Synthesis, characterization, and dielectric properties of N-butyl aniline capped CdS nanoparticles

Damian C. Onwudiwe [a,*], Tanvir Arfin [b,1], Christien A. Strydom [a]

[a] Chemical Resource Beneficiation (CRB) Research Focus Area, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa
[b] Department of Applied Chemistry, University of Johannesburg, PO Box 17011, Doornfontein, 2028, South Africa

ARTICLE INFO

ABSTRACT

CdS nanoparticles were prepared by chemical reaction between some cadmium salt ($CdSO_4$ 8/3 H_2O and $CdNO_3 \cdot 4H_2O$) and thioacetamide (TAA), in the presence of N-butyl aniline (NBA) as a capping group; and denoted by CdS1 and CdS2 respectively. The structural and morphological properties were studied by powdered X-ray diffraction, transmission and scanning electron microscopy (SEM). The optical properties were studied by the ultraviolet–visible and photoluminescence spectroscopy. The particle sizes were influenced by the nature of the cadmium source. The photoluminescence spectra of the nanoparticles show peaks at 630 and 635 nm respectively, which are attributed to the surface defects of the CdS nanoparticles. The dielectric properties of CdS nanoparticles were studied in the temperature range of 25–150 °C, and at a single frequency of 1 kHz. The dielectric constant, capacitance and conductivity were found to increase with an increase in temperature at 1 kHz, and opposite behaviour were obtained for the dissipation factor and electrical modulus. The dissipation factor and electrical modulus decreased with an increase in temperature at 1 kHz. The activation energies were obtained from conductivity and capacitance. The activation energies obtained from capacitances were slightly higher than the values obtained from conductivity measurements. The electrical conductivity was found to be dependent on the size of the prepared nanoparticles.

1. Introduction

Nanocrystals exhibit novel electronic, magnetic, optical, chemical, and mechanical properties that cannot be obtained in their bulk counterparts. Their properties and applications are largely dependent on the size, shape, structure of the particles as well as the chemical composition [1]. When the size of a semiconductor nanocrystal is comparable with the diameter of the bulk exciton, splitting of the continuum of electronic energy levels into discrete states occurs and the effective band gap blue shifts from that of the bulk [2,3]. This is ascribed to confinement of the charge carriers in the limited space of the nanocrystal. Thus, quantum confinement will affect all electronic transitions throughout the entire Brillouin zone and, thus, decide the dielectric function of a semiconductor nanocrystal in a broad energy range [4]

CdS is an important Group II–VI semiconductor compound with a wide band gap (Band gap energy is 2.42 eV). It has attracted much research interest due to its excellent properties for opto-electronics, being used in both photosensitive and photovoltaic

devices. It has also been extensively studied due to its potential applications in field effect transistors, light emitting diodes, biological sensors and heterogeneous photocatalysis [5,6].

Chemical synthesis is one important technique for the synthesis of nanomaterials and nanostructures. Although CdS nanoparticles can be prepared by solvo-thermal techniques [7], pyrolysis [8], microwave [9], hydrothermal methods [10], and synthesis in polymer or glass matrices [11–13], synthesis of semiconductor nanoparticles by chemical route is simple, inexpensive, needs less instrumentation and is considered to have good viability. Synthesis by chemical means allows for the variation of parameters such as time, temperature, and concentration of reactants to obtain different sizes and shapes of nanoparticles. It is a synthetic route that works in mild and normal environments, and no special conditions of pressure, irradiation, or high temperature are required. Also, the H_2S, which is created via the hydrolysis of the thio-acetamide (when used as the sulphur source), is released gradually, as opposed to the direct reactant derived from sulphide solution or toxic H_2S gas [14].

AC conductivity is one of the investigation approaches done on solids in order to characterize the bulk resistance of the material sample, and allows for measurement of the electrical properties. Measurement of AC conductivity can be done by different techniques. The currently and widely used technique is complex

* Corresponding author. Tel.: +27783789500.
E-mail address: dconwudiwe@webmail.co.za (D.C. Onwudiwe).
[1] ISE Member

impedance spectroscopy. This measurement technique also gives information on electrical properties of materials and their interface with electronically conducting electrodes [15]. The dielectric constant is defined as the ratio of the capacitance of the material under investigation with and without the dielectric material placed between the plates of a parallel plate condenser. The dielectric properties of every solid are known to be very sensitive to local electric field distribution in the sample. Therefore, the temperature and frequency dependence of the dielectric constant can expose useful information about structural changes, transport mechanisms and defect behavior. The dissipation factor is one of the important electric properties of materials due to its use to predict behavior in encapsulates for electric components and interlay dielectrics [16]. Impedance spectroscopy has been used as a powerful technique to study the charged carrier relaxation and transportation in electronic devices [4,17,18]. The study of dielectric relaxation processes in semiconductor nanoparticles would improve the understanding of the molecular motions and their interactions which are affected by chemical composition, molecular structure and morphology of the sample. In this paper we have prepared CdS nanoparticles via the chemical reaction route, and studied the dielectric properties such as dielectric constant, ε, dissipation factor, $\tan\delta$, AC conductivity, σ, and capacitance, C.

2. Experimental

2.1. Materials

The raw materials used in this work such as thioacetamide (CH_3CSNH_2), cadmium sulphate, cadmium nitrate, N-butylaniline, and dimethyl formamide (DMF) were obtained with high purities, therefore no further purification was required.

