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Full Length Article

Role of CdSe quantum dots in the structure and antibacterial activity of chitosan/poly ε-caprolactone thin films

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ABSTRACT

Chitosan/polycaprolactone (Ch/PCL) semi-natural polymeric blend containing gradient concentrations of CdSe quantum dots (QDs) dopant were synthesized via hot injection method. Synthesized samples containing different concentration of CdSe QDs were characterized by X-ray diffraction and FTIR absorption spectroscopy. FTIR experimental data of synthesized samples shows the maintenance of characteristic vibrational band with a marginal variation in both intensity and position related to the increase in dopant concentration. XRD patterns reveals amorphous nature of prepared virgin blend and blend samples that contain small amount of QDs. Samples with higher QDs concentration, namely (0.008, 0.016) wt% shows appearance of crystalline bands related to the (1 1 1) reflection plane and in agreement with JCPDS card no. 19-0191. Scanning electron microscopy (SEM) indicates that morphology of synthesized biocomposites is critically affected by addition of CdSe QDs.

Antibacterial tests reveals different inhibition zone related to increasing concentration of CdSe QDs and type of bacteria under investigation. Evaluation of The activity index % were also studied.

1. Introduction

Chitosan is a natural polymer classified as polysaccharide that composed of a random distribution of β-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine with a chemical formula $(C_6H_{11}O_4N)_n$ [1] which can be obtained from deacetylation process of chitin that considered as the second most abundant polysaccharide primarily extracted from exoskeleton of sea creatures [2–4]. Chitosan gained its cationic nature due to amino groups that grants biological activity at low pH values that results in a high capacity to interact with negatively charged compounds including proteins or anionic polysaccharides.

Poly ε-caprolactone (PCL) is a hydrophobic synthetic semi-crystalline polyester with the chemical formula $(C_6H_{10}O_2)_n$ that synthesized by ring opening polymerization of monomer (ε-caprolactone) via cationic, anionic and co-ordination catalysts or by free radical ring-opening polymerization of 2-methylene-1-3-dioxepane [5]. PCL usually characterized by slow degradation rate combined with high plasticity and ductility that can help counter balance the rapid degradation of natural polymers and increase the structural stability of the scaffolds obtained from their blends [6,7].

Blending of natural and synthetic polymers namely PCL with cellulose, starch and chitin may result in a new class of materials suitable with desired properties for bio-application as unique [8–12]. The hydrophobic character of PCL decreases the physicochemical interactions with cells laying on its surface and their blends considered as a good candidate for the construction of 3D scaffolds results from slow degradation rate and its ability to maintain its morphology and mechanical properties after implanted that enhance mechanical properties of chitosan based scaffolds especially in the wet state [13]. PCL/Ch blends have been used as scaffold materials in the controlled release of drugs like Ofloxacin [14] and in nerve tissue reconstruction [15]. Ch/PCL ratio of 75/25 has higher hydrophilicity and better mechanical properties and cell adhesion and proliferation than PCL scaffolds.

Quantum dots (QDs) are spherical nano-sized crystals that may be formed of almost all semiconducting metals including CdSe, CdS, CdTe, PbS and ZnS while, alloys or any other metals may be used [16,17]. Cadmium selenide (CdSe) may be considered as an archetypal quantum dot with size range from 2 to 10 nm in diameter (10–50 atoms). Many types of quantum dot will emit light of specific frequencies if electricity or light is applied to them. These frequencies can be precisely tuned by changing the dot's size, [18,19], giving rise to many applications. QDs were introduced to

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biological cell as alternative fluorescent probes in recent years. It uses in biological imaging, bio-sensing and intracellular detection and targeting, solar cells, quantum computing, transistors, LEDs and diode lasers [20]. Density function theory (DFT) is computational quantum mechanical method utilized as a part of physical science, material science to research the electronic structure (the ground state) of numerous body system, specifically particles, and atoms. It is a standout amongst the most well-known and effective quantum mechanical ways to deal with matter.

The present work aims to introduce a routine characterization for a novel semi-natural polymeric blend containing gradient concentration of CdSe QDs. FTIR, density functional theory (DFT) and XRD was employed to approve the reaction mechanisms between both constituents of organic matrix and that with inorganic dopant. In addition, the antimicrobial tests were performed to study the effect CdSe QDs on different gram-positive, gram-negative and fungi.

2. Experiment and method

2.1. Materials

Chitosan of molecular weight 6.0×10^5 [2-Amino-2-deoxy-(1-4)glucopyranan] with the chemical formula $(C_8H_{11}NO)_n$, supplied by Aldrich Co. Poly ε-caprolactone of average molecular weight 45,000 with chemical formula $(C_6H_{10}O_2)_n$, supplied by Aldrich in pellets form. Acetic acid, ethanol and other solvents of high purity were supplied by Sham Lab. Co.

