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RESEARCH ARTICLE

Synthesis of Cds Nanoparticle by the Hydrothermal Method and the Contribution in Different Biological Uses

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Abstract: Cadmium sulfide CdS nanoparticles were synthesized in aqueous medium at pH constant, the obtained nanoparticles has been characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Cadmium sulfide nanoparticles were screened for their antibacterial and tested for antioxidant activity using 1,1-diphenyl-2-picrylhydrazyl (DPPH), hydroxyl radical ($OH^{\cdot}$) and hydrogen peroxide (H_2O_2) scavenging activity, ferric reducing power (FRP) assay and ferrous ion chelating (FIC) methods. The sizes of the crystallites were estimated to 12 nm using the Debye-Scherrer formula based on the XRD data. Transmission electron microscopy (TEM) results indicate that the CdS nanocrystals distribute uniformly and the size is 12 nm. The obtained CdS quantum dots present an antioxidant activity especially in oxido reduction power. It was found that CdS nanoparticles showed relatively higher antioxidant activities that this nanomaterial' scan react at the interface with the life entities.

Keywords: Nanoparticles, Semiconductors, Antioxidant activity

Introduction

The semiconductor nanoparticles also called quantum dots (QDs) have been characterized by sizes generally inferior to 100 nm. Due to this small size, they exhibit specific properties different from those of the corresponding bulk materials[1-3]. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material. The synthesis and properties of II-VI semiconductor quantum dots (QDs) have been extensively investigated over the last 30 years. The reason for this seems to be their special optical and electronic properties which arise from the quantum confinement of electrons and the large surface area[4-12]. The semiconducting nanocrystals of CdS are one of the more prominently studied and reported QDs for various applications. In bulk form, the CdS crystalisa hexagonal Wurtzite type structure with band gap energy Eg of 2.42 eV[13].

In absence of any surface passivation, most of the nanoparticle systems undergo aggregation leading to an impact on the optical properties. Thus, it is of paramount significance to develop methods for the surface passivation of nanoparticles. Organic stabilizers have been the most frequently reported capping agent for the above purpose[14]. Apart from maintaining the desired size distribution, the capping with stabilizers provides specific functional groups that may be exploited for various biological labeling[15]. In particular, CdS have been extensively studied due to their potential applications in several technological areas such as solar photovoltaic cells, nano bar codes, field effect transistors, light emitting diodes, photocatalysis and *in vivo* biomedical detection fluorescent tags in biology and the development of chemical and biological sensors[15-18].

In this context, the present study was focused on the contribution of CdS nanoparticles in biological uses, for that, nanoparticles has been synthesized and structurally characterized before been used in the *in vitro* evaluation of their antioxidant activities using 1,1-diphenyl-2-picrylhydrazyl (DPPH), hydroxyl radical (OH.) scavenging activity, ferric reducing power (FRP) assay and ferrous ion chelating (FIC). The study has been reinforced by screening in vivo tests for inactivation profiling with bacteria and fungus selected species.

Experimental

Cadmium chloride hydrate ($CdCl_2.H_2O$, 98%), thiourea (CH_4N_2S, ≥99%) propanoic acid ($C_3H_6O_2$, ≥99.5%) and sodium hydroxide solution (NaOH). All solutions were prepared using distilled water as the solvent.

Synthesis of CdS nanoparticale

CdS nanoparticles are prepared as follows. 5 mL of 0.1 M $CdCl_2.H_2O$ and 20 mL of 0.1 M $C_3H_6O_2$ were combined. The pH of this solution was adjusted to 10 using 2 M NaOH. Next, 4.5 mL of 0.1 M CH_4N_2S were quickly injected into the solution. The result precursor mixture was stirred at room temperature for 24 h, placed into a Teflon lined autoclave and finally subjected at 180 °C for 7 h. The nanocrystals were collected by centrifugation, washed 3 times with ethanol and then dried in air at 80 °C.

Characterizations

We have examined the structure, the average particle sizes and the phase composition of the resulting product by powder XRD using a Philips 1710 diffractometer with CuK_α radiation and FEI Tecnai G_2 transmission electron microscopy. The particles morphology study was carried out using FEI Tecnai G2 Transmission electron microscope (TEM) operating at 200 Kv.

