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HYBRID POLY (O-TOLUIDINE)/MWCNT/COPPER OXIDE NANO COMPOSITE ELECTRODE FOR ELECTROCHEMICAL SUPERCAPACITOR

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ABSTRACT

Hybrid nanocomposite containing poly o-toluidine, copper nanocomposite (CuONC), and multiwalled carbon nanotubes (MWCNT) was fabricated by i*n-situ* oxidative synthesis method. The electrochemical performance of the hybrid composite was inspected as a supercapacitor material by three-electrode cyclic voltammogram analysis. Physicochemical aspects of synthesized OT/MWCNT/CuO nanocomposite were justified by FTIR, UV-vis. spectroscopy, XRD, FESEM and EDX techniques. The composite comprising of metal oxide, polymer and MWCNTs offers a promising alternate for developing better supercapacitor electrode materials. The highest specific capacitance of 1900 F/g at a scanning rate of 5 mV/s and 1800 F/g and current density of 1A /g was achieved in an aqueous solution of 0.5M H_2SO_4 with good cycle stability.

Keywords: O-toluidine, Carbon Nanotubes, Supercapacitor, Voltammetry, Charge-discharge, Impedance.

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INTRODUCTION

Recently, supercapacitors have been widely used and drawn high renewed attention due to its ultra-high power density, extended life cycle, ease of operation, and high dynamics of charge transfer. The supercapacitor is a novel device for energy-storage that endures numerous charge and discharge cycles at high current and short duration. The demand for better energy storage devices electronic gadgets, electric automobiles as well as hybrid energy-based vehicles (HEV), have been growing rapidly to meet this demand, supercapacitors which are also known as electric double-layer capacitors (ELDC), deal with favorable substitute. The conjugated polymers as advanced electroactive electrode materials have been used in supercapacitors.[1,2] Conjugated polyaniline has been broadly studied due to its high conductivity, simple amalgamation, great ecological stability and minimal cost.[3,4] To achieve extra insight into polyaniline, -CH_3 group substituted polyaniline at ortho-position known as poly (o-toluidine) (OT) reported being superior to aniline, due to its faster switching time between its oxidized and reduced conditions. Despite having these characteristics this conducting polymer suffers a major disadvantage. During the doping and de-doping process, it degrades mechanically due to which its electrochemical execution blocks.[5,6]

Carbon-based nonmaterials *viz* graphene, graphene oxide (GO), (MWCNT) and activated carbon (AC) are broadly utilized for improving the performance of supercapacitors. They act as fillers for polymer-based composites due to their unique thermal,[7,8] Electronical, mechanical, and reinforcement properties.[9,10] Also Metal oxide used for developing supercapacitive electrode material due to their specific capacitance and therefore use for quick and changeable redox reactions.[11,12] Among various metal oxides copper oxide (CuO) based nanocomposite has been attracting much attention due to its great electrical conductivity, remarkable handling capacity and ease of preparation.[13,14] Copper in different forms has already been broadly utilized as a part of gadgets, biomedical applications, supercapacitors, biosensor, miniature devices and catalysis.[15,16] The improvement of polymer nanocomposite comprising of nanoscale metal

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oxide open new window, towards the fabrication of extraordinary electrode material with novel sophisticated properties.[17,18] OT is an appropriate "polymeric" conducting material for nanoscale metal oxide amalgamations. It enables consolidated metal salts to attain nanoscale. Thus results in changing its electrical and optical properties.[19,20] These materials apart from having unique thermal, electrical, mechanical, structural and reinforcement property, also are very good filler materials, especially for pseudo-capacitors. Using conducting polymer and transition metal together as electrode materials and developing such methodologies that can combine their virtues can be helpful for a further up-gradation of electrical conductivity and stability of the electrode.[21,22]

The motive of the present study was to synthesize tri-hybrid composite, comprising of conducting polymer, metal and MWCNTs (OT/MWCNT/CuO) to develop hybrid electrode material. The fabricated composite act as an excellent electrode material due to the distinctive structural and excellent electro-capacitive properties.

EXPERIMENTAL

Material and Methods

O-Toluidine, MWCNTs (extent 10-12 nm and length 1 μm), acetylene black and polyvinylidene fluoride (PVDF), were procured from Sigma Aldrich. Other required chemicals as ammonium persulphate (APS), Hydrochloric acid (HCl), Sulphuric (H_2SO_4), Nitric acid ($HNO_{3)}$, N,N-dimethylformamide (DMF). All the aqueous solutions were prepared using Millipore deionized water.

