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Synthesis and evaluation of AgCu-MWCNTs doped with Poly (Ortho-Toluidine)

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ABSTRACT
The aim of this work to purpose a material for electrode in solar energy sector. For this purpose, we prepared Ag-Cu-MWCNTs alloy doped with Poly (Ortho-toluidine) composite. The phase, chemical bonding and structural morphology of composite were characterized. The X-ray diffraction (XRD) results showed that our sample have good crystalline behavior. A SEM analysis reveals that the formation of fibrous phase composite in which particles are uniformly disturbed. The FTIR studies shows that good interaction exists between POT and AgCu-MWCNTs particles. Our studies potentially form a basis for a simple, efficient, and cost-effective approach for fabricating electrode composites.
Keywords*: Silver-Copper alloy, MWCNTs, Poly (Ortho-Toluidine), electrodes*

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I. Introduction

The economy of a country is highly influenced by energy. Due to increase in the population of world and the demand in energy sector continuously arise day by day. Due to which energy crisis all over the world is serious concern. Usage of the conventional resources of energy are not reliable because the combustion of fossil fuels also leads to unpleasant environmental effects such as acid rain, pollution, and greenhouse effect [1]. Therefore, to resolve both the energy crisis as well as environment problems alternative renewable and green energy source must be adopted. Solar cell, geothermal, hydropower, biomass, biofuel, and wind power are all examples of renewable energy sources that can be employed to decrease these concerns. Solar energy is the most widely used and infinite source of energy, owing to its low cost, clean supply, high power conversion efficiency, and ease of manufacture. The fundamental challenge for solar cells has been the high cost, low conductivity, and low power conversion efficiency of the electrode materials used in solar cells [2].

For an ideal electrode material should possess the characteristics of good electrical conductivity, excellent catalytic activity and low cost [3]. Platinized (Pt) catalysts are commonly used as an electrode in solar cells, however because platinum (Pt) is an extremely expensive noble metal with limited reserves, there is a need to construct Pt-free materials for solar cell electrodes [4]. There are many good alternatives to Pt including carbonaceous materials [5]such as carbon black, carbon nanotubes (CNTs), graphene, conducting polymers [6] , carbides [7], nitrides [8] and metals alloys [9].Among them Metal nanoparticles (NPs) have received significant attention in solar panels because of their higher reactivity, electrical and thermal properties. Silver (Ag), copper (Cu), and gold (Au) are the most widely known metals. As compared to monometallic the bimetallic nanostructures reveal good photo electrochemical catalytic activity [10]. So, Ag-Cu alloy gain great interest for electrode due to their remarkable catalytic activity [11] but difficulty of Ag-Cu alloys to be used as electrode materials is due to their insufficient conductivity [12]. Combining it with other carbon-based materials like carbon powder [13], mesoporous carbon [14], graphene [15] and MWCNTs [16] is an effective way to overcome this problem. Among them multiple-wall carbon nanotubes (MWCNTs) are very effective candidates because of their excellent conductivity [17]. Pure MWCNTs, on the other hand, have trouble dispersing in metal nanoparticles due to a lack of compatibility between metal NPs and MWCNTs [18]. Surfactants and polymers are used to disperse MWCNTs effectively [19].

Polyaniline (PANI) [20] and its derivatives poly ortho-toluidine (POT) and Polypyyrole (PPy) [21] are the most attractive conducting polymers due to their ease of synthesis, high electrical conductivity, thermal stability, and environmental stability. Poly-ortho-toluidine has attracted interest due to better solubility in a wide range of solvents and ease of processing over PPy and PANI [22].

The purpose of present study to synthesize and characterization of Ag-Cu-MWCNTs alloy doped with Poly (Ortho-toluidine). There is no research on the topic synthesis of AgCu-MWCNTs alloy doped with POT is available. We are proposing that the synthesized Nano composite is low cost thus would be a better choice for electrode in solar energy sector.

II. Material and method

2.1. Chemicals

All the chemicals, copper nitrate Cu $(NO_3).3H_2O$, Silver nitrate $(AgNO_3)$, Sodium poly acrylate $(C_3H_3NaO_2)$, Sodium Borohydride $(NaBH_4)$, Sodium dodecyl benzene sulfonate $(C_{18}H_{28}NaO_3S)$, Multiwall carbon Nanotubes (MWCNTs), Sulphuric acid (H_2SO_4), Ammonium per sulphate (APS), O-Toluidine (C_7H_9N), Acetone and Deionized water were purchased in Pakistan. All these reagents were analytical grade and used without purification.