Results and discussion

Structural characterization: XRD and TEM

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials *etc*., Figure (1-a) shown the powder x-ray diffraction pattern of pure CdS nanoparticle. The diffraction peaks positioned at 2θ values of 24.91^0, 26.57^0, 28.25^0, 36.47^0, 43.87^0, 48.047 and 52.1^0 match well with hexagonal wurtzite phase of CdS (JCPDS card no.89-2944) and can be indexed respectively to the (1 0 0), (0 0 2), (101), (102), (110), (103) and (112) crystal planes. The average sizes of the CdS nanoparticles were estimated using the Debye-Scherrer formula[19].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ is the x-ray wavelength in nanometer, β is the peak width of the diffraction peak profile at half maximum height in 2θ axis and θ is the Bragg angle. The average crystal size in semiconductor nano-sized CdS particles obtained from Scherrer formula equation is 10 nm. According to the Figure 1, the lattice parameters of CdS with hexagonal structure are a = 4.121 Å and c = 6.682, which is in good agreement with the TEM measurements.

Figure (1-b) shows TEM images of CdS nanoparticles. As can be seen, all nanocrystals are nearly monodispersed with spherical or oval shape. The average diameters of the CdS were determined to be 12 nm, based on statistical analyses of more than 100 nanoparticles in a region (Figure (1-b)).

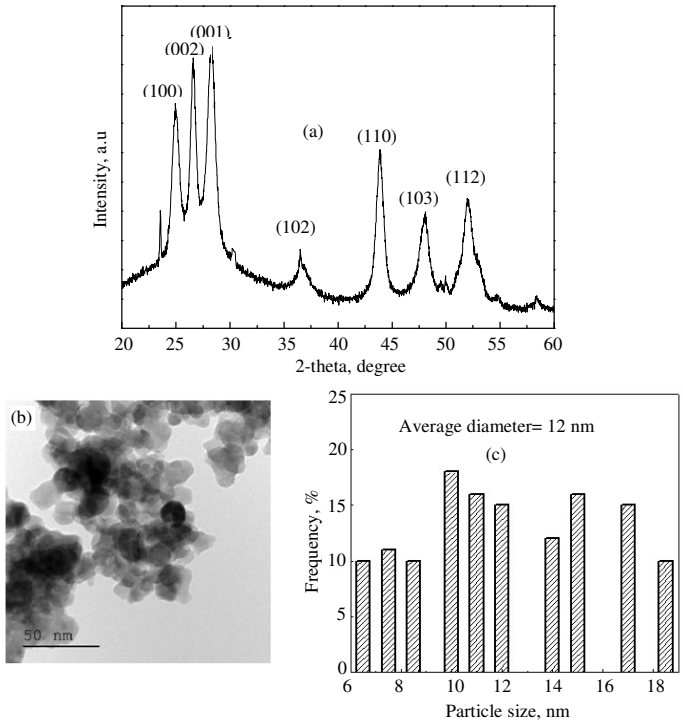

Figure 1. (a) XRD pattern, (b) TEM and (c) the corresponding size distribution of the nanocrystal CdS

In vitro antioxidant activity

Antioxidants are used to prevent the formation of reactive oxygen species (ROS) as HO•, H_2O_2 and NO, which are generated in living organisms during metabolism[20]. Excessive amounts of ROS are harmful because they can initiate biomolecular oxidations which lead to cell injury and death and create oxidative stress which results in numerous diseases and disorders such as cancer, diabetes, mycocardial infarction, stroke, *etc*[21,22].

The objective of this study was to evaluate the antioxidant activity of new compound Cd-S. The antioxidant properties were determined via the DPPH radical scavenging, the ABTS radical scavenging, ferric reducing power (FRP), hydroxyl radical scavenging and ferrous ion chelating activity (FIC).

DPPH radical scavenging activity

The DPPH free-radical scavenging activity: the hydrogen atom or electron donation abilities were measured by the bleaching of a purple colored methanol solution of DPPH. The free-radical scavenging activity of the various concentrations of new compound (Cd-S) and ascorbic acid was measured with the stable radical diphenylpicrylhydrazyl (DPPH) in terms of radical scavenging activity. 3 mL of DPPH (in methanol) was added to 100 µL of compound (dissolved in methanol), at different concentrations (1-0.2 mg/mL). After incubation 30 min, the absorbance was measured at 517 nm according to a described procedure[23]. Ascorbic acid was used as a positive control. Each study corresponded to three experiments, performed in duplicate. The scavenging activity was estimated based on the percentage of DPPH radicals scavenged by the following formula:

% Scavenging = $[(A_0 - A_s)/A_0] \times 100$ where A_0 is absorption of control, AS is absorption of tested extract solution.

