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Biocompatible multi-walled carbon nanotube–CdTe quantum dot–polymer hybrids for medical applications

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ABSTRACT

Herein we report the synthesis of polymer coated quantum dots (QDs)–carbon nanotube composite material with high biocompatibility and low cellular toxicity. The synthesized multi-walled carbon nanotube (MWCNT)–QD-(-poly(glycidyl methacrylate)) (pGMA) hybrids were characterized using X-ray photoelectron spectroscopy, laser scanning confocal microscopy, transmission electron microscopy and scanning electron microscopy. The results showed that quantum dots were well-distributed on nanotube surfaces in high density. The toxicological assessments of QDs and MWCNT–QD–polymer hybrids in human mammary carcinoma cells and their fluorescence imaging in living cell system were carried out. MWCNT–QD–polymer hybrids possess intense red fluorescence signal under confocal microscopy and good fluorescence stability over 6-h exposure in living cell system. The toxicity comparison of QDs and MWCNT–QD–polymer hybrids has shown that the existence of PGMA thin coating on MWCNT–QD hybrid surface decreased the cellular toxicity and increased biocompatibility.

1. Introduction

Carbon nanotubes (CNTs) have shown interesting applications in many fields because of their extraordinary physical, chemical, and mechanical properties [1–8]. A large number of applications are dependent on chemical modification of CNTs with organic and inorganic materials [9]. Among inorganic compounds, metals, metal salts, oxides and metal based quantum dots (QDs) are used to modify the surfaces of CNTs. There are also various organic components such as aliphatic hydrocarbons, aromatic and heteroaromatic compounds, carotenoids, and several others, particularly polymers [10] to modify carbon nanotube surfaces. Potential applications of biocompatible CNTs in biomedical studies are biosensing, drug delivery [11], antimicrobial activity [12,13], gene transfection and tissue engineering, including cellular tracking and imaging [14–20]. The applications of CNTs are dependent on functional groups on their surfaces and functionalizing of CNTs surfaces is a significant step to produce biocompatible CNTs [21–23]. But analysis of CNTs in applications for biological fields has some disadvantages because visualization in biological environments using simple fluorescence microscopy is not easy without any functionalization or modification of CNTs surfaces [24]. Therefore, different types of fluorophores to functionalize CNTs were developed for the purpose of imaging [25,26]. Transmission electron microscopy technique is used to analyze CNTs in cells; however real-time analysis is not possible with this technique [27]. Therefore, fluorescence molecule–CNT hybrids have been developed to make real-time analysis possible [11–12]. But fluorescent quantum yield of organic molecules dramatically decreases when bonded to CNT surfaces, which limits the sensitivity and also reliability of the analysis. On the other hand, semiconductor quantum dots exhibit size dependent fluorescence emission with narrow bands, high fluorescence quantum yield and photo-stability [28–34].

Biological studies, in which quantum dots are used together with carbon nanotube-polymer composite materials, are rare [35–37]. Moreover, to our knowledge, cytotoxicity of the CNT–QD hybrids and their fluorescence stabilities in living cells have not been explored in detail yet [36].

In this paper, we have successfully functionalized surfaces of multi-walled carbon nanotubes (MWCNT) with QDs and encapsulated the QD functionalized MWCNT surfaces with poly(glycidyl methacrylate)

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(pGMA) to obtain biocompatible materials. pGMA was coated on MWCNT surfaces using an initiated chemical vapor deposition method. Chemical vapor deposition (CVD) is a dry method to produce thin films. The substrates with complex geometries can be coated by initiated chemical vapor deposition (iCVD) with high uniformity, without solvent related damages, which are observed in conventional wet processes. In the iCVD method, substrate is cooled to promote adsorption of the species for the film growth. Therefore the substrate to be coated remains isolated from high temperatures, plasma or light sources, which can alter the chemical and/or physical nature of the substrates. Therefore, iCVD was selected to be an ideal method to functionalize and encapsulate the surfaces of MWCNTs. Morphological characterization of the obtained composite materials was made by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and confocal microscopy. Chemical structure of the encapsulation polymer PGMA was analyzed with X-ray photoelectron spectroscopy (XPS). Finally QDs and QD–CNT hybrids were applied to mammary carcinoma cell line MCF-7 in dose and time dependent manner. Results demonstrate that QD–CNT hybrid composite has lower toxicity on cells. Also the hybrid composites were visualized in living cells by confocal microscopy. These results prove that QD–CNT hybrid composite may be a candidate material to be used in diagnosis of cancer cells.

2. Material and method

2.1. Chemicals and materials

Cadmium chloride ($CdCl_2 \cdot 5/2H_2O$), 3-mercaptopropionic acid (MPA, 99%), tellurium powder (Te, 99.5%), and sodium borohydride ($NaBH_4$ 99.99%) were purchased from Sigma-Aldrich. To adjust the pH of reaction mixture, 0.1 mol L^{-1} KOH was used. All aqueous solutions were prepared with ultrapure water and all solutions used for chemical procedures were fresh. For polymer synthesis, the monomer glycidyl methacrylate (GMA) and the initiator tertbutyl peroxide (TBPO) were purchased from Sigma-Aldrich. Both the initiator and the monomer were used as-received without further purification. Ultrahigh purity hydrogen and ethylene gases were obtained from Linde Gas for MWCNT synthesis.

2.2. Preparation of MWCNT–QD hybrids (composite materials)

CdTe quantum dots (QDs) were prepared according to procedure reported previously by our group [38]. All synthesis reactions were carried out under nitrogen gas. The $Cd(MPA)_2$ precursor was prepared by mixing n moles $CdCl_2 \cdot 5/2H_2O$ with $2n$ moles MPA in water. pH of the solution was adjusted to 12 with 0.1 mol L^{-1} KOH. The prepared solution of Cd–thiolate complex was loaded in a three-necked flask. It was left under nitrogen gas environment for 30 min and heated to 100 °C. To prepare 10.0 ml of fresh NaHTe aqueous solution, $NaBH_4$ and Te powder (0.2 mmol) were used and the procedure was carried out under nitrogen. The precursor solutions were injected into the reaction system by vigorously stirring, and reaction solution was refluxed at 100 °C. The prepared QDs were precipitated and washed with 2-propanol more than three times. The QDs were dried overnight at room temperature.

The MWCNTs were synthesized in a hot wall chemical vapor deposition reactor from hydrogen and ethylene gases over Fe/Al_2O_3 (Fe/Al = 1:1) catalyst at 650 °C. In order to remove the catalyst impurities, nanotubes were treated with dilute hydrofluoric acid and hydrochloric acid solutions separately. Final MWCNTs were obtained after extensive washing with water and ethanol, and drying at 60 °C overnight.

QDs solution was prepared in Milli-Q ultrapure water (10 mg/ml). To functionalize surfaces of MWCNTs, QDs solution was dropped on MWCNTs and the mixture was left under vacuum overnight at room temperature.

Surfaces of MWCNTs were coated by a thin PGMA film by using the iCVD method. The details of the iCVD coating process are given elsewhere [39]. The monomer GMA was vaporized at 65 °C in a stainless steel jar and fed to the reactor. TBPO was used as the initiator and vaporized at room temperature in a glass jar. Flow

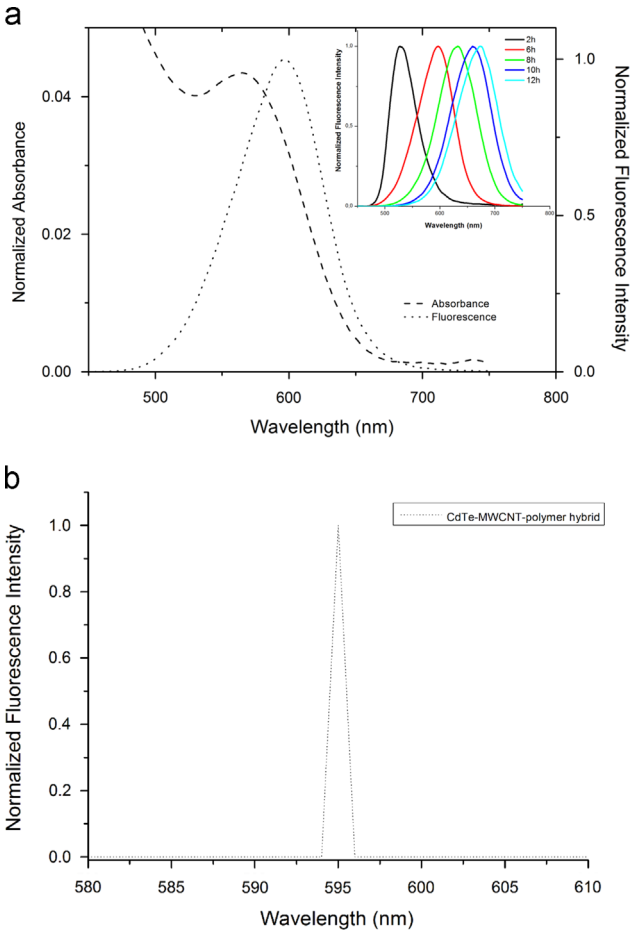

Fig. 1. (a) Absorption and photoluminescence spectra of CdTe QDs and (b) photoluminescence spectra of MWCNT–QD–pGMA nanohybrids.

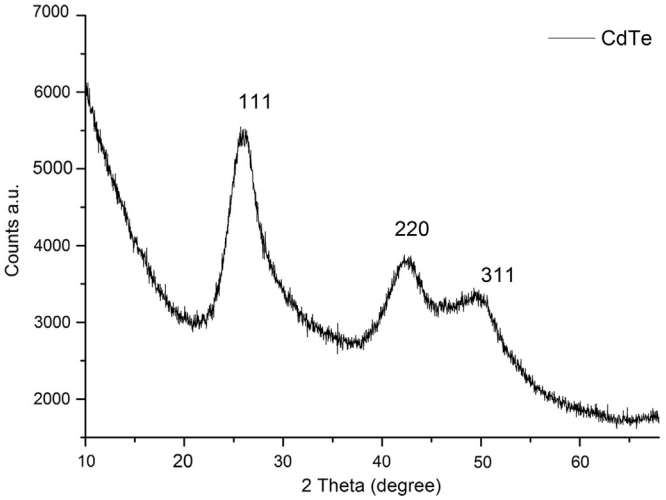

Fig. 2. XRD image of CdTe QDs.