2.2. Physical Measurements

Powder X-ray diffraction (XRD) data were obtained with a Bruker D8 advanced powder diffractometer with copper target and $K\alpha$ radiation ($\lambda = 1.54056$ Å, nickel filter). The samples were scanned from a high angle 2θ range of 20–75º using a scan speed of 0.01º s^{-1}. Scanning electron microscopy (SEM) characterization was performed with a Quanta FEG 250 Environmental Scanning Electron Microscope (ESEM). Transmission electron microscopy (TEM) measurement was performed on a TECNAI 20 (ACI) instrument operated at a voltage of 200 kV. UV-Vis measurements were made with a Perkin Elmer Lambda 20 UV-Vis Spectrophotometer using a quartz cell (10 mm path). Photoluminescence were measured on a Jobinyvon-spex-Fluorolog-3-Spectrofluorimeter with a xenon lamp (150 W). All experiments were performed at room temperature. Dielectric properties measurements were conducted by employing a GenRad LCR Digbridge in the temperature range 25-150 °C at single frequency of 1 kHz. The pellet was mounted on a stainless steel holder between two copper leads using two polished platinum electrodes. The copper leads were insulated from the sample holder by Teflon sheets. The pellet was annealed between the platinum electrodes for two hours at 80 °C to enhance the connectivity between the pellet and the electrodes.

2.3. Preparation of samples

In a typical procedure, 1.5 mmol of the cadmium source ($CdSO_4$·8/3 H_2O or $CdNO_3$·4H_2O) was dissolved in dimethyl-formamide, DMF (10 mL), and in a separate vial 15 mL of N-butylaniline was dissolved in 10 mL of DMF. The two solutions were mixed together to form a homogeneous solution at elevated temperature, to allow the Cd^{2+} ions to adsorb onto the amino groups of the N-butylaniline. After purging the solution with N_2 gas for a few minutes, 3 mmol of thioacetamide, TAA, dissolved in 20 mL of DMF was added and the solution was acidified to control the decomposition of TAA that generated the sulphide anions. The reaction time was fixed at 45 min, after which the product was placed in an ice-bath (< 10 °C) to terminate the reaction of TAA. Then, the precipitated CdS powders were centrifuged and washed thoroughly with ethanol and warm distilled water, respectively to eliminate the excess TAA. Finally, the sample was dried in vacuum at 50 °C until complete evaporation of the solvent was achieved. The synthesized nanoparticles from $CdSO_4$ (as Cd^{2+} source) were represented as CdS1, while CdS2 represents the nanoparticles obtained from $CdNO_3$·4H_2O as Cd^{2+} source.

3. Results and discussion

3.1. Synthesis

Cadmium sulphide (CdS) nanoparticles were obtained by precipitation from homogeneous solutions of cadmium salt and S^{2-} as a precipitating anion, formed by decomposition of thioacetamide (TAA) under acidic conditions (pH $\approx$ 2). The overall scheme for the synthesis of the CdS nanoparticles is depicted in Scheme 1. The reaction was based on the chemistry of TAA and the ability of a secondary amine (N-butyl aniline) to act as a surfactant for the synthesis of mono-dispersed nanoparticles [19]. To investigate the effect of the type of the cadmium source on the chemical reaction and consequently on the nanoparticles obtained, the experiments were conducted under the same operational conditions, including reactant concentrations, pH, temperature, and reaction time.

3.2. Optical Properties

UV–Vis absorption spectra of the as-synthesized CdS particles are shown in Fig. 1(a). By applying 2nd-order differentiation on the absorption spectrum, the absorption edges were found to be 488 (CdS1), and 481 nm (CdS2), respectively. There is thus a blue shift compared with the absorption edge of the bulk CdS (520 nm) [20]. A broad band centred at about 475 nm for both samples can be assigned to the 1s–1s exciton absorption [21]. The absorption edge is formed by the optical transitions between the levels in the valence and conduction bands and depends on the size of CdS nanocrystals. The calculated energy gap corresponding to the absorption edges are 2.54 eV (CdS1), and 2.57 eV (CdS2). The Brus equation [22], which relates the optical energy gap with the dimension of the nanoparticles, was used to estimate the sizes of the CdS nanocrystallites. The sizes were estimated as 5.8 nm (CdS1) and 5.2 nm (CdS2), respectively. The photoluminescence (PL) spectra of the samples are shown in Fig. 1(b). The PL spectra show strong peaks at 635 nm (CdS1) and 630 nm (CdS2) respectively. The PL peak around this region is generally accepted to originate from sulphur-deficient defects at the surface of CdS nanocrystallites [23–25]. This indicates that the emissions of the CdS nanoparticles were driven by trap-state emissions associated with electron transitions between
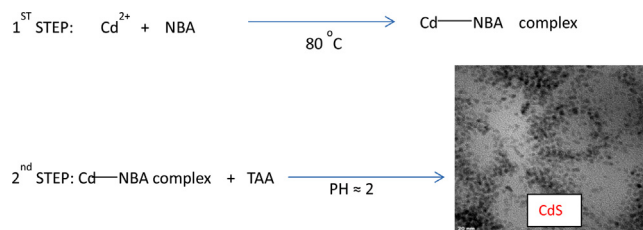
Scheme 1. The overall scheme for the synthesis of mono-dispersed NBA-CdS nanoparticles and TEM image.