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Multi walled carbon nanotube decorated with TiO_2 based Biosensors for Imaging

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ABSTRACT

Carbon nanotubes fluorescence in a region of the near-infrared, where human tissue and biological fluids are particularly transparent to their emission, but especially in the last decade it has attracted scientific and economic interest triggered by a rapid increase in response to specific biomolecules. A suitable scheme to conjugate the drug and the nanotube is required to make CNTs into viable delivery vehicles. In this present work, multi walled carbon nanotube decorated with titanium dioxide (TiO_2-MWNTs) particles have been synthesized and employed as acceptor type materials in organic bulk heterojunction. The donor type material employed in the blend was regioregular poly (3-Octyl Thiophene) (RR-P_3OT). X-ray diffraction (XRD), UV-Visible spectroscopy, FT-IR spectroscopy and scanning electron microscopy (SEM) characterized and analyzed.

Introduction

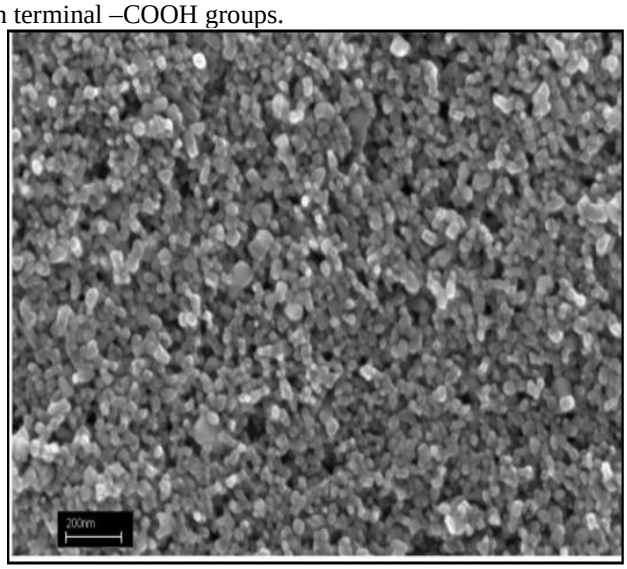
The nanotubes are hydrophobic and therefore insoluble in liquid biological media, so various methods have been exploited to functionalize the nanotubes, both covalently and noncovalently to make them soluble [1]. TiO_2 is widely used as white pigment because of its brightness. TiO_2 nano particles are typically sized less than 100 nm. As the size of the particles reduces to the nanometer scale, new photochemical characteristics occur in the particles. For example, (rutile) nano. Additionally, as TiO_2 is exposed to ultraviolet light, it becomes increasingly hydrophilic (attractive to water), thus it can be used for anti-fogging coatings and self-cleaning windows[2]. ZnO Nanoparticles are used as a pigment in paints. They are less opaque then TiO_2. ZnO absorbs both UVA and UVB rays of UV-light. Additionally, since zinc oxide has antimicrobial and antifungal activities [3].

The optical properties of nanotubes impart promising advantages to their use in imaging applications within live cells and tissues [4]. The unique photostability of SWNT photoluminescence allows for longer excitation time at higher laser fluorescence than either organic fluorophores or quantum dots. Also, in the range of 700–1400 nm, visibly opaque tissue exhibits greatly attenuated absorption, auto fluorescence, and scattering characteristics. This range overlaps with the fluorescence profiles of many semiconducting nanotubes, allowing their observation in whole blood and thick tissue directly imaged nanotubes after incorporation by macrophages, observing no photo bleaching – a phenomenon that plagues conventional biological imaging. Nanotube fluorescence was also used to image SWNT in tissue sections as well as measure their concentration in blood [5]. The majority of the solar radiation lies in the visible and IR regions, whereas that of P_3OT poly (3-Octyl Thiophene) falls in the visible region. With the incorporation of MWNTs and metal oxide decorated MWNTs, the band gap is expected to decrease towards the IR region. Hence, we have employed titanium dioxide decorated on MWNTs (TiO_2-MWNTs) as acceptor type materials in organic bulk heterojunction.

Experimental

Preparation of multi-walled carbon nanotube

MWNTs were synthesized by catalytic chemical vapor deposition (CVD) technique which involves the decomposition of hydrocarbon gases on the substrate in the presence of metal catalyst particles (Fe, Ni, Co) [6]. They were purified by air oxidation at 450 °C followed by acid treatment. For further functionalization, the MWNTs were dispersed into nitric acids and refluxed for 16 hours at 80° C to eliminate impurities and to produce shortened MWNTs with terminal –COOH groups.



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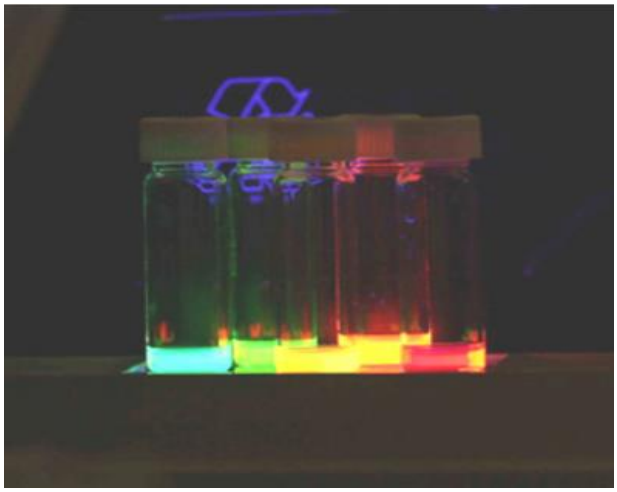

a) ***Electron micrograph of (anatase) titanium dioxide (TiO2) nanoparticles; b) Colloidal quantum dots irradiated with a UV light. Different sized quantum dots emit different color light due to quantum confinement***

Incorporation of titanium dioxide on multi-walled carbon nanotubes

The Sol-Gel solution (SGS) was prepared using titanium tetraisopropoxide Ti $(OPr)_4$, isopropanol (IPA), nitric acid (HNO_3) and distilled water (H_2O). The weight ratio for the SGS preparation is kept as 1:10:1:0.2 for $Ti(OPr)_4$: IPA: H_2O: HNO_3. The solution was reflux at the temperature 80° C for a period of 1 hour, using a magnetic stirrer. For each sample, 0.2 g of MWNTs were mixed with 50 ml of SGS and stirred in close vials for 3 hours. The impregnated MWNTs were separated from the solution by filtration process [7]. To obtain TiO_2-MWNTs the filtered nanotubes were dried in an oven at 80° C for 1 hour under atmospheric conditions followed by thermal treatment at 450° C for 1 hour. The dried TiO_2-MWNTs can be easily dissolved in chloroform to prepare solution.

Synthesis of TiO2-MWNTs doped P_3OT solution

P_3OT dissolved in chloroform and was added into the (1) MWNTs solution, (2) TiO_2-MWNTs solution and mixed under sonication for 30 min to prepare P_3OT –MWNTs and TiO_2-MWNTs doped P_3OT solution.

Fabrication of TiO_2-MWNTs doped P_3HT and P_3HTdoped MWNTs

The ITO glass substrate was ultrasonically cleaned in a series of organic solvents (ethanol, methanol and acetone) [8]. A 40 nm thick layer of PEDOT: PSS was spin coated onto the ITO glass consecutively to modify the ITO substrate surface. After baking at 120° C for 30 min in the oven, the sample was transferred to a nitrogen filled glove box for active layer deposition. Two kinds of active layer materials: (1) P_3OT/MWNTs, (2) TiO_2-MWNTs doped P_3HT, were spin-coated on the ITO glass. The thin film formed was then dried in a covered glass Petri-dish.

Results and discussion

The surface morphology of the prepared samples were studied by scanning electron microscopy (SEM). Fig.1 gives the SEM image of the MWNTs wherein densely packed MWNTs are clearly seen. The morphology of TiO_2- MWNTs is clearly seen from Fig.2. The TiO_2- MWNTs nanoparticles are uniformly dispersed on MWNTs. The confirmation of the presence of TiO_2 was done by an EDX (Energy Dispersion X-ray Analysis) (Fig. 3).

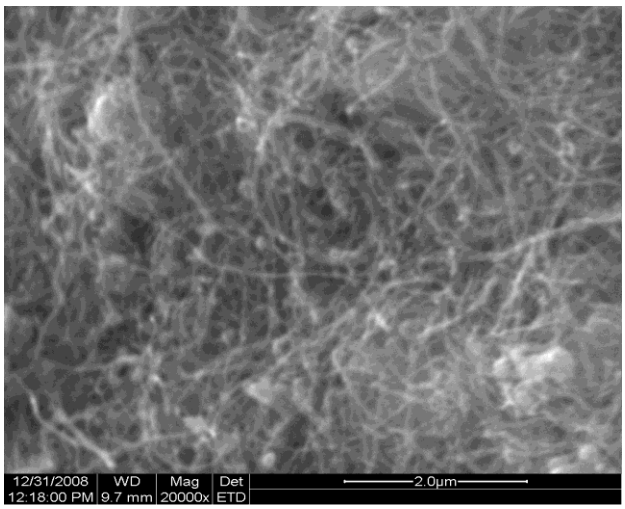

Fig 1. SEM image of MWNTs

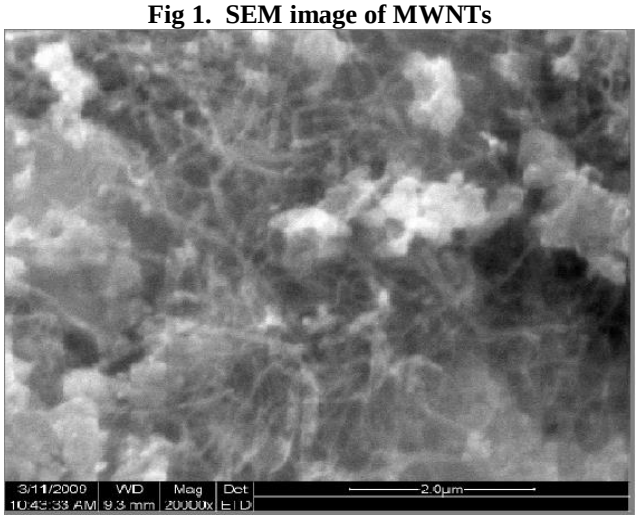

Fig 2. SEM images of TiO_2-MWNTs

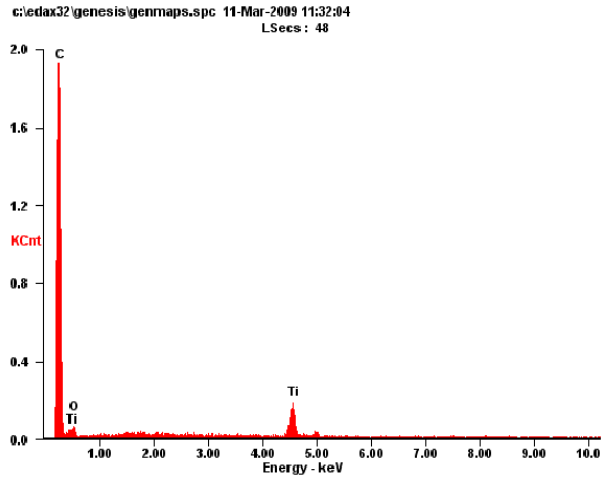

Fig 3. EDX image of TiO_2-MWNTs

XRD

The powder X-ray diffractograms of the samples are shown in Fig. 4. The XRD pattern of functionalized MWNTs shown in Fig. 4(a) wherein the planes have been indexed to that of hexagonal graphite. With th planes C (002) and C (101) are prominent. Fig.4 (b) shows the XRD pattern of TiO_2-MWNTs wherein the characteristic planes of TiO_2 are clearly seen along with those of MWNTs. The broad size of the peaks indicates smaller the particle size as further confirmed from Scherrer formula.

