



Structural dependent, dielectric and conduction analysis of CdSe based quantum dots

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Abstract

Nowadays, the effect of temperature on nanocrystal's dielectric has become a routine study while their structural effects on dielectric properties, lacks the attention of researchers. The correlation of different shell arrangement on dielectric enhancement in CdSe based quantum dots, is addressed in this letter. Detrimental impact of surface defects on dielectric properties of quantum dots is investigated and shown that surface defects of bare core increases dielectric loss, dissipation factor and decreases conductivity of the quantum dots. Dielectric properties of quantum dots is evaluated after deposition of different shells and multishells. It is observed that loss factor is declined in core/shell(multishell) quantum dots due to passivation of surface defects and consequently ease in charge carrier tunneling. Higher conductivity of the core/shell and multishell structures has also been demonstrated here. Structural and optical investigation of the quantum dots after shell deposition is also considered.

Keywords Dielectric studies · CdSe QDs · Core/shell (multishell) · Nano-composites

1 Introduction

Colloidal semiconductor nanocrystals, commonly known as quantum dots (QDs), have been the origin in much of the studies over the past two decades. Semiconductors, owing to a wide range of customizable features including electronic devices and nanocircuits [1], biotechnology [2, 3], solar cells and light-emitting diodes [4–8], QDs are of the outmost importance. Many of these applications are greatly benefited by existence of quantum dots with their extensive and unique properties. For instance, dielectric characteristics of QDs can enhance the electro-optical properties of nano-composites like, liquid crystals [9, 10], polymer matrix [11–13], graphene and hybrid graphene [14–16]. Polymeric nano-composites consisting of conductive nanoparticles are mostly used in electronic devices offering wide and low-budget fabrication techniques. At the meantime, addition of QDs in nano-composite liquid crystals, paves the way improving their dielectric, optical

and electro-optical properties. It has shown in literatures that, in some cases dispersion of CdSe based QDs in nano-composite reduces the relative permittivity [9], whereas in some, this value is enhanced after addition of CdSe based QDs [11–13]. Therefore, understanding of the quantum dots electrical properties and their interaction with variety of matrices, help fabricating of efficiently enhanced electronic devices.

Study of the optical and structural properties of Cd(Zn) Se based bare and core/shell (multishell) heterostructures are at the center of attention in our group. In previous studies, considering QDs different structural arrangement, lattice mismatch induced strain amount in the boundary of core and shell is calculated using continuum elastic theory. Obtained strain is introduced in effective mass approximation method to find and predict squeeze and stretch amount in the capped core of different structural arrangement [17–20]. Along with it, band gap tuning dependent

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structural analysis are also took place in binary core and ternary shell arrangement nanocrystals as well [18, 20].

In the present study, structural arrangement effect on QDs electrical properties drew our attention. Dielectric and conductivity properties of CdSe based QDs is observed with different structural arrangements (core, core/shell and multishell). Up until now, frequency and temperature dependency of dielectric properties in QDs have been evaluated in many reports. In this letter, dielectric permittivity, dielectric loss, dissipation factor ($\tan \delta$) and AC conductivity of bare CdSe, CdSe/Cd(Zn)S core/shell and CdSe/Cd(Zn)S/Zn(Cd)S core/multishell is investigated. Surface defects and their role in trapping charge carriers and their influence on dielectric parameters are shown. Meantime, concise detail of the chemicals, synthesize and characterizations of the QDs are presented. All the experiments took place at room temperature unless stated otherwise.

2 Experimental details

2.1 Chemicals and synthesize technique

2.1.1 Chemicals

Cadmium oxide (CdO, 99.5%), Selenium powder (Se, 99.99%), Sulfur powder (S, purum, 99.5%) and tributylphosphine (TBP) were purchased from Aldrich. Paraffin liquid (chemical pure), stearic acid (analytical grade), zinc acetate dehydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, analytical grade), were obtained from Sinopharm Chemical. Methanol (analytical reagent), n-hexane (analytical reagent) and acetone (analytical grade) were also purchased from Merck Chemicals. Chemical elements were used without any refinement in our synthesis.

