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Surface functionalized bare and core–shell quantum dots in poly(ethylene-co-vinyl acetate) for light selective nanocomposite films

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ABSTRACT

Light-selective polymer films based on poly(ethylene-vinyl acetate) (PEVA) are of significant interest in emerging solar materials, including PV encapsulants and greenhouse plastic films. Quantum dots (QDs) have been shown to absorb UV light while transmitting light of higher wavelengths which potentially can be advantageous for enhancing PV efficiencies or in the case of greenhouse films, controlling plant growth. However, a simple procedure for integration of the QD nanocrystals into PEVA films with retention of the light selective properties has been elusive. In this work we report a simple procedure for loading QD nanocrystals into PEVA using a novel silane functionalized QD approach by simple melt-mixing in a twin-screw extruder. Both bare CdS and core–shell CdS–ZnS QDs were synthesized by colloidal chemistry using a facile single-molecular precursor method, and then functionalized with (3-mercaptopropyl)trimethoxysilane to improve their compatibility with PEVA. These nanocrystals were then melt-mixed into PEVA in a mini-compounder, with the resulting blends extruded and pressed into thin films using a Universal Film Maker and a Carver hydraulic press. Both experimental and commercial greenhouse films were analyzed by electron, confocal and atomic force microscopy, showing that the silane ligand enhanced dispersibility of QDs throughout the PEVA. The bare and core–shell QDs were studied at various loading levels from 0.1% to 0.5%, showing high light transmissions (90%) and decreased UV transmission with increased QD loading.

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1. Introduction

Polymer coatings and films with light harvesting properties are of tremendous current interest in which UV radiation from the sun is converted efficiently into more useful higher wavelengths. These higher wavelengths are favorable for plant growth in greenhouse films [1] and can also help potentially enhance PV panel efficiencies through downregulation [2]. Defined as small semiconducting nanocrystals, quantum dots (QDs), such as CdS, show promise as a converting material to convert UV energy into longer wavelength lights, such as red or blue [3]. However, a simple procedure for integration of heterojunction QD nanocrystals into polymer films without aggregation while retaining their light selective properties has been elusive. We previously examined silane coupling approaches in supercritical carbon dioxide (scCO₂), where the QDs were directly attached to vinyl acetate polymer chains [4]. However, aggregation was still observed and the approach suffered from problems with using commercial ethylene vinyl acetate resins suitable for greenhouse application or PV encapsulants.

In order to integrate the QDs with polymers to produce functional nanocomposites with suitable properties, the QDs need

to be functionalized with specific organic ligands to improve their binding ability [4,5]. The addition of a higher band gap inorganic material shell in core–shell structured QDs is advantageous and has been shown to improve the optical properties and reduce the toxicity of the bare QD cores [4,6,7]. The fluorescence quantum yield is increased by negating surface defects on the optically active core, which reduces the effects of blinking [4,6–8]. The shell of the QDs improves the photostability and effective lifetime by providing a physical barrier that separates the core from the surrounding environment, protecting the optical properties from the negative effects caused by prolonged exposure to light and water [6]. Furthermore, the addition of the inorganic shell reduces the tendency of the nanoparticles to aggregate and makes them more robust, improving their tolerance to processing conditions necessary for incorporation into polymers [4].

Of particular interest for this work was integration of QDs into polymer greenhouse films. Recent studies using light emitting diodes (LEDs) in greenhouses have demonstrated that increased photosynthesis rates can be achieved, as well as improvements to plant growth and development, resulting in greater fruit yield of superior quality [9–11]. However, LED lighting is far too energy intensive and expensive for commercial operations, creating a need to investigate alternative methods for spectral manipulation. As nearly all available greenhouse plastics and PV encapsulants consist of ethylene-vinyl acetate (EVA) films [12,13], it would be

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useful to integrate the QDs into this polymer matrix. EVA plastics show high compatibility with fillers and additives [14,15], making them an excellent candidate for incorporation of QDs. The addition of the vinyl acetate (VA) component to ethylene decreases polymer crystallinity, enhancing the transparency of the films [11,12,16].

In this work CdS bare and CdS–ZnS core–shell structured quantum dots with size-dependent tunable optical properties were synthesized using a single-molecular precursor method, and then functionalized with 3-(mercaptopropyl)trimethoxysilane (MPS) to improve their compatibility prior to their incorporation into polymer films. We have previously reported that MPS was successfully employed as a ligand for both CdS bare and CdS–ZnS core–shell QDs in poly(vinyl acetate). By attaching the polar siloxyl group to the surface of the QDs, it was expected to improve the dispersibility of the QDs in PEVA matrix. These nanocrystals were melt-mixed into PEVA in a mini twin-screw extruder, and then pressed into thin films, which were characterized in terms of their optical properties and compared to the commercial greenhouse plastic films as regards performance.

2. Experimental

2.1. Materials

Argon (ultra-high purity, 99.9%, PRAXAIR), cadmium chloride (tech grade, A.C.S. reagent, Aldrich), sodium diethyldithiocarbamate trihydrate (A.C.S. reagent, Sigma-Aldrich), zinc diethyldithiocarbamate (98%, Aldrich), trioctylamine (TOA; 98%, Aldrich), trioctylphosphine (TOP; 97%, Aldrich), anhydrous ethanol ($\geq 99.5\%$, Sigma-Aldrich), methanol ($\geq 99.9\%$, CHROMOSOLV, Sigma-Aldrich), and toluene ($\geq 99\%$, Sigma-Aldrich) were used for the synthesis of bare CdS and CdS–ZnS core–shell quantum dots. 3-(Mercaptopropyl)trimethoxysilane (MPS; purum $\geq 95\%$, Fluka), anhydrous pentane ($\geq 99\%$, DriSolv) and toluene ($\geq 99\%$, Sigma-Aldrich) were used for ligand exchange to introduce new surface functionality to the QDs to facilitate their incorporation into the polymer films. Polyethylene (PE 220) and ethylene vinyl acetate co-polymer (Ateva[®] 1075, Ateva[®] 1941, Ateva[®] 2821, and Ateva[®] 3325) resins were provided by AT Plastics for use in the preparation of experimental greenhouse plastics.