2.2 Synthesis of AgCu alloy NPs

AgCu NPs were produced by chemical reduction method. In this method first take 0.7 M of Cu $(NO_3)_2.3H_2O$ and 0.7 M of $C_3H_3NaO_2$ solutions in (10ml) deionized water were prepared and mixed under constant stirring at 25℃ for 50 minutes. After 50 minutes add 1.68 M of $NaBH_4$ solution in 10ml deionized water was rapidly injected into solution and stirred for 20 minutes. After that add (2.17M) $AgNO_3$ solution in 10ml deionized water and then added into above solution stirred for last 25 minutes at room temperature. The formations of black precipitates of AgCu were separated via centrifugation.

2.3 Preparation of POT coated AgCu-MWCNTs nanocomposite

For making POT coated nanocomposites firstly, Ortho-toluidine (1 M) acts as monomer was dissolved in 10ml deionized water 25℃, then a sulfuric acid H_2SO_4 (1 M) was add and stirred at 25℃ for 25 minutes. After that as prepared AgCu alloy NPs were dissolved with Ortho-toluidine solution stirred for next 50 minutes. Then polymerization step occurs when adding drop wise Ammonium per sulphate (APS) solution of (0.5 M) left the solution for continuous stirring for 15 hours. MWCNTs disperse via anionic surfactants name as Sodium dodecyl benzene sulfonate (SDBS). For this add MWCNTs into SDBS solution then solution was sonicated for 90 minutes at 35^0C. After that POT coated AgCu solution was added and stirred at 35^0C for next 90 minutes. At the end we get required AgCu-MWCNTs coated POT nanocomposite which was washed several times with acetone to remove residual and dried over night at 45^0C.

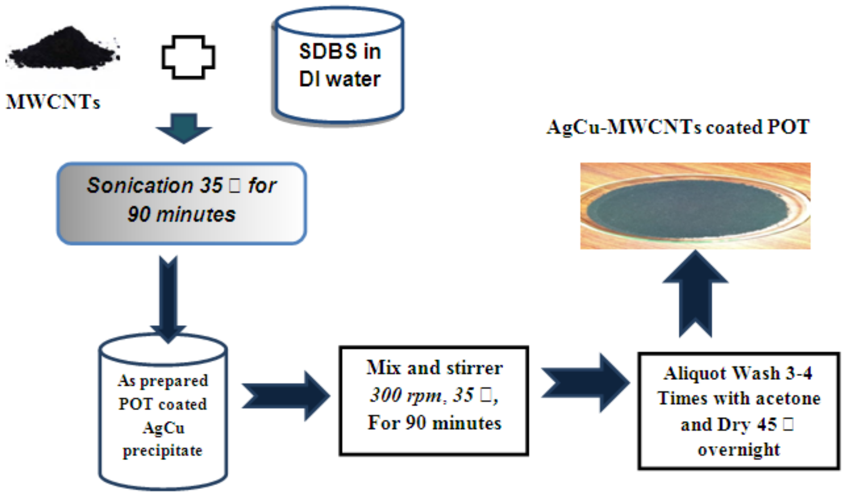

Fig. 1 – Flow chart of preparation of AgCu-MWCNTs coated POT composite.

III. Characterization

X-ray was employed to examine the phase, crystal structure and crystalline size of sample. The X-ray diffractometer used for this analysis was Bruker D8 Advance Diffractometer prepared with copper tube ((λ = 1.5406A) and average range was set from 20^0 to 80^0 along with step size of 0.02^0. Fourier Transform Infrared Spectroscopy was used to detect compositional analysis. The spectrometer used for analysis was Perkin-Elmer double beam spectrophotometer in combination with KBr disc. Range of the spectral series was taken from 4000-400 cm^{-1} at room temperature. Scanning electron microscopy was employed to examine the surface morphology of the nanocomposite. VEGA 3 TESCAN (Czech Republic) 10 nanometers at 30 kV was used to take the SEM micrographs and the double carbon coated sticky tapes were used to analyze the sample and evade charging.

IV. Results and Discussion

4.1. phase Identification

XRD of AgCu-MWCNTs Coated POT nanocomposite was done for phase identification and crystalline behavior. **Error! Reference source not found.** reveals the XRD pattern of the AgCu-MWCNTs Coated POT nanocomposite.

The reflecting planes (200), (220), (311) corresponding to 2θ angles 44.51°, 64.52°, and 78.01° respectively shows the characteristic peaks of Ag nanoparticles which is reference by (JCPDS no.04-0783.

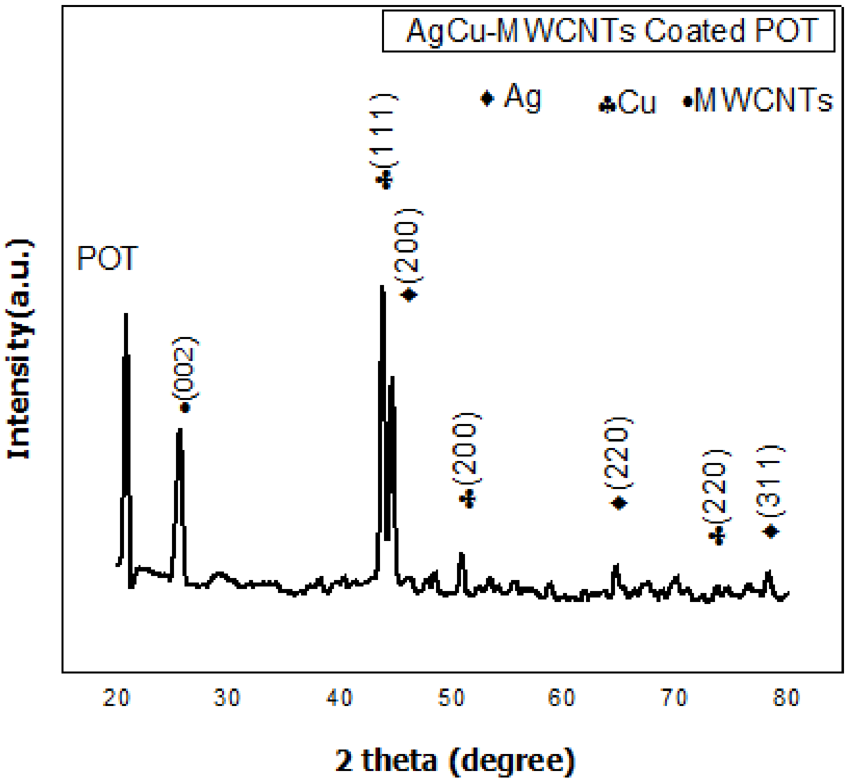

Fig. *2*– XRD pattern of AgCu- MWCNTs Coated POT composite

The reflecting planes (111), (200) and (220) corresponding to 2θ angles 43.66°, 50.01°, and 73.62° respectively shows the characteristic peaks of cu nanoparticles (JCPDS no.04 -0836[23]. Diffraction peaks are present at value of 25.4° corresponding to planes of (002) confirmed by presence of MWCNTs matched with JCPDS 96-101-1061 [24]. The other intense peaks at 2θ around 20° an associated with POT. The size was found using Scherrer Equation and found to be 25.21nm. The presence of fine and intense lines was shown during the analysis of this powder x - ray diffraction, indicating that our sample had a good crystallization. Furthermore, no further lines indicating the creation of secondary phases were observed, confirming the purity of the acquired phase.

4.2. Compositional Studies

Fourier-Transform Infrared spectroscopy (FTIR) was used to analyze the composition of the AgCu-MWCNTs Coated POT nanocomposite. Infrared rays interact with particles and provide information on the presence of elements in a composite.

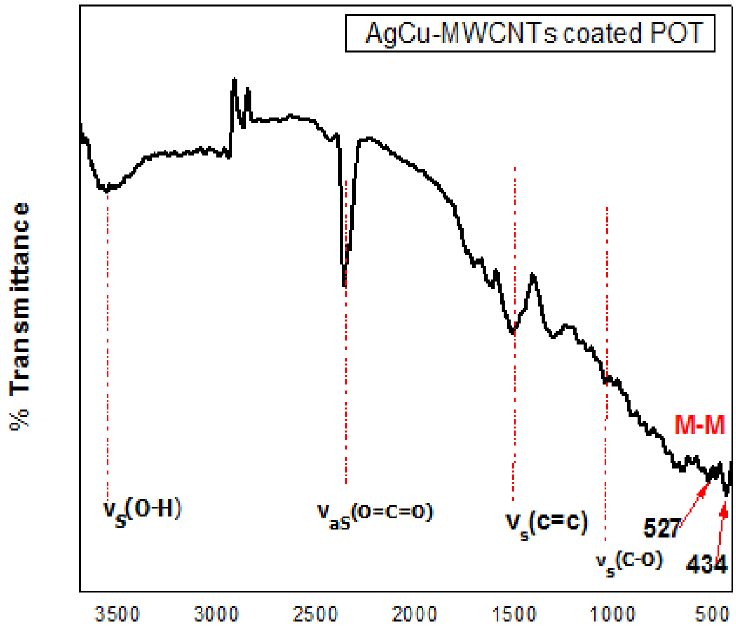

Fig. *3*– FTIR of AgCu- MWCNTs Coated POT composite

Fig. 3 illustrate the FTIR spectra of the AgCu-MWCNTs Coated POT composite. The absorption peaks observed at 527 cm^{-1} and 434 cm^{-1} indicate the presence of **Metal-to-Metal** bonding [25]. The peak appeared at 1046 cm^{-1} corresponding to C-O stretching. The presence of **C=C** was revealed by the absorption spectra at **1535cm-1** which indicate the presence of the **MWCNTs**. A medium peak observed at **2312cm^{-1}** is due the carbon dioxide absorbs from surrounding. A broad band at **3200** cm^{-1} to **3,500** cm^{-1} is assigned to **O–H** stretching frequency indicating the presence of **hydroxyl groups**.

4.3 Morphology studies

The surface morphological behavior of the AgCu NPs and AgCu-MWCNTs Coated POT composite were reveals through SEM analysis which are shown in Fig,4 and Fig.5 respectively.

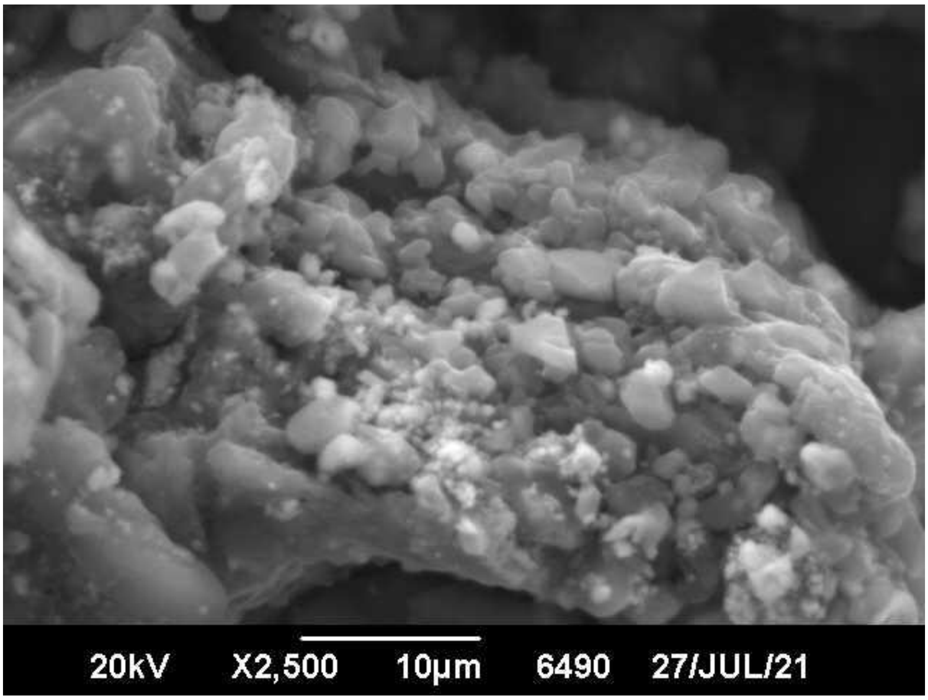

Fig 4. SEM image of AgCu alloy

It is clear from fig.4 that the formation of both crystalline and amorphous regions containing particles with uniformly disturbed. The morphology of AgCu NPs has changed by the introduction of MWCNTs as displayed in Fig.5.it can be seen that MWCNTS exert a strong effect on the morphology of AgCu in the nanocomposite. The spherical crystal structure was observed signifying the formation of AgCu alloy which are well dispersed on POT polymer. MWCNTs are well dispersed in the conducting polymer. The SEM image of AgCu-MWCNTs Coated POT nanocomposite shows the formation of interwoven fibrous structure that would help nanoparticles to enhanced conductivity. The formation of fibrous phase composite is due to interaction between O-toluidine monomer and MWCNTs. Some O-toluidine monomers may have polymerized on the surface of MWCNTs, and the remaining amount of O-toluidine monomer may have polymerized into the fibrous structures.