2.1.2 Synthesis of CdSe, CdSe/ZnS and CdSe/CdS core/shell QDs

Zhu et al. [21] method is followed for synthesizing CdSe QDs. Core/shell structure were obtained, adding shell layer of ZnS and CdS to the core NCs. CdSe/ZnS structure, were prepared following the same [22] method. CdSe/CdS core/shell were synthesized, applying Yordanov et al. method.

2.1.3 Synthesis of core/MultiShell NCs

CdSe/Cd(Zn)S/Zn(Cd)S QDs are also synthesized by repeating the mentioned sequences above. In order to stop further growth of the QDs, n-hexane were added to the reaction mixture. Quantum dots were separated by decantation of the solution waste after being washed for multiple sequences with acetone and methanol in order to be applied in characterization analysis.

2.2 Optical investigations

2.2.1 Absorption and photoluminescence measurements

The absorption and photoluminescence (PL) spectra of the synthesized QDs diluted in n-hexane were measured using the Shimadzu UV-3600 UV-Vis NIR Spectrometer and Varian Cary eclipse photoluminescence spectrometer. Base line of the experiment were measured filling quartz cuvettes with n-hexane under emission of light in visible spectrum, in air at room temperature.

Figure 1a, b demonstrate absorption and PL of synthesized core/shell (multishell) QDs, respectively. The observed red shift in absorption and PL spectra of the QDs is an evidence for an effective capping process of bare core and core/shell structure. Capping CdSe with ZnS and CdS shows 26 nm and 7 nm of red shift

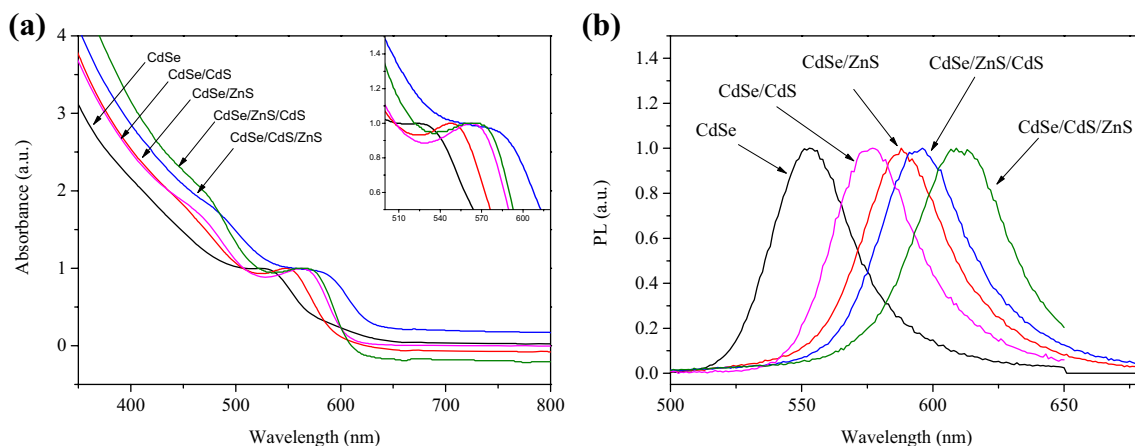


Fig. 1 Comparison of the normalized UV (a) and PL (b) spectrum of bare CdSe core and CdSe/Cd(Zn)S and CdSe/Cd(Zn)S/Zn(Cd)S QDs

in exciton wavelength of UV spectra, respectively. Capping CdSe/ZnS with CdS shows low red shift in UV and PL spectra due to rise of potential barrier energy created by ZnS which already suppress excitons leakage (electron–hole pairs) from CdSe core.

Observed distinct absorption peak and moderate red shift in absorption and PL spectra of the CdSe after being capped with shell (multishell), represents type I semiconductors, in which exciton pairs are generated in core. Therefore, red shift in absorption and PL spectra peaks of type I QDs, shows band exciton energy and size change of capped core influenced with shell deposition, since electron–hole pairs are excited inside the core region.

2.3 Structural study

2.3.1 X-ray diffraction measurements

X-ray diffraction is a non-destructive analytical technique which can yield the unique fingerprint of Bragg reflections associated with a crystal structure. Structural analysis of the XRD patterns of as produced QDs were carried out using X'Pert³ MRD (XL) X-ray diffractometer operating at 45 kV/40 mA using Copper Ka line ($\lambda = 1.5406 \text{ \AA}$). The XRD pattern depicted in Fig. 2a, b show cubic crystal phase of the synthesized NCs. The XRD pattern of CdSe exhibits broad peaks at 2θ values of 25° related to $\langle 111 \rangle$, 42° to $\langle 220 \rangle$ and 49° to $\langle 311 \rangle$ crystalline plane for low temperature synthesized ZB CdSe (Joint Committee on Powder Diffraction Standards File No. 77-2100). Authors would like to mention that, though QDs were washed several times with acetone and methanol, paraffin shows its effect in suppressing XRD patterns intensity of QDs.

2.3.2 TEM measurements of the bare core

Figure 3 shows typical SEM image of bare (pre-capped) CdSe core in good shape uniformity (spherical) and a narrow size distribution ($\sim 3.8 \text{ nm}$). The shell and mulshell of CdS and ZnS semiconductors are deposited on the core shown in Fig. 3.

In Fig. 4a, b TEM image of the CdSe/CdS and CdSe/ZnS is shown with good crystalline structure, respectively. As it can be seen from Fig. 4a, single crystal of CdS is shown with a d -spacing of 0.33 nm corresponding to the $\langle 111 \rangle$ lattice plane with the fast Fourier transform (FFT) of cubic CdS [23, 24]. Lattice spacing of 0.183 nm , corresponding to the $\langle 220 \rangle$ plane and the FFT of cubic ZnS is seen in Fig. 4b [25, 26].

2.4 Dielectric characterizations

Measurements were carried out using an HP impedance analyzer HP-4192A with a test fixture 16047A connected to measuring cells. The experiment took place in frequency intervals from mHz to MHz. The mentioned measuring cells were made in a parallel silver electrode, dielectric cell (1 mL) specially designed measuring cell for this experiment. The diluted concentration of the QDs dissolved in n-hexane, filled the cell to reach the level of the upper silver electrode. The electrodes were the flat faces of two silver pistons fitted inside a polymeric cylinder fitted horizontally to the measuring assembly. The diameter of the electrodes were slightly smaller than the inner diameter of the tubing, so that the electrodes were partially immersed in the liquid sample in such a way that no air bubbles were retained in the measuring compartment. The cell was electrically screened and the screen connected to the common ground of the set up [27]. The impedance analyzer was

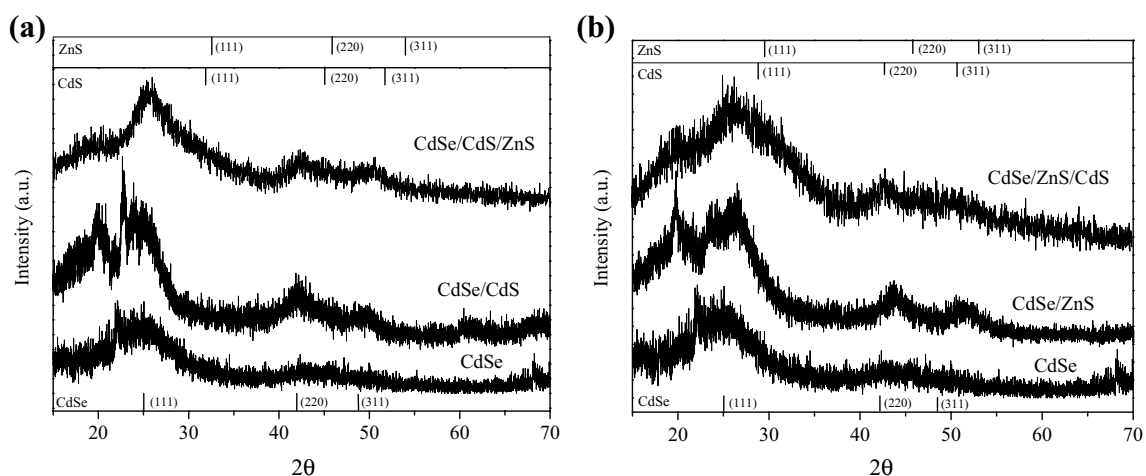


Fig. 2 X-ray diffraction of **a** CdSe, CdSe/CdS and CdSe/CdS/ZnS structure and **b** CdSe, CdSe/ZnS and CdSe/ZnS/CdS nanocrystals

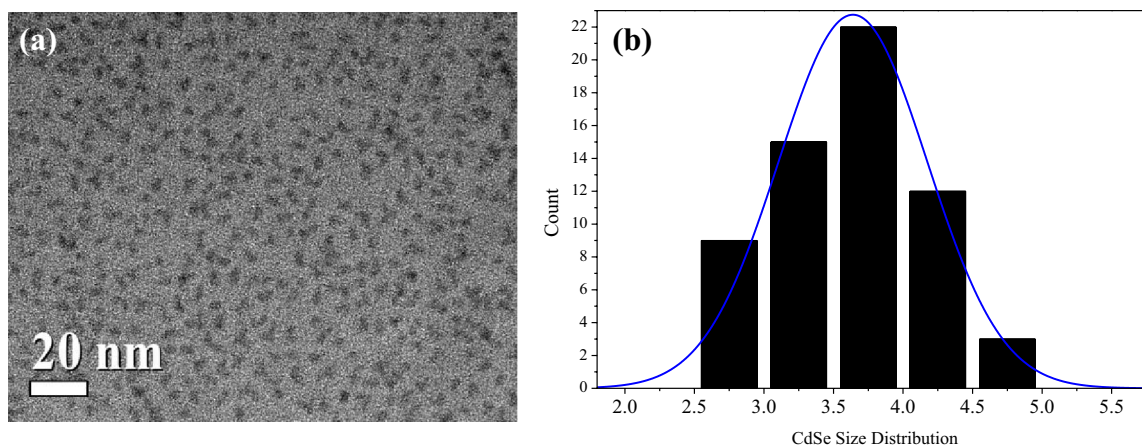


Fig. 3 SEM image (a) and size histogram (~3.8 nm) of bare CdSe core (b)

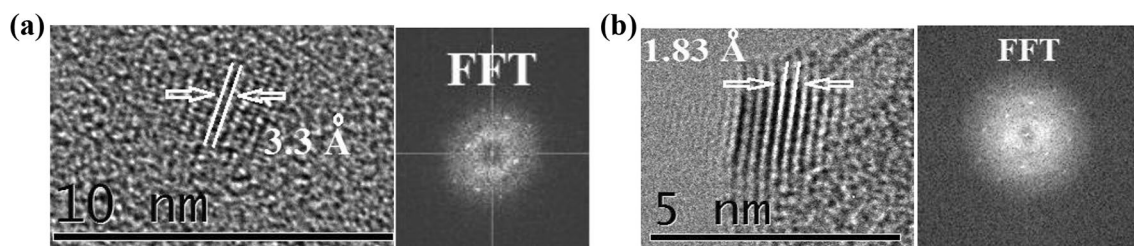


Fig. 4 TEM images of CdSe/CdS with FFT patterns of cubic CdS (a) and CdSe/ZnS with FFT of cubic ZnS (b)

interfaced with a computer for automatic data acquisition. Measurements were started as soon as the cell was filled with solution. Solution should be in a way that QDs are being floated in it with respectively the lowest effect on dielectric measurements. Here, the solution consists of QDs dispersed in Hexane. Hexane is just hydrogens and carbons with no much charge imbalance in it and the carbon-hydrogen bonds that are not much polarized. Therefore, it has insignificant interference in dielectric study of the QDs. Paraffin oil effect on dielectric study of QDs dispersed in hexane is neglected for two reasons: (a) paraffin amount is the same in all mixtures and (b) the matrix for dielectric study consists of QDs in hexane, with a negligible paraffin amount.

3 Results and discussion

3.1 Dielectric study of the QDs

It has been shown in articles that, addition of QDs to polymer matrices enhance dielectric properties of the matrix through imposing different types of polarizations like; interface, dipole, ionic, atomic and electronic [12, 13, 28]. Dielectric analysis is a comprehensive method

to counterpart conduction and dielectric properties of materials. The margin of dielectric constant (ϵ'), dielectric loss factor (ϵ''), dissipation factor ($\tan \delta$) and AC conductivity versus frequency, reveals information about charge carrier mobility in the structure [29]. Here, the complex permittivity of the synthesized QDs is expressed in terms of real and imaginary part in accordance with frequency variations (Fig. 5). Systematic and exponentially decrease of dielectric constant (ϵ') and loss factor (ϵ'') with increase in frequency is noticeable in Fