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Green Synthesis of CdS Nanoparticles using Avocado Peel Extract

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Abstract

Cadmium sulfide (CdS) nanometre-sized particles have been prepared using an eco-friendly and low-cost method. This method relies on using parts of plants as reducing agents and protecting agents. Here, the synthesis of CdS nanoparticles using avocado peel extract, which converts Cd^{2+} to Cd atoms and then forms CdS nanoparticles, has been reported. The influence of pH, concentration of peel extract, and reaction time on the formation process of as-prepared CdS nanoparticles were studied. The structural properties of CdS nanoparticles were investigated using electron microscopic techniques (FE-SEM and TEM), and a majority of CdS particles with elongated to spherical shapes were observed. The crystalline structure of CdS nanoparticles (Face Center Cubic-FCC) was confirmed using XRD, and the nanoparticle size was estimated from the Debye-Scherrer equation at nearly 2.5 nm.

Keywords

Avocado peel, CdS nanoparticles, Structural properties, X-ray Diffraction

Introduction

Semiconductor materials have captivated researchers attention due to their unique optical and electronic properties. These properties rely strongly on shape, size, and crystalline structure. Semiconductor quantum dots possess many applications in lasers [1], electrochemical cells [2], biological labels [3], and optoelectronic devices. Among the semiconductor materials, CdS (II-VI semiconductor materials) have been gaining broad attention with regard to their potential properties. One of the key properties of CdS particles is their wide band gap energy (for bulk CdS is 2.42 eV at room temperature) [4], which makes them an essential component in optoelectronic devices [5, 6] and in solar cells (in which they are used as a window material) [7]. CdS nanoparticles are used as a pigment in engineered plastic and paints because of their chemical and thermal stability [8].

Moreover, CdS nanocrystals have incredible optical properties which lead to their use in lasers [9], sensors [10], optical filters [11], and light-emitting diodes [12, 13].

Finally, the photocatalytic properties of CdS open the door to their use in reducing the levels of pollutants in water, in addition to generating hydrogen by splitting water molecules with the help of solar energy [14, 15].

In nature, CdS has been found in three crystalline phases: zinc blende, high pressure rock salt, and wurtzite. The latter has been found in bulk and nano size CdS while the other two phases have been observed in nano-crystalline CdS [16, 17].

However, the most stable of the three is the wurtzite phase, though it has been found that the phases can be transformed from zinc blende to wurtzite phases or vice versa by changing the particle size [18], the concentration of the capping agent [19-21], reaction temperature [22, 23], or the components of the starting material [14]. Several chemical and physical techniques have been used to prepare CdS nano- structures, for instance, sol-gel [24], microwave heating [25], micro-emulsions [26], and sonoche- mical preparation [27], etc. Although most of these techniques are still used successfully, there are a considerable number of problems associated with them, such as the need to use various hazardous materials and solvents which may result in biological risk, some of which use high heat or ultrasonic waves that could affect the crystalline structures of the prepared nano-crystals. Furthermore, some nanoparticle preparation techniques employ high-power lasers [28, 29] to peel or deposit nanoparticles which incur additional costs or are not safe with such power. An alternative technique can be used to synthesize nanostructures. This technique is called a plant extract method (Green Synthesis), which are widely used in the fabrication of metal and semiconductor nanoparticles [30, 31]. This technique depends on the use of plant parts such as roots, leaves, and peels as capping agents and reducing agents. It is considered an easy, cheap, and eco-friendly method for fabricating materials on the nano sscale. There are many studies in the literature on the formation of semiconductor particles from plant extracts. However, little work had been conducted into the use of the plant extract method for preparing CdS nanoparticles. Therefore, here, it is reported, for the first time, the preparation of cadmium sulfide nanoparticles from avocado peel extract. Avocado is an active fruit contains many bioactive compounds such as phenols, hydroxybenzoic acid and flavonoid, [32], which is possibly serve as a capping agent to prevent or reduce the aggregation of CdS nanoparticles and control their stability.

Methodology

Avocado extract

An appropriate amount of avocado plant was bought from the local market. This fruit was washed several times with tap water followed by de-ionized water to remove any impurities and dust. The peel was then collected and dried for two days, then crashed into a fine powder. 10 g of the powder was dissolved in 100 ml deionized water, stirred, and heated for 8 minutes at 70 ^{o}C. After cooling, the avocado solution was filtered using filter paper. The supernatant was kept in a fridge at 40 ^{o}C.

Synthesis of CdS nano-objects

0.001 M of cadmium chloride and sodium sulfide were prepared separately, each being kept under vigorous stirring for half an hour at ambient temperature. To the cadmium chloride solution, an appropriate amount of the avocado peel extract was added and stirred for 10 minutes. To that solution, sodium sulfide was added slowly, and the solution was then left on magnetic stirring for a period of time. Centrifuging at 4000 rpm was used to separate the particles from the supernatant. In order to remove unwanted materials, such as organic materials, which could be bound to the prepared particles, the sample was washed three times with deionized water. The sample was then dried for 3 hours at 100^{o}C and kept in a dry place.

Optimum conditions for preparing CdS nanoparticles

To determine the optimum conditions for preparing and improving CdS nanocrystals, various parameters were studied such as the effect of reaction time, pH, and the concentration of the avocado peel extract.

The influence of reaction time on the absorption of CdS nanoparticles

The effect of the reaction time on the absorption of CdS nanoparticles was the first experiment conducted in this work. To determine the most favourable time to form large and stable CdS particles, the reaction flask, which contains $CdCl_2$, avocado extract, and Na_2S, was left on a magnetic stirrer for different interval times (0 h, 2 h, 4 h, and 6 h) before testing the resultant solution using a UV-vis spectrophotometer.

The effect of avocado extract concentration on the CdS nanoparticles absorption

The effect of avocado extract concentration on the formation of CdS nanoparticles was studied by varying the amount of the extract (2.5 ml, 5 ml, and 10 ml). The reaction was carried out at room temperature with 6 hours shaking.

The influence of pH on CdS nanoparticle absorption

Aliquots of the prepared solution was placed into six different flasks. The pH was adjusted using 0.1 M of NaOH and 0.1 M of HCl, to make the pH of the solutions 3, 5, 7, 8, 9, 11, and 12 (pH of the original solution was found to be 5) in each flask. All these solutions were measured at room temperature after 6 hours of mixing using a UV-vis spectr ophotometer.

Characterization of CdS nanoparticles

The formation of cadmium sulfide was monitored using the UV-vis spectrometer (UV-1800 Shimadzu spectrophotometer, Japan). An FT-IR spectropho- tometer (IRAffinity-1S, SHIMADZU) was used to identify the functional groups of the peel extract and to confirm the formation of CdS particles. The size and morphology of the prepared particles were obtained using transmission electron microscopy (TEM) and the ImageJ software program [33]. A field emission scanning electron microscope (FE-SEM) (Zeiss Model Sigma VP) was used to detect the surface morphology of the as-prepared CdS particles. The crystalline structure of our particles was determined via XRD (X pert pro-PANalytical company).

Results and Discussion

In order to establish the optimum conditions to produce large CdS nanocrystals, the reaction time was studied using a UV-vis spectrophotometer. After the addition of sodium sulfide to the solution containing cadmium chloride and avocado peel extract, the absorption spectra were recorded immediately

(0 h) then after 2, 4, and 6 hours. It is clear (see Figure 1) that the absorption band of cadmium sulfide nanoparticles relies strongly on the reaction time; the longer the reaction time, the more overlapping of CdS particles and more absorbance.

Therefore, for the following experiments, the reaction time was set at 6 hours, which gives an absorption wavelength of ~ 405 nm.

Figure 2 shows the effects of the concentration of the avocado peel extract on the formation process of CdS nanoparticles after 6 hours of mixing at room temperature. For the low extract concentration (2.5ml), no absorption peak was observed. When 5 ml of the peel extract was used, a weak band was observed at approximately 323 nm, which showed the nascent formation of CdS particles. A further increase in the avocado extract (to 10 ml) showed a significant increase in the absorbance, and a blue shift in the absorbance feature of about 120 nm compared to bulk CdS was noted. This blue shift could be attributed to the quantum confinement effect (which appeared when the particle size decreases to less than 10 nm) [34].