Synthesis of POT/MWCNT/CuO Nanocomposites

Step-1: Firstly, acid treatment was given to MWCNTs by keeping the calculated amount of MWCNTs soaked in a mixture of conc. H_2SO_4 and HNO_3 in the ratio of 1:3 for 10 h at room temp. Then this mixture was ultrasonicated for 3-4 h, Afterward, the functionalized MWCNTs were filtered, washed up to neutralized pH of MWCNTs and then dried at 80 °C to get functionalized MWCNT for further use.

Step-2: Separately, CuO nanoparticle was synthesized by making an aqueous solution of the calculated stoichiometric amount of Cu $(NO_3)_2.9H_2O$ and CH_4N_2O separately. Then the above solution was mixed well to acquire a homogeneous product. The obtained product was transferred to autoclave & placed in a muffle furnace at 500ºC for 12 h and then the product was obtained.

Step-3: OT/MWCNT/CuO nanocomposite was synthesized by varying the concentration of CuO (as listed in Table No.1) MWCNTs, and as depicted in Table-1. For the preparation of, OT (OT), OT/MWCNTs (OT1), OT/CuO (OT2) and OT/MWCNT/CuO nanocomposites (OT3).

Table-1: Formation of Samples

Sample	Poly(O-toluidine)	MWCNTs	CuNP
OT	0.1M	-	-
OT1	0.1M	0.05g	-
OT2	0.1M	-	0.035g
OT3	0.1M	0.05g	0.035g

At first 0.1M of POT was taken and dissolved in DI water, followed by calculating the amount mixture of MWCNTs and CuO in the above aqueous solution. All the chemical oxidation procedure of OT carried out in a highly acidic solution of 1M HCl at 5°C followed by the addition of 1M $(NH_4)_2S_2O_8$ drop wise under continuous stirring at 100 rpm and kept on stirring for 24 h at room temp. After complete polymerization the precipitate of the obtained product was cleansed with DI water, followed by acetone to remove oligomeric contaminations. The filtered composite outcome was dried inside a vacuum oven at 60°C for up to 10 h. The end product was crushed well to get the powder form of the nanocomposite electrode material.

Material Characterization

Electrode material was characterized by different techniques to explore its properties. The UV–Visible absorption/transmission spectra recorded on spectrophotometer Shimadzu UV-(3101). X-ray beam diffraction studies were obtained using (Phillips X'pert Pro) with Cu Kα radiation of (1.54060 nm) and

emission wavelength 1.75 A° at an accelerating voltage of 45 Kv. Morphology and crystal structure of composites remained was explored by field-emission scanning electron microscope (FESEM, JEOL JMS-7600 F). The chemicals composition in the composite was determined by energy-dispersive X-ray beam spectroscopy (EDS, Zeiss Instruments, attached to the FESEM).Whole electrochemical experimentations were performed in a conventional three-electrode cell system handling by the potentiostat. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and (EIS) investigations were completed in a tri-electrode assembly (Autolab, PGSTAT 86, 472).

Electrochemical Measurement

The hybrid OT/MWCNT/CuONC nanocomposites were added with 20 wt% of activated carbon (AC) as conductive and agent filler and 10% binder poly (vinyldiene fluoride) (PVDF) in N-N Di-methyl formamide (DMF) solvent. The enhanced proportion by wt % of covering gel solution is containing the nanocomposite material (60%), AC (20%), and PVDF (20%), liquefied in DMF. The mixture was ultrasonicated for 2 h. to form homogenous slurry. The electrodes were prepared via coating slurry on 1cm ×1cm of graphite sheet as a current storage. The electrode was let dry in an air vacuum at 70°C for 16 h. Each electrochemical analysis was made using three-electrode cell assembly of the as-prepared composite referred to as anode, silver/silver chloride as the reference electrode and Pt acting as the cathode dipped in an aqueous solution of 0.5M H_2SO_4 utilized as an electrolyte at room temp.

