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Deposition and characteristics investigations of nano-carbons deposited by electrochemical route

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The nano-carbons / carbon nano tubes (CNT) have been synthesized by a noble electrochemical route using a non-aqueous bath. We have synthesized the carbon nano tubes (CNT) by making use of the monomer precursor as the potassium iodide (KI) in different molar concentrations. The nano-carbons / CNTs have been investigated electrochemically by using cyclic- voltammetry and current-time transient response. The cyclic voltammetry results show that the potential lower than -1.5 V leads for the intercalation of the potassium precursor in to the graphite sheets. Also performed current-time transient response results for the periodic oscillations the interval of 70 seconds. Optical absorbance studies result for the semi conducting nature of deposited nano carbons. Photoluminescence (PL) studies indicate luminescent nature of nano carbons in the visible region. X-ray diffraction (XRD) pattern shows close resemblance with the JCPDS data of (C_{60}) fullerenes i.e. carbon nanotubes. The investigated surface morphological (STM) study results needle shaped structure or the cylindrical shaped structure of the nano carbons deposited in the ITO substrate.

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1. Introduction

Since the discovery of carbon nanotubes in 1991 by S. lijima [1], the understanding of the unique physical properties of wrapped graphene like materials [2–4] and their metal filled derivates [5,6] have attracted large attention among researchers. Carbon nanotubes have unique nanostructures with remarkable electronic and mechanical properties. The research communities have been focused enormous interest on their unusual electronic properties, since nanotubes can be considered as prototypes for a one-dimensional quantum wire. As other useful properties have been discovered, particularly strength, interest has grown in potential applications. Carbon nano-tubes could be used for conducting lightweight and strong materials [7] and nanometer-sized electronics or to strengthen polymer materials [8-11].

Carbon nano tubes are attracting interest as constituents of novel nano-scale materials [12-14], device applications [15–16], novel-mechanic, electronic, magnetic and chemical properties [17]. At present, there are several approaches to produce nano-tubes. The arc discharge method [3], carbon vapor method [4] and the use of pyrolisis hydrocarbons like benzene at approx. 1000 ^{o}C or laser vaporization have been earlier workers used for these synthesis of carbon nano-tubes. A common drawback of all the mentioned methods are a number of impurities incorporated in the nano tube material, whose type and amount depend on the deposition technique. The most common are of carbonic nature such as graphitic or amorphous nano-particles.

In this present paper we represent an alternative method for the growth of nano-cabons/ carbon nano-tubes. In this process carbon nano-tubes have been deposited on Indium Tin Oxide (ITO) coated glass substrate as a thin film. It is very pure phase contains only nano-tubes or needle-like structures and adheres very well to the substrate. Moreover, this electrochemical effort resulted out for the synthesis of the CNT or nano-carbons. The experimental details and the results of the electrochemical, optical and structural characterizations of the films have been described.

2. Experimental detials

The nano-carbons have been synthesized by involving three-electrode geometry in an electro-deposition route. The electrolyte was prepared using 0.5 M solution of Potassium Iodide in ethylene glycol at 200 ^{o}C in the electrochemical cell. The electrochemical cell involved the graphite as the working electrode and molybdenum electrode as the counter electrode. The potential has been applied on working electrode with respect to the saturated calomel electrode. The current time transients have been recorded by applying a constant potential of –1.7 V involving the graphite electrode and ITO electrode. The current time transient response was recorded using a data acquisition system.

The cyclic voltammetry and current time transient response was carried out by potentiostat / galvanostat (EC&G USA Model 362) with a function generator in a serial interface. The optical absorption spectroscopy was

carried out by UV- Visible spectrophotometer (UVPC-1601 Shimatzu) in the spectral range of 300 nm to 1100 nm using the spectral band with of 2 nm. The photoluminescence measurements (PL) were performed by computer controlled luminescence spectrometer (LS-55 Perkin Elmer Instruments, UK) at room temperature. The X- ray diffraction (XRD) studies were performed out in grazing angle mode for the nano carbon thin film grown on the ITO substrate. The particular scan range for nano-carbon sample was kept $2\theta = 20^{o}$-35^{o} for the unannealed and annealed sample at 500 ^{o}C respectively. The morphological profile has been investigated by scanning tunneling microscopy (STM) by using SPM 9500 J2 Shimatzu instrument.