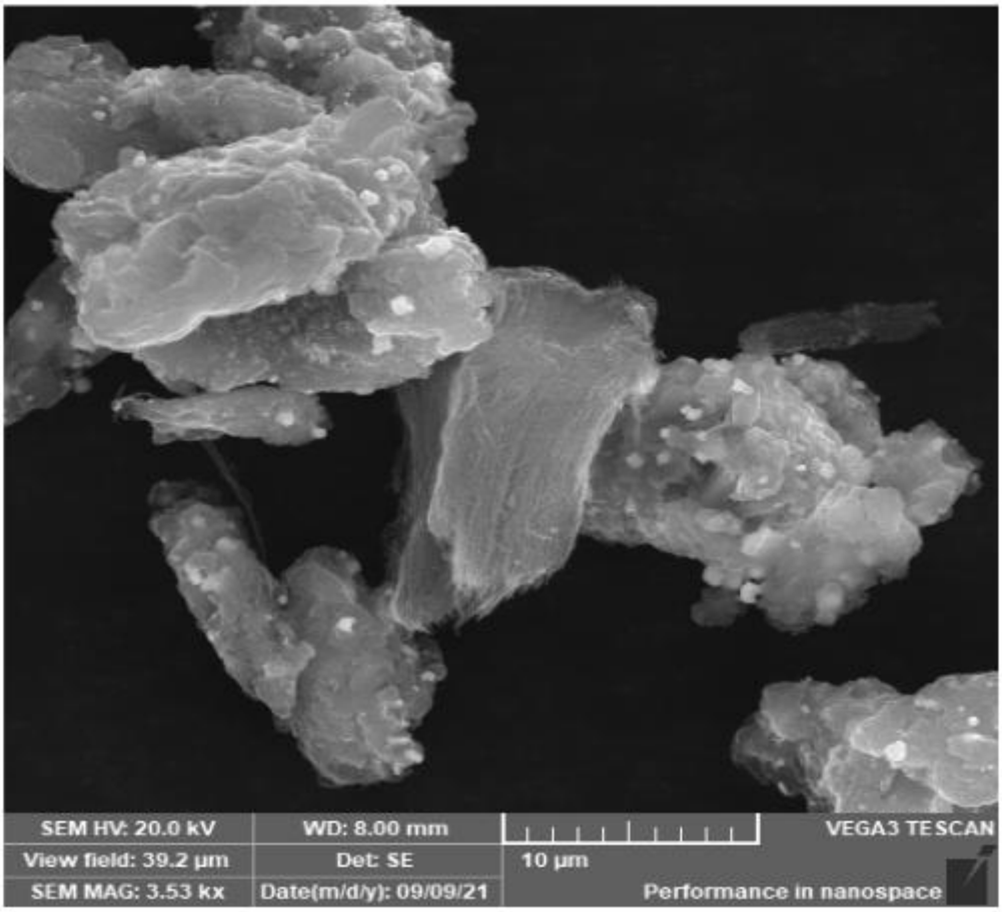

Fig 5. SEM image of AgCu-MWCNTs coated POT composite

V. Conclusion

In this work, we successfully synthesized AgCu-MWCNTs Coated POT nanocomposite via in situ polymerization of O-toluidine monomer and AgCu-MWCNTs composite. The XRD studies reveals that the structure of nanocomposite has intense single phase which indicates our sample have good crystalline behavior. The size of particles was found to be 25.21nm. The FTIR analysis indicate that good interaction exists between POT and AgCu-MWCNTs particles. The surface morphology confirmed the formation interwoven fibrous structures in which O-toluidine monomer and MWCNTs are well compactable also MWCNTs are well dispersed in composite. So, our synthesized AgCu-MWCNTs Coated POT nanocomposite would be great potential for electrode materials in solar application because of its low cost and easy production.

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