RESULTS AND DISCUSSION

The polymer when combined with CuONC the XRD showed in Fig.-1. This indicates that composite has a polycrystalline nature.[23,24] In X-ray diffraction patterns, monoclinic and orthorhombic structures related by different crystallization parts were shown, The polycrystalline nature acquired after the addition of OT was also confirmed by prior reports.[25,26] shown in Fig.-1.

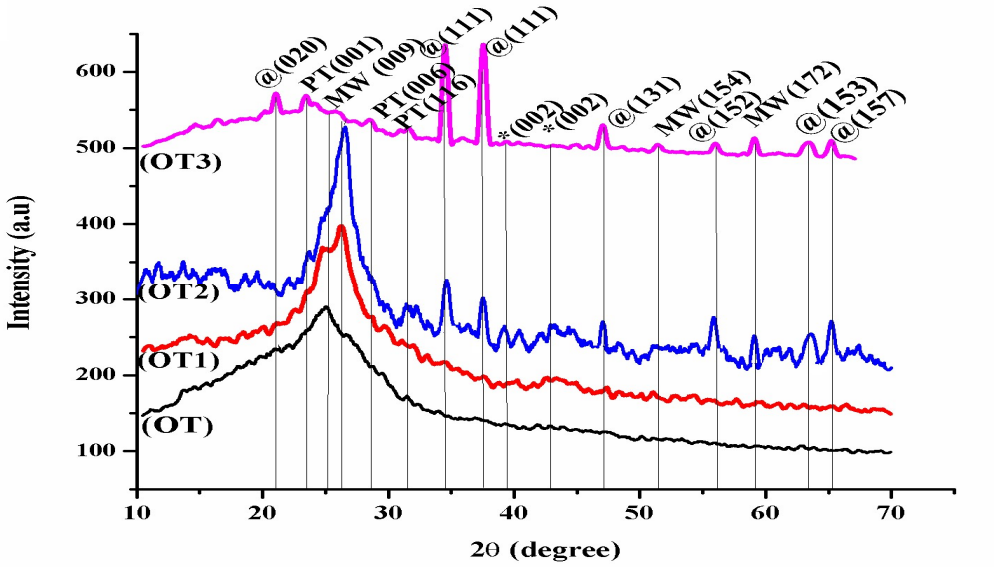

Fig.-1: XRD Diffraction of (OT) Pure o-Toluidine, (OT1) OT/MWCNTs, (OT2) OT/CuO and (OT3) OT/MWCNTs/CuONC Composite

The pattern of XRD OT shows a more vast band around the scope of 2θ from 10° to 35° arising due to pure ortho toluidine. The composite OT/CuNC creates just two characteristic peaks at 2θ= 64° and 66° corresponding to copper.[27,28,29] The lattice structure expanding the amount of CuONC, crystalline highlights to nanocomposite rises fine peaks. The crystalline structure investigated the development of lattice stages identified with copper oxide (shown as @), $Cu(OH)_2$ (shown as*), MWCNTs (shown as (MW) and Poly o-toluidine by (OT) confirmed with JCPDS Number respectively are 05-0661, 89-5895 and 11-0933.[30,31] It generally is known that insulating consistent in CuONC was observed to that

considerably greater molecules measure in nanoscale.[32,33] CuONC attract to each other in nano size. The attraction between the nanoparticles is considerable in nano region, the amount of CuONC the normal conduct between particles diminishes bringing about high attraction among the nanoparticles, well-ordered shape organized out lattice structure system inside conducting polymer framework.[34,35]

FESEM micrograph has been achieved to analyze surface morphology of prepared composites. FESEM was implemented to elucidate the morphology of the CuONC/MWCNTs/OT nanocomposite and the pictures are shown in Fig.-2. The FESEM pictures at high magnification demonstrate that the morphology of CuONC/MWCNTs/OT nanocomposite was changed in the type of nanomaterial thicker and denser contrasted with the untreated MWCNTs currently published.[36,37] The average spread of the nanocomposite is perceived to be ~100 nm. Therefore, the system of OT expelling has existed in the interlayer of CuONC/MWCNTs. A qualitative EDAX investigation of CuONC/MWCNTs/OT nanocomposite conforms in Fig.-3(a,b,c,d) That they contain a proportion of carbon, oxygen and nitrogen to turns out to be 45.19%, 4.53%, and 1.19%, which indicate CuONC/MWCNTs/OT nanocomposite contains just target martial no other component was traced out proposing CuONC/MWCNTs/OT nanocomposite.