The result showed remarkable scavenging activity was presented in Figure 2. The compound had the highest capacity of scavenging DPPH radicals with percentage of inhibition 45.05±1.85% (IC50=0.994 mg/mL) at the concentration (1 mg/mL) and compared with ascorbic acid at the same concentration 66.43±0.83% (IC50=0.67 mg/mL).

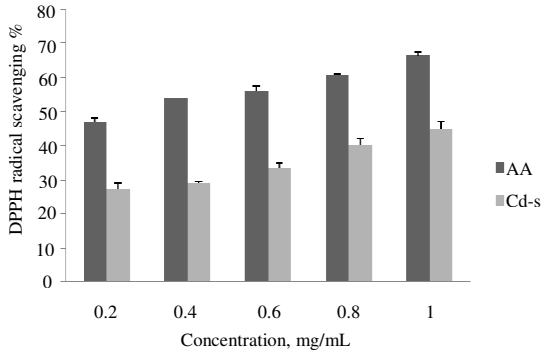

Figure 2. DPPH radical scavenging activity: tested compound (Cd-S), AA: ascorbic acid)

ABTS radical scavenging activity

ABTS assay was performed according to the protocol [24]. The stock solution was prepared by mixing equal volumes of 7 mM ABTS solution and 2.45 mM potassium persulfate solution followed by incubation for 12 h at room temperature in the dark to yield a dark-colored solution containing ABTS•+ radicals. Working solution was prepared freshly before each assay by diluting the stock solution by mixing of stock solution to 50% methanol. Free radical scavenging activity was assessed by mixing 300 µL of compound (Cd-S) at various concentrations (1-0.2 mg/mL in methanol) with 3.0 mL of ABTS working standard. The absorbance was measured at 734 nm. Data for each assay was recorded in triplicate. Ascorbic acid was used as positive controls. The scavenging activity was estimated based on the percentage of ABTS radicals scavenged by the following formula:

% Scavenging = [(A0-As)/A0]×100, where A0 is absorption of control, AS is absorption of tested compound.

Differences for the $ABTS^{\bullet+}$ (2,2-azobis-(3-ethylbenzothiozoline-6-sulphonic acid) radical scavenging capacities of each sample was recorded in Figure 3. The compound (Cd-S) was presented the highest capacity of scavenging at the high concentration (1 mg/mL)

with Value 55.92±1.65% (IC50=0.768) and ascorbic acid at the same concentration 69.38±0.214% (IC_{50}=0.778).

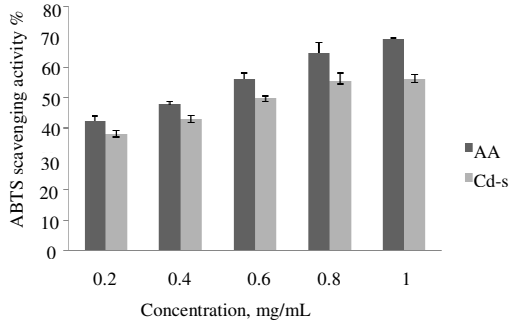

Figure 3. ABTS radical scavenging ability: tested compound (Cd-S), AA: ascorbic acid)

Hydroxyl radical scavenging ability

The effect of compound on hydroxyl radicals was assayed by using the deoxyribose method described by Halliwell and Gutteridge[25]. 2-Deoxyribose is degraded on exposure to hydroxyl radicals generated by Fenton's reaction. The compound (Cd-S) and ascorbic acid (AA) was prepared in methanol. The reaction mixture contained 450 µL of 0.2 M sodium phosphate buffer (pH 7.0), 150 µL of 10 mM 2-deoxyribose, 150 µL of 10 mM $FeSO_4$-EDTA, 150 µL of 10 mM H_2O_2, 525 µL of H_2O and 75 µL of sample solution (0.2 -1 mg/mL). The reaction was started by the addition of H_2O_2. After incubation at 37 °C for 30 min, the reaction was stopped by adding 750 µL of 2.8% trichloroacetic acid and 750 µL of 1% TBA in 50 mM NaOH, the solution was boiled for 10 min and then cooled in water. The absorbance of the solution was measured at 520 nm. Ascorbic acid (0.2-1 mg/mL) was used as a positive control. The ability to scavenge the hydroxyl radical was calculated using the following equation:

Percentage OH radical scavenging ability (%) = [(Abs cont-Abs test) /Abs cont] × 100
Abs cont = absorbance of the control (reacting mixture without the test sample) and Abs test = absorbance of reacting mixture with the test sample.

The results were summarized in the Figure 4 demonstrated that the most effective for hydroxyl radical scavenging activity followed at highest concentration (1 mg/mL) 34.46± 1.13% (IC_{50}=1.24) and compared with ascorbic acid at the same concentration (1mg/mL) the percentage of inhibition was 55.28±1.86% (IC_{50}=0.85).

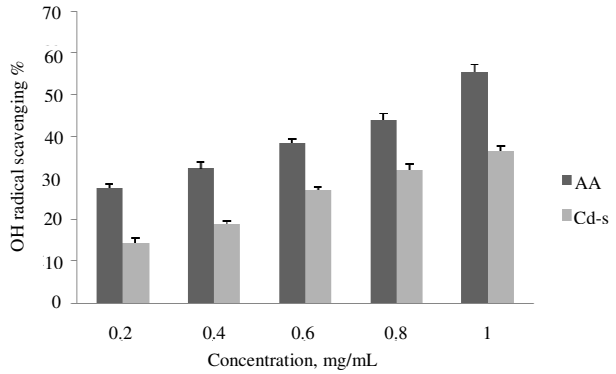

Figure 4. OH radical scavenging ability: tested compound (Cd-S), AA: ascorbic acid)

Reducing propriety

The reducing power of new compound (Cd-S) was assayed according to the method of Pulido *et al.*[26] Briefly, a methanolic solution of compound (Cd-S) (1 mL) at different concentration (0.2-1 mg/mL) was mixed with 2.5 mL of phosphate buffer (0.2 M) and 2.5 mL of 1% potassium ferricyanide and incubated at 50 °C for 20 min. To this mixture, 2.5 mL of 10% trichloroacetic acid was added and the mixture was centrifuged at 3000 rpm for 20 min. The upper layer (2.5 mL) was mixed with 2.5 mL of deionized water and 0.5 mL of 0.1% Ferric chloride and the same treatment was performed to a standard ascorbic acid solution and the absorbance taken at 700 nm. The reducing property was measured using the following equation:

Reducing power %= [(Abs cont−Abs test) /Abs cont] × 100

Where Abs cont = absorbance of the control (reacting mixture without the test sample) and Abs test sample = absorbance of reacting mixture with the test sample.

The results was presented in Figure 5 reported that Cd-S has a slight reducing property to compare to that of ascorbic acid and the percentage in the highest concentration (1 mg/mL) is AA 49.28±0.85% (IC_{50}=0.88) and Cd-S 48.76±0.929% (IC_{50}=1.122).

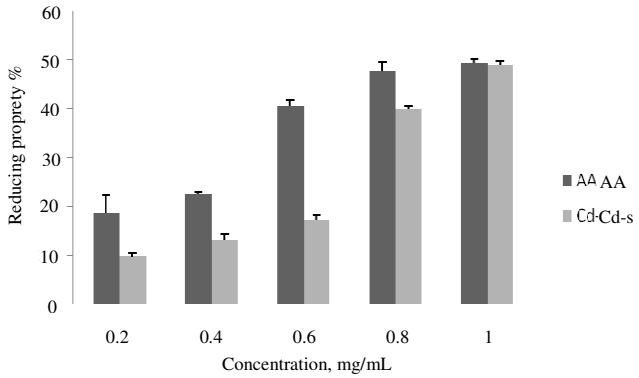

Figure 5. Reducing power assay: tested compound (Cd-S), AA: ascorbic acid)

Conclusion

CdS nanoparticles with average grain size of about 12 nm were successfully synthesized by hydrothermal method. The results presented highlight the possible uses of CdS nanoparticles in different biological level of study. Our results aimed to show the antioxidant activity in vitro of new compound (Cd-S). Our data showed that compound complex has an antioxidant character; this is demonstrated by scavenging DPPH radicals, ABTS radicals, hydroxyl radical scavenging and reducing property to that of ascorbic acid.

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Conflict of interest statement the authors declare that there is no conflict of interest regarding the publication of this document.

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