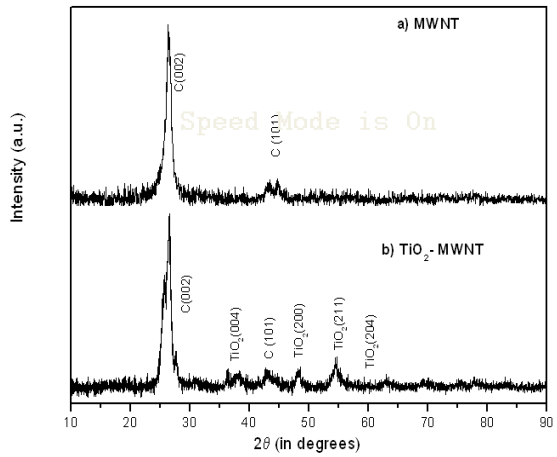

Fig 4. XRD patterns of a) MWNTs and b) TiO_2-MWNTs

FT-IR

FT-IR spectra of the samples are shown in fig. 3. Fig. 3(a) gives the FT-IR spectra of functionalized MWNTs wherein the various functional groups are clearly seen. On the dispersion of TiO_2 particles onto MWNTs new peaks appear and also the intensity of some of the peaks reduces. This indicates that TiO_2 particles have attached to these anchoring sites. It is known that MWNTs have hydrophobic surface and poor dispersion stability. To avoid these problems the pretreatment of MWNTs is needed for many applications. Carboxylic acid groups could be generated easily by oxidation of MWNTs, by acid treatment [9]. Acid treated MWNTs have a hydrophilic surface. The carboxylic acid groups on the surface of MWNTs have a polar covalent bonding by the electro negativity difference. Thus, we could consider that acid treated MWNTs have a generally negatively charged surface. The negatively charged surface of MWNTs enhances the stability of dispersion.

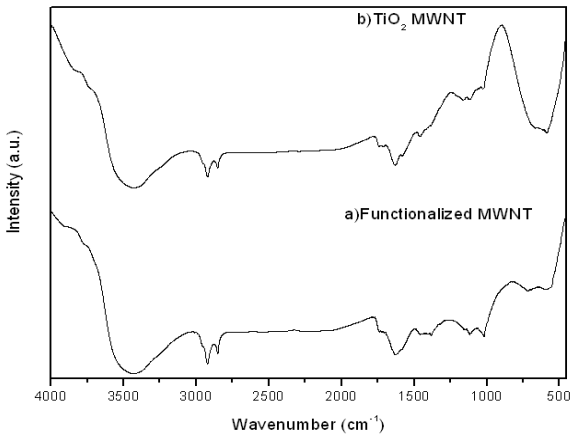

Fig 5. FT-IR spectra of a) MWNTs and b) TiO_2-MWNTs

Conclusion

The sensor could be implanted into tissue, excited with a near-infrared light source, and provide real-time, continuous sensing of blood glucose level by fluorescence response. The therapeutic effect of drugs is constantly being increased through the development of new delivery vehicles. Previously, these vehicles included viral vectors, liposome, cationic lipids, polymers, and nanoparticles. While viral vectors have an inbuilt transfection capability, there have been safety concerns surrounding their use, opening the door for other vehicles [10]. Although nonviral vehicles have versatility of shape, size and materials, one issue of concern is the poor penetration of some therapeutic agents into cells. Carbon nanotubes are readily internalized by cells; and after surface modification, they exhibit low cytotoxicity over the period of a few days [11-12]. In addition, they have a higher surface area to volume ratio than spheres, giving nanotubes the potential to be conjugated with more functional agents than spheres [13] and to accommodate higher loadings of therapeutic agents [14]. For these reasons, nanotubes have received a lot of attention as potential Potential Applications of Carbon Nanotubes vehicles for drug delivery.

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