The FESEM picture of CuONC doped MWCNTs with nanoparticles in FESEM microhraphs color circles shown in Fig.-2d. The nearness of CuONC inside the MWCNTs, showing up as snowy spots.[38] It examine shaped crystal structures of CuONP in little size, irregular shapes the presence of CuONP nanoparticles in the nanocomposite materials.

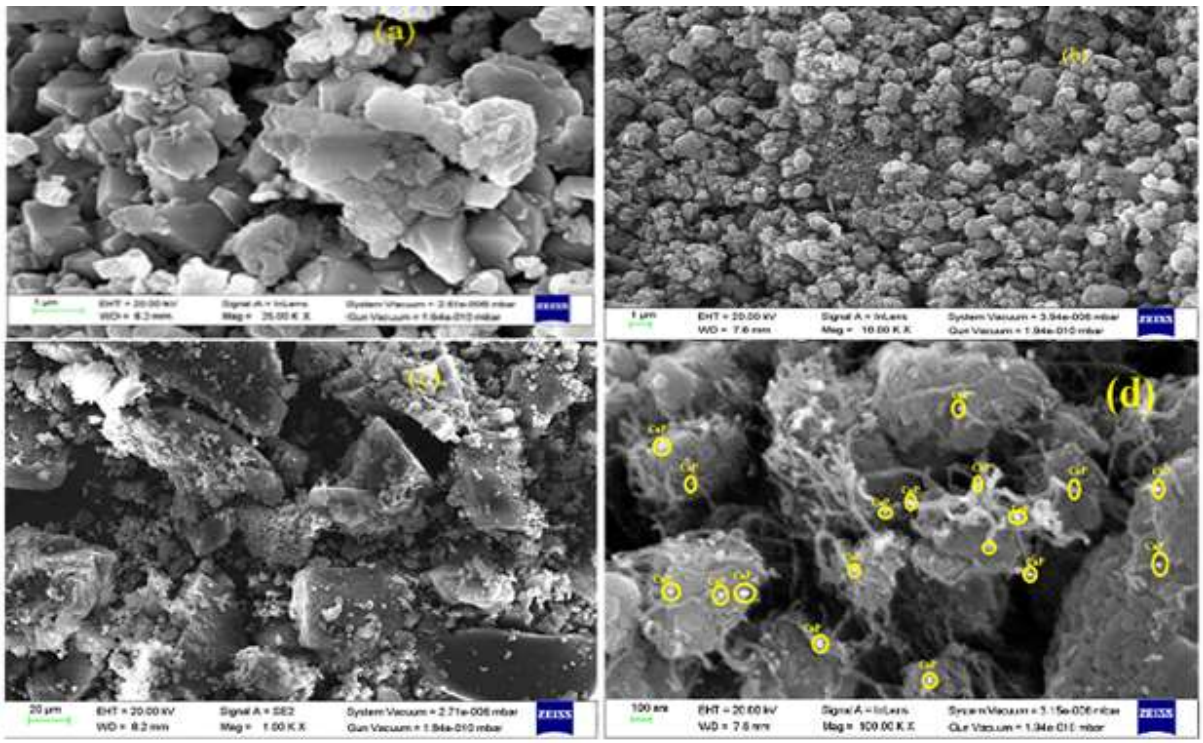

Fig.-2: FESEM of the Composite (a) Pure Polyo-toluidine, (b) MWCNTs Doped OT, (c) CuONC Doped OT, (d) OT/MWCNTs/CuNC Nanocomposite

The acquired FTIR spectra of the OT/CuONC/MWCNTs composites are shown in Fig.-3(a to d). The characteristic band MWCNTs and their position are 1109 cm^{-1} C-O stretching vibration, 1183 cm^{-1} justification the MWCNT and 1556,1593 cm^{-1} indicate the characteristic C=C stretching vibration of the carbon skeleton,1592 $cm^{-1}$the C=O stretching vibrations of quinone group over the surface of MWCNTs,1732,1693 cm^{-1} extending vibrational of carboxylic (COOH) acidic groups. For OT in IR graph 505 $cm^{-1,}$ C-C stretching in benzenoid rings.648,777 cm^{-1} exclude of plane deformation of C-H in the 1,2,4 substituted benzene ring, 821 cm^{-1} C-C stretching in benzenoid rings.1057 cm^{-1} B-NH-Q or else B-NH-B bond in-plane modes.1180 cm^{-1} stretching vibration of quinoid rings in C-H plane.1155cm^{-1}

charge delocalization in polymer backbone. 1307 cm^{-1} C-N is the secondary aromatic aminestretching.1558,1587 cm^{-1} C=C or else–C-N- quinoid structure of stretching vibrations. At 1732 & 1815 cm^{-1} C=O the stretching mode. The composite of OT/MWCNTs indicates in composition by IR graph 540,648 and 677 cm^{-1} in the fingerprint of OT then peaks are imposed to C-H out of plane deformation 705cm^{-1}. The 1,2,4-substitution in benzenoid rings, 813 cm^{-1} out of plane C-H vibrational mode 893,941 cm^{-1} the substitution in benzenoid rings 1004,1035 cm^{-1}plane C-H vibrations of quinoid rings.

UV-visible spectroscopy was utilized to govern interfacial interaction between different components. The absorption around 250 nm is allocated to the π-π* electronic transition that corresponds to the excitation of the electron over forbidden gap and promotion from π bonding orbital to an antibonding π*orbital .[39] However following band occurs about 600 nm because electron exchange form benzenoid to quinoid rings is a consequence of inter-band exchange form n-π*.[40] Comparable benzenoid and quinoid absorption groups with a little red shift shown in the spectra of OT/MWCNTs nanocomposite Fig.-3. This red shift shows the manageable interface between the quinoid rings of the OT and MWCNTs and efforts the doping impact on the MWCNTs on the conducting polymer.

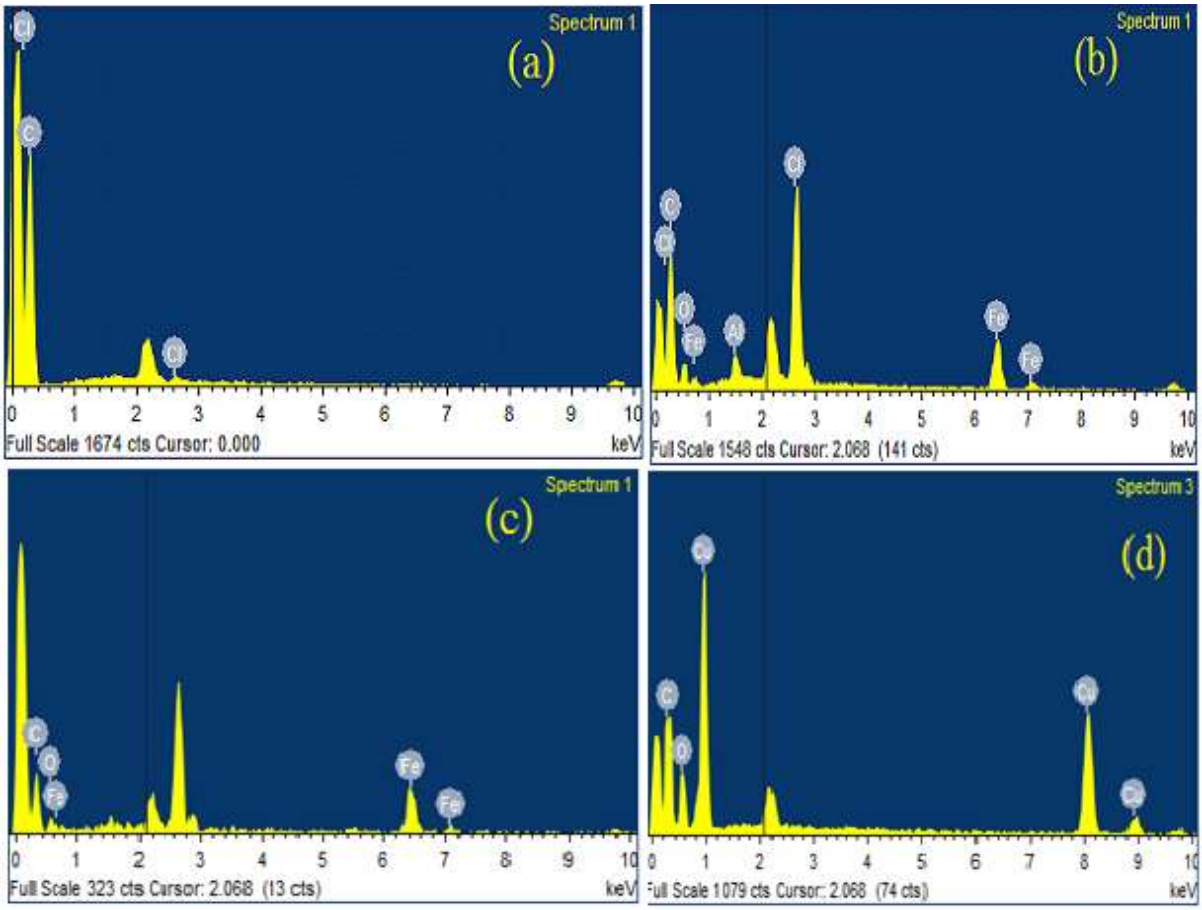

Fig.-3: EDX of Graph of Pure Poly o-toluidine OT (a) MWCNTs Doped OT (b) CuONC Dope OT (c) OT/MWCNTs/CuNC (d) Nanocomposite

Electrochemical Studies

The electrochemical execution OT/MWCNTs/CuONC nanocomposite evaluated using (CV), galvanostatic charge-discharge (GCD) in a tri-electrode chemical cell mechanism, the cyclic voltammetry measurements (CV) have been performed on various scan frequency in a fixed potential window range of -0.4 to 0.6 V in 0.5 M H_2SO_4. The CVs the results were shown in Fig.-3. Symmetrical figures indicate

enhanced intrinsic electrical conductivity of electroactive composite thin-layer and batter kinetic reversibility, which isan imperative component for supercapacitors.[41-43] Oxidation and reduction are also seen in CVs composite by varying current. It is observed that composite OT4 shows excellent outcomes as electroactive material. The specific capacitance (Sc.) was analyzed from CVs through the utilized the given formula:

$$Cs = I/m \times v \quad (1)$$

Where, (Cs) specific capacitance in farad per gram, *m* (g) the total mass of electroactive material, I apply current (mA), as well as v is the scan frequency in mV/s. the specific capacitance of composite OT4 is shown as 1514, 1233, 693, 444 F/g at different scan frequencies at 5, 10, 20,40 and 80 mV/s respectively. The growth MWCNTs can enormously control the morphology of the composite to give maximum span region and enhance electrical conductivity, the copper nanocomposite (CuONC) present pseudocapacitance in faradic procedure in electrolyte v/s electrode interaction. Furthermore, the CuONC was decorated by OT. Additionally, the substance of CuONC shows the noteworthy part in three electrochemical cell execution, it is observed that OT4 shows most elevation particularly in specific capacitance of 1514 F/g among the different nanocomposites. The uniform structure shown in OT4 was comparatively shown that disorder agglomerated structure in OT4 shows a fast transition of charge.[44, 45, 46]

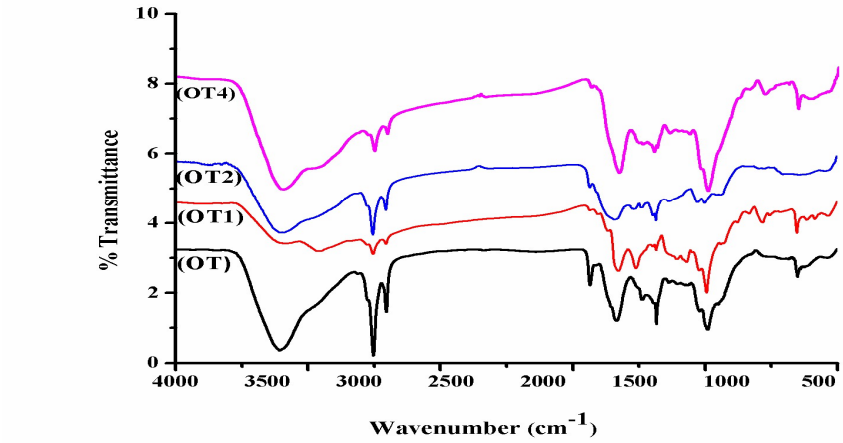

Fig.-4: FT-IR Spectra of Pure o-toluidine (OT1), OT/MWCNTs (OT2), OT/CuONC (OT3), OT/CuONC/MWCNTs (OT4)

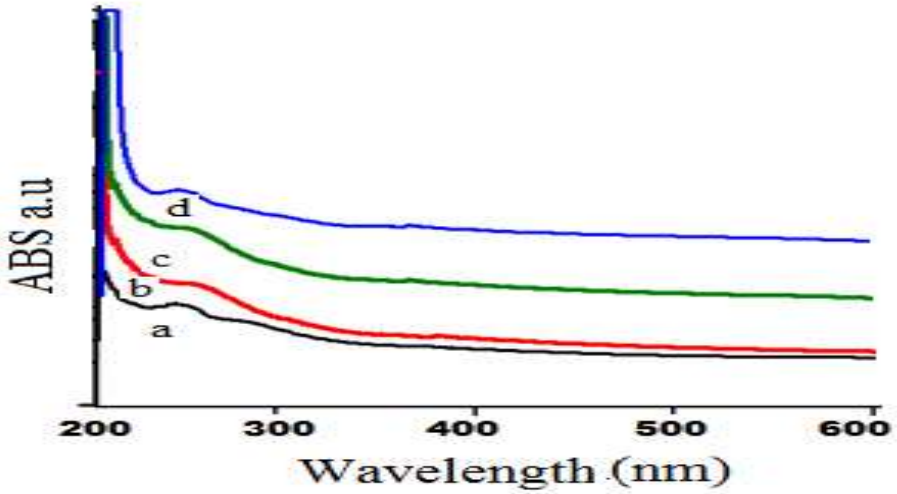

Fig.-5: UV-Visible Absorption Spectra of Pure O-toluidine (a), OT/MWCNTs (b), OT/CuONC (c) OT/MWCNTs/CuNC (d) Nanocomposite.

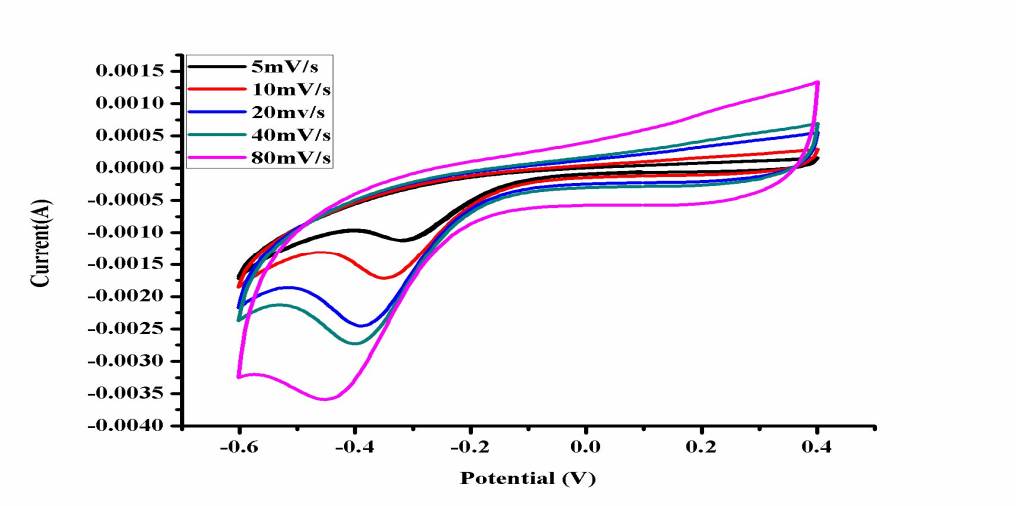

Fig.-6: CVs of Poly O-toulidine /MWCNTs/CuONC (OT3) at Different Scan Rate

CONCLUSION

This investigation demonstrated a simple procedure to fabricate a composite of CuONC with conducting polymer in MWCNTs by adding the mixture in oxidative synthesis manner. The different compositions of material containing MWCNTs/CuONC were investigated to substantial impact at morphology also the electrochemical performance of electroactive material. Among the produced nanocomposites, OT4 displayed a maximum capacitance of 1514 F/g at a current density of 1A/g with enhanced rate potential and cycle strength. This interesting property was achieved form the good-shape and design, excellent conductivity due to improved synergistic inputs form specific segments in the nanocomposite, which creates a reasonable possibility to application in a charge storage mechanism.

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