2.2. Synthesis of quantum dots and polymer nanocomposite films

Both the bare CdS and CdS–ZnS core–shell quantum dots were prepared using colloidal chemistry following a single-molecular precursor method described by Xu and Charpentier [4] and Medina-Gonzalez et al. [17]. To formulate the cadmium diethyldithiocarbamate single-molecular precursor ($\text{Cd}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$) for QD synthesis, a 0.1 M aqueous solution of sodium diethyldithiocarbamate and 0.1 M cadmium chloride solution were prepared and dissolved using sonication. Stoichiometric amounts of each solution were reacted while stirring, yielding a white precipitate. The precipitate was collected using vacuum filtration, further purified by washing with distilled water, and then dried in a vacuum oven overnight at 40 °C. For the preparation of the core–shell CdS–ZnS QDs, 50 mL of trioctylamine (TOA) was heated while stirring in a 250 mL 3-necked round-bottom flask and inert argon atmosphere equipped with a reflux condenser, vacuum, thermocouple and temperature controller. When the temperature was stable at 220 °C, a solution of 1 g of cadmium diethyldithiocarbamate in 18 mL of TOP was rapidly injected into the flask, forming the cadmium sulfide cores. The cores were allowed to grow for 5 min, and then a solution of 0.4 g of $\text{Zn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ in 6 mL of trioctylphosphine (TOP) was slowly added, dropwise. After

a further reaction time of 10 min the heat was removed and the solution was cooled. When the temperature of the reaction mixture was approximately 75 °C, a large excess of methanol was added. The QDs were separated using centrifugation, washed using methanol and then re-centrifuged. Sonication was used to break up any aggregated material and help remove poorly capped and large particles. The product was then dispersed in toluene. For the synthesis of bare CdS QDs, a similar procedure was followed using a higher temperature of 240 °C and a reaction time of 15 min with no addition of $\text{Zn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$. For ligand exchange, the synthesized quantum dots were then reacted with 5 mM MPS while stirring in argon at 70 °C for 24 h. The mixture was cooled to room temperature and a large excess of pentane was added. The QDs were separated using centrifugation and re-dispersed in toluene. This process was repeated three times.

For the synthesis of the light selective experimental film, 5 g of PEVA pellets containing 9% VA content by weight was added to a Thermo Scientific HAAKE Mini-Lab II twin-screw micro-compounder at 130 °C. The pure polymer was allowed to melt and cycle for 5 min at a speed of 50 RPM and torque of 35 N cm. Varying concentrations of 0.1%, 0.2% and 0.5% of CdS or CdS–ZnS QDs were added by weight to the melted PEVA. The polymer and nanoparticles were left to cycle for a further 15 min under the previous conditions and then flushed from the extruder. The resulting blend was cut and weighed into 0.030 and 0.065 g pieces and pressed into thin films using a Spectra-Tech Universal Film Maker (UFM) kit and Carver hydraulic press. The platens of the UFM were heated to 120 °C and placed under 2000 psi for 4 min using 100 or 250 μm spacers. The films were left to cool under pressure for 10 min, and then transferred to a cooling chamber for a further 5 min.

2.3. Materials characterization

X-ray diffraction (XRD) was used to study the quantum dot crystal structure, confirm the chemical composition, and determine the approximate average particle size of the samples. Analysis was done in a Bruker D2 Phaser powder diffractometer using $\text{Cu K}\alpha$ radiation (λ for $\text{K}\alpha$ is equal to 1.54059 Å) over $2\theta = 0$ –100. Estimates for particle size were calculated from XRD diffraction patterns using Debye–Scherrer's equation in the Diffraction EVA XRD analysis software. A Phillips CM10 transmission electron microscope (TEM) was used to image the QD particles to observe particle size and shape at 80 kV. The nanoparticles were suspended in methanol and dispersed on a copper grid. Thin strips of the nano-composite experimental films were placed in an airtight gelatin capsule and filled with LR white, a polyhydroxy-aromatic acrylic embedding resin. The medium was placed in an oven to polymerize for 48 h at 60 °C. This was used as a support for the experimental films so they could be sectioned into thin slices using a Reichert Jung UltraCut Ultramicrotome with a diamond knife. The shavings were placed on a copper grid and imaged using TEM in order to view the particle dispersion below the surface of the films. Scanning electron microscopy was used to study the morphology of the QD samples. This was done using a Hitachi S-4500 field emission SEM. Elemental composition of the nanoparticles before and after ligand exchange was confirmed and quantified using the energy dispersive x-ray detection (EDX) feature of the SEM to monitor the change in elemental ratios present in each sample. A Shimadzu UV-3600 UV–vis–NIR spectrophotometer was used to measure the absorption spectrum of the QDs dispersed in toluene in the ultra-violet and visible range from 280 to 700 nm. The integrating sphere compartment of the spectrophotometer was used to measure the absorption behavior in the UV range as well as the visible transmittance and haze values of the commercial and experimental film samples. A PTI photoluminescence (PL) spectrophotometer was

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