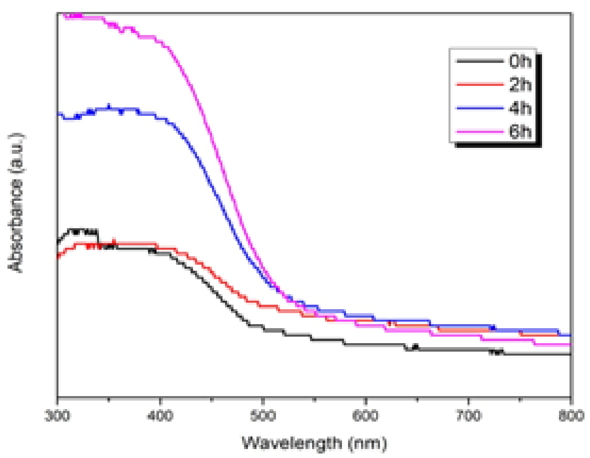

Figure 1: UV-vis spectra for cadmium sulfide nanoparticles as a function of the reaction time.

The effect of pH on the CdS nanoparticles absorption band was investigated by moderating the pH of the solution using HCl and NaOH, while the concentration of the peel extract was kept constant (10 ml) at room temperature.

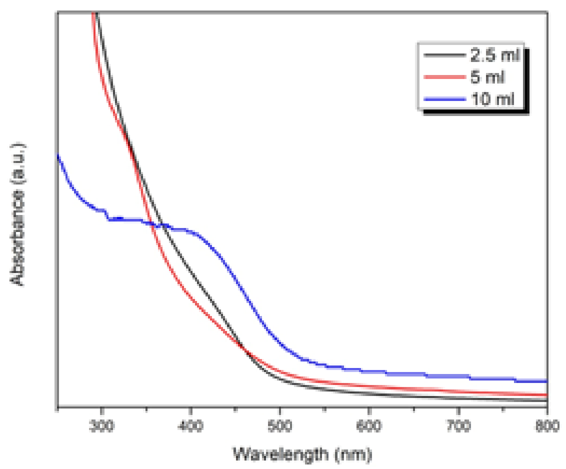

Figure 2: UV-vis spectra for cadmium sulfide nano- particles using different amounts of avocado peel extract (2.5, 5, and 10 ml).

In figure 3, different pH values of 3, 5, 7, 8, 9, 11, and 12 were studied (the pH of the original prepared CdS solution was 5). Under acidic conditions, small absorption peaks were found at around 325 nm, which indicates the formation of CdS particles.

As the alkalinity of the solution increases, the intensity of the absorbance of CdS particles increases due to an increased growth rate of CdS particles. At a pH of 11, a strong absorption peak at 395 nm was observed which indicates the formation of large-sized CdS nanoparticles compared to those formed at low pH. On the other hand, a strong red shift (~ 10 nm) compared to bulk CdS was observed when the pH was adjusted to 12, with a significant decline in the intensity of the CdS peak. This decline could be attributed to the formation of $Cd(OH)_2$ as a result of increasing the OH- concentration, which would accordingly reduce number of Cd^{2+} ions in solution. As a consequence, the quantity of CdS nanoparticles would also be significantly reduced [35].

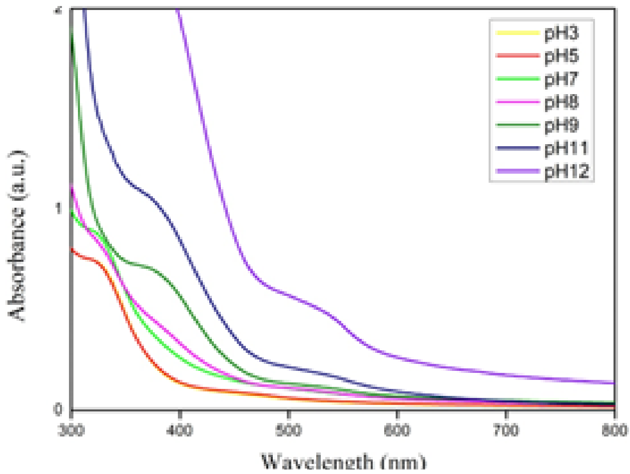

Figure 3: UV-vis spectra for cadmium sulfide nanoparticles prepared in the presence of avocado peel extract as a function of the pH.

Tuac's equation [36], as shown below, was used to estimate the band gap energy of cadmium sulfide particles at pH =11 and 10 ml extract.

$\alpha h\nu = C (h\nu - Eg)n$ ....(1)

Where, hν is the photon energy, n is equal to 0.5, which represents a direct electronic transition [37], Eg is the band gap energy, and α is the coefficient of absorption. It is clear from figure 4 that the band gap energy of as-prepared particles (3.25 eV) is larger than that of bulk CdS (2.24 eV), which is due to the quantum confinement effect [38].

It is obvious from figure 5 that as-prepared CdS particles are crystalline. Four peaks were seen in the XRD pattern, at 2θ = 27.6° (111), 31.8° (200), 45.6° (220), and 54.4° (311), corresponding to the cubic (zinc blende) phase [39]. The size of as-prepared CdS crystals was estimated from the Debye-Scherrer equation [40] for the diffraction peak (111), and is roughly 2.5 nm.

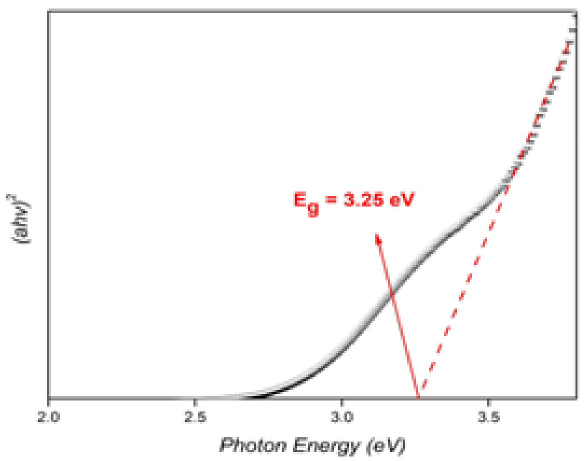

Figure 4: The band gap energy of CdS nanoparticles was calculated from the Tauc equation by extrapolating the linear portion of the UV-vis curve to the photon energy axis.

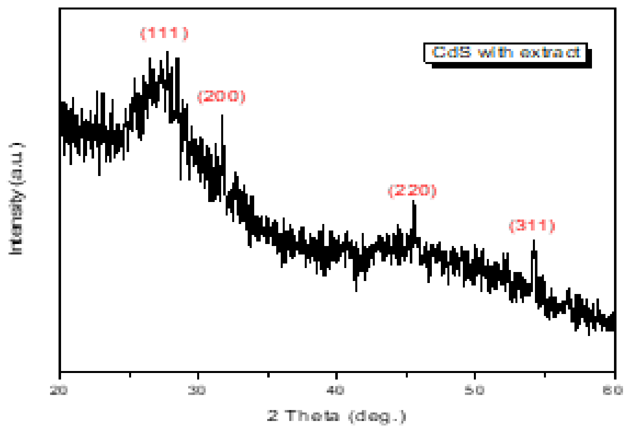

Figure 5: XRD pattern for CdS particles formed in the presence of avocado peel extract as a capping agent.

The TEM images in figure 6 show that CdS particles have a nearly spherical shape with ~ 6.5 nm in diameter. Particles agglomeration was not observed because of the presence of the avocado peel extract, which serves as a protecting agent. The large lump that appeared in the right-hand image may be the result of the association of CdS crystals during the drying process on the TEM grid [41, 42].