2.2. Sample preparation

CdSe QDs were synthesized via ordinary hot injection route previously reported [21,22]. In the synthesis route 0.8 mmol of CdO was added to about 20 mmol of stearic acid in a tri-neck flask with smooth heating (70–110 °C) in nitrogen atmosphere. The temperature was raised gradually to 180 °C after the formation of cadmium stearate (colorless solution). One mmol of Se metal powder and 3 mL of trioctylphosphine (TOP) were injected to the flask. Six equal amount of reaction mixture were collected every 15 min to permit the QDs formation and growth. The samples were instantaneously diluted and cooled with toluene to discontinue CdSe particles growth. Obtained QDs were washed in methanol media and centrifuged.

Chitosan and poly ε-caprolactone were dissolved in 0.2 M aqueous acetic acid and glacial acetic acid respectively. Ch/ PCL (75/25) poly blend was prepared using casting technique. Gradient concentration of the QDs were added to form thin film of desired concentrations. Samples were kept in evacuated dissector until use. Table 1 lists the abbreviation and sample composition.

2.3. Physical measurements

Single beam (Nicolet *iS*10, USA) spectrophotometer was used to record the FTIR experiment data in the spectral range (4000–400) cm^{-1} and with resolution of 2 cm^{-1} to study the vibrational mode of the specimens.

X-ray diffraction scans were obtained using PANalytical X'Pert PRO XRD system using Cu K_α target with secondary monochromator (where, λ = 1.540 Å, the tube operated at 45 kV–40 mA (Holland), the Bragg's angle (2θ) in the range of (5–80°). In this analysis, the peak locations (2θ) in X-ray diffraction spectra are used to identify the different crystalline structures in the pure and doped films.

The morphology of the films was characterized by scanning electron microscope using SEM Model Quanta 250 FEG (Field Emission Gun) with accelerating voltage 30 kV, magnification 14× up to 1,000,000 and resolution for Gun.1n). Size and shape of QDs determined using HRTEM (JEOL-JEM-2100) with accelerating voltage 200 kV while UV/Vis. measurement was performed using JASCO V770 Spectrophotometer.

Table 1
Sample notation and composition.

Sample	Chitosan	PCL	CdSe
	wt%		
CdSe0	75	25	0.000
CdSe1	75	25	0.001
CdSe2	75	25	0.002
CdSe4	75	25	0.004
CdSe8	75	25	0.008
CdSe16	75	25	0.016

3. Results and discussions

3.1. Characterization of prepared QDs

Fig. 1 revels UV UV/Vis optical absorption spectra of prepared CdSe QDs combined with high resolution transmission electron micrographs (HRTEM). Obtained micrograph shows that synthesized material are of spherical shape with size ranging from 4 to 5 nm. UV/Vis. optical absorption spectrum was found to be in agreement with that reported for the same sample previously reported [21,22].

3.2. Fourier transform-infrared spectroscopy (FTIR)

FTIR absorption experimental data of prepared pristine polymeric matrices and their blend films shown in Fig. 2 reveals the maintenance of basic vibrational groups belong to the backbone matrices of both Ch and PCL. The absorption bands observed in the chitosan spectra at 2951, 2872 cm^{-1} can be assigned to the stretching vibrations of CH_3, while bands at 1648, 1555 cm^{-1} may be attributed to (—C=O) secondary amide and (—C=O) protonated amine stretching respectively. Other bands located at 1165, 1025 cm^{-1} are assigned to C—O—C asymmetric stretching and (C—O—C) a symmetric and (C—O—C) symmetric vibration respectively. The band at 3429, 1724, 1412 cm^{-1} is assigned to (O—H) overlapped to the (N—H) stretching vibrations, (C=O) carbonyl stretching and (CH_3) symmetric deformation. Same observation with marginal variation in peak position and/or intensity may be

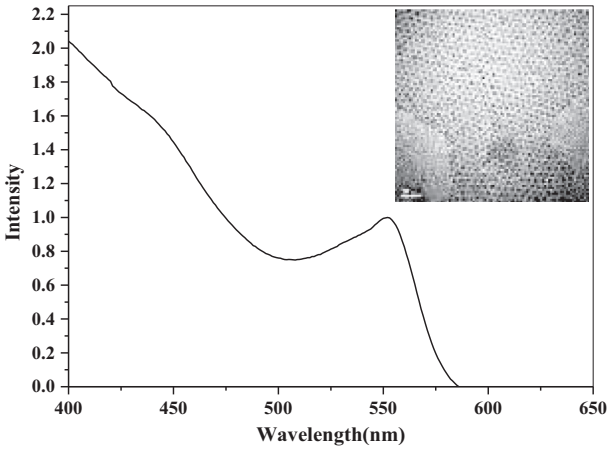

Fig. 1. Revels UV UV/Vis optical absorption spectra of prepared CdSe QDs combined with high resolution transmission electron micrographs.