3. Results and disscussion

3.1. Cyclic voltammetry

Cyclic voltammetry studies give information about the electrochemical reactions occurring at working electrode. The cyclic voltammetry recorded by using the scan rate 10 mV/sec as shown in Fig. 1.

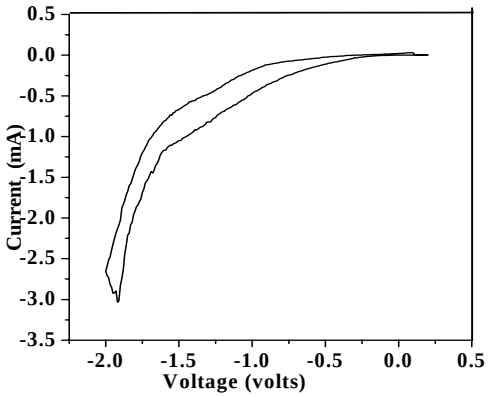

Fig. 1. The cyclic voltammetry recorded using scan rate of 10mV/sec.

The graphite and molybdenum electrodes have been used as the working and reference electrode in particular potential range of -2.0 V to +2.0 V. The cyclic voltammetry studies have been revealed out several interesting features. The occurrence of particular electrochemical process is revealed by the onset of the current or a peak in the cyclic voltammograme. The cyclic voltammetric plot did not result any noticeable peak except a sharp exponential rise of cathodic current at potential beyond –1.5 V, which corresponds to intercalation of potassium in graphite planes. Interestingly, It is also noted that during reverse sweep current still rises on decreasing the voltage. This shows that intercalation can be carried out in the potential window of –1.5 V to –2.0 V. Therefore, the current time transient response has been recorded at a constant working electrode potential of – 1.7 V using ITO coated glass as a working electrode.

The current time transient response recorded at constant potential of 1.7 V is as shown in Fig. 2. The resulted response exhibits periodic oscillations with an interval of 70 seconds. These periodic oscillations correspond to the maximum possible concentration of the intercalated potassium, which can reside within the graphite layers. Higher degree of intercalation leads to breaking of the graphite atomic planes, hence the drop in current was observed. The process is repeated as evidenced by current time response in Fig. 2.

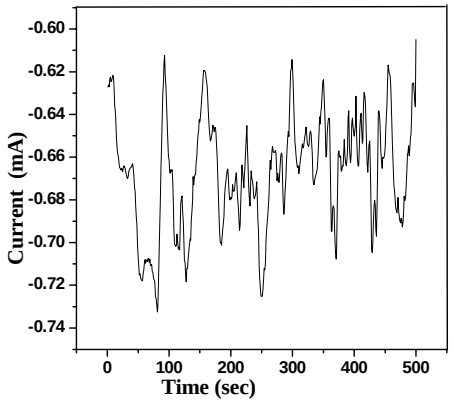

Fig. 2. The current and time transient response recorded at graphite electrode.

3.2. X-Ray diffraction

Fig. 3 shows the recorded XRD pattern of graphite substrate and the nano-crystalline film deposited on the Ni substrate in the deposited condition and annealed at 500 ^{o}C. The graphite substrate exhibited a single well-defined peak at $2\theta = 26.59^{0}$ corresponding d-value of 3.35 Å. The above-described sharp peak corresponds to (002) plane, which shows good agreement with the respective JCPDS data.

