the passage of maximum number of ions through the electrode, while the interaction became frail between electro-active material and the ions. The Nyquist plot of CrFe_2O_4 showed greater value of R_{ct}

as compared to that of MWCNT-based nanohybrids, which indicated the enhanced electrochemical behavior. It was also observed that bare CrFe_2O_4 electrode exhibited higher value of R_{ct} , which was decreased with increasing contents of MWCNTs due to good inter-particle electrical contact between nanoparticles and MWCNTs. These results indicate that $\text{CrFe}_2\text{O}_4/(\text{MWCNTs})_x$ nanohybrids are the potential candidates for the high-performance energy storage devices especially for Li-ion batteries.

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