The surface morphology of CdS nanoparticles was examined by field emission scanning electron microscopy (FE-SEM), as shown in figure 7. It seems that the majority of CdS particles have elongated shapes, in addition to the spherical shape. Conclusive evidence for the production of CdS was found via FTIR. A significant peak appears at 405 cm^{-1}, which can be attributed to the Cd-S bond [43, 44]. Shown in the expanded view in figure 8. However, no corresponding peak was observed in the same region in the spectrum of the sample that included avocado peel extract. FTIR analysis of the peel extract and CdS particles with the extract shows a broad peak at 1639 cm^{-1} which can be assigned to the C = N asymmetric stretch [45]. The sharp peak at 1015 cm^{-1} can be assigned to the C-C-N asymmetric stretch of the species present in the avocado peel extract [46].

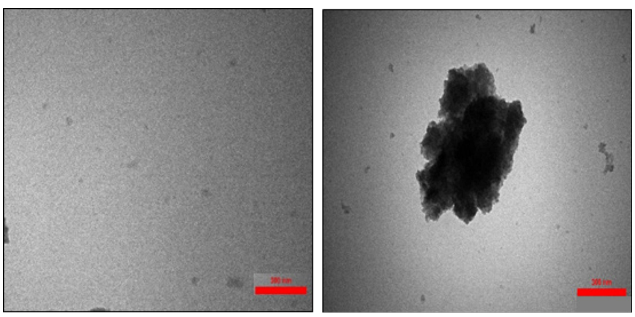

Figure 6: TEM images for CdS particles formed in the presence of avocado peel extract. The scale bar represents 300 nm.

The peaks that appear at 2922 cm^{-1} and 2853 cm^{-1} correspond to symmetric CH_2 stretching and asymmetric CH stretching vibrations. The broad band located at 3320 cm^{-1} is assigned to the stretching vibration of the OH functional group [47]. A strong band centered at 2350 cm^{-1} can be assigned to the S-H bond [43].

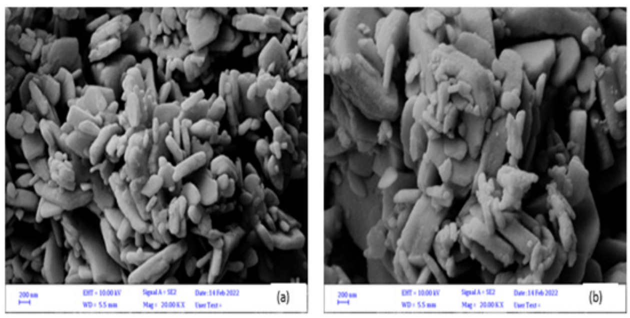

Figure 7: FE-SEM images of CdS particles at 20000 x.

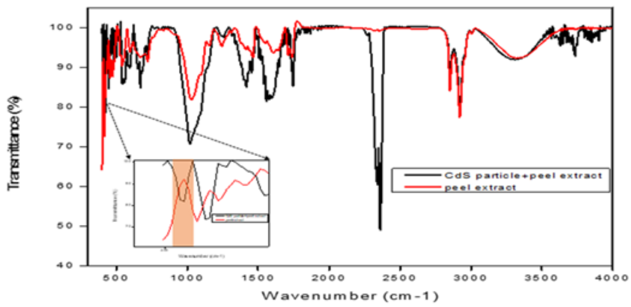

Figure 8: FT-IR spectra. The red line represents the avocado peel extract only and the black line represents the spectrum of CdS nanoparticles formed in the presence of avocado peel extract. The inset shows a significant peak appears at 405 cm^{-1}, which can be attributed to the Cd-S bond.

Conclusion

Avocado peel extract was used for the first time as a reducing agent to fabricate cadmium sulfide nanocrystals. Three physicochemical factors that are expected to affect the formation process of CdS nanoparticles were optimized: concentration of the peel extract, pH of the solution, and reaction time. pH 11 was found to represent the most favourable conditions under which to form CdS particles in the presence of 10 ml avocado peel extract. The XRD curve shows that the prepared CdS particles are crystalline with a size of approximately 2.5 nm. Microscopic techniques showed the formation of CdS nanoparticles with different morphologies (ranging from spherical to elongated structures). FTIR analysis shows evidence for the formation of CdS particles in the presence of avocado peel extract through the peak that appears at 405 cm^{-1}.

Acknowledgement

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Conflict of Interest

Nano.

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