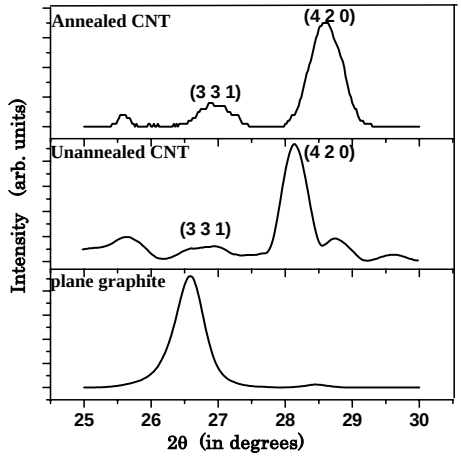

Fig. 3. XRD spectra recorded for (a) plane graphite nano-crystalline film on the Ni substrate (b) as deposited condition (c) annealed at 500 ^{o}C temperatures.

This diffraction peak is attributed due to the graphite structure of MWNT [18]. The peaks recorded for nano-crystalline carbon film in un-annealed and annealed do not show any resemblance to the peak corresponds to the plane graphite substrate. This implied that the nano-crystalline carbon film have been formed by reorganization of the atoms originated from the graphite atomic planes. The reorganization of atoms is followed by the intercalation of the potassium in the graphite planes. Interestingly, the X-Ray diffraction data recorded for the deposited films obtained at $2\theta = 28.12^0$ showed close resemblance with standard data of C_{60}. Also, we observed five new diffraction peaks of un-annealed film at $2\theta = 25.12^0$, 27.12^0, 28.12^0, 28.75^0 and 29.60^0 corresponding to inter-planar spacing of 3.48, 3.30, 3.17, 3.10 and 3.01 Å respectively. The film annealed at 500 ^oC results three new diffraction peaks at $2\theta = 25.57^0$, 26.96^0 and 28.58^0 corresponding d-values of 3.46 Å, 3.30 Å and 3.17 Å respectively. The two diffraction peaks recorded for unannealed film at $2\theta = 27.12^0$ and 28.12^0 and for annealed film $2\theta = 26.96^0$ and 28.58^0 matches with the corresponding JCPDS data of C_{60}. The above described peaks correspond to miller indices are (331) and (420) respectively. These two planes indicate electrochemical recycling of graphite atoms enables the formation of C_{60}. It is clear from the annealed film that diffraction peaks become sharper with increasing the temperature of heat treatment. Moreover, several new peaks corresponding to $2\theta = 25.12^0$, 28.75^0 and 29.60^0 could not be identified. The XRD spectra for annealed film revealed that the peak position shifted toward higher angle side and inter-planner spacing decreases respectively, which may be attributed to change in crystallinity or may be due to rearrangement of atoms within the C_{60}.

3.3. Absorbance spectroscopy

Fig. 4 shows the absorption spectra of the sample. The absorption spectra resulted two-absorption onsets at 385 nm and 260 nm, which corresponds to energy value 3.21 eV and 4.75 eV respectively.

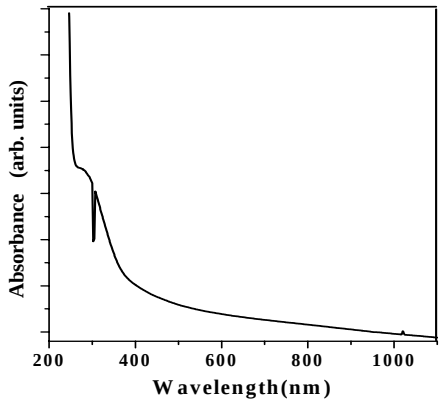

Fig. 4. Measured optical absorbance spectra for electrodeposited nano carbon film deposited on ITO substrate.

The onset position was determined by taking second derivative of absorbance spectrum. For carbon nano tubes, excitonic effects play an important role in the optical spectrum of metallic tubes. The peak corresponding to energy value 3.21 eV is shown resulted from a bound excitonic peak of metallic tubes. This onset resulted out the fundamental absorption band gap of electrodeposited carbon nano tube is 3.25 eV approximately, which is the same as reported by J.B. Neaton et al [19]. The broad wide band up to 3.21 eV is due to the inter-band transitions. The onset at 4.75 eV is due to π to π^* transitions or weak Vander Waals bonding nature [20]. Hence the excitonic effects are essential in explaining and predicting the optical response of carbon nano tubes. The obtained energy values showed that sample of nano-crystalline carbon particles are semiconducting in nature.

3.4. Photoluminescence spectroscopy

Photoluminescence (PL) spectra recorded within the spectral range of 300 to 500 nm as shown in Fig. 5.

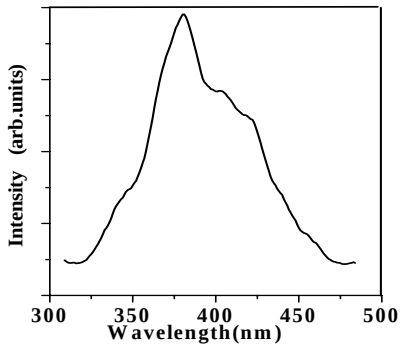

Fig. 5. Measured photoluminescence (PL) spectra for electrodeposited nano carbon particles.

The PL intensity is assumed to be the product of the induced photon absorption, relaxation rate and spontaneous photon emission. The graph shows broad band recorded at excitation wavelength 250 nm, which corresponds to tunnel absorption onset. The PL spectra revealed four peaks centered at 340 nm, 381 nm, 404 nm and 422 nm with energy value of 3.65 eV, 3.25 eV, 3.06 eV and 2.94 eV respectively. The sharp intense peak at 3.25 eV is stronger for the single walled and semi conducting nano tubes carbon nano tubes. Moreover, this PL intensity of the sharp peak in decreases with decrease in the chiral angle, which is similar as observed by Y. Oyama et al [21]. These nano tubes exhibit low PL intensities due to their very small relaxation rates. These resulted PL peaks showed the luminescent nature of deposited nano carbons in the visible region range.

3.5. Scanning tunneling microscopy

The STM image of a typical annealed film of nano-carbon composed of very fine needle shaped objects. A high-resolution image of a typical needle shaped structure

has been shown in Fig. 6. The area scanned was 158.20 × 158.20 nm. The diameter of the tubular structure was measured 4.0 Å approximately. The lattice atomic image of this tube has also been shown in the inset of Fig. 6. The separation between the two atomic sites is founded as 3.0 Å, which shows close resemblance with our X-ray diffraction results. Thus STM image actually corresponds to the carbon atom and the structure is a carbon nano-tube. Hence these investigations leads for the deposited sample film are cylindrical carbon nano tube.

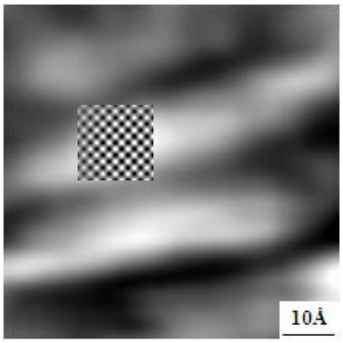

Fig. 6. The morphological image obtained by scanning tunneling microscopy of electrodeposited film of nano carbon particles on ITO coated glass substrate. Inset image shows the higher resolution image of cylindrical carbon nano tube.

4. Conclusion

We have synthesized cylindrical carbon nanotubes/ nano carbons successfully by using an electrochemical route. The cyclic voltammetry studies resulted out about the intercalation of the potassium precursor in the graphite layers with the period of 70 seconds. X-ray diffraction studies showed the close resemblance of observed peaks with JCPDS data of the carbon nano tubes (C_{60}). Optical studies resulted out the optical band gap of 3.27 eV, which reveals the semiconducting nature of deposited nano carbons. A Photoluminescence spectrum shows the luminescent behavior in the visible region. Scanning tunneling microscopic image of nano-carbons annealed at 500 ^{o}C composed of very fine needle shaped objects. The measured tubular diameter and separation between the two atomic sites was founded to be 4 Å and 3 Å respectively. In this present paper, we have successfully determined out the possibility of making carbon nano-tubes structures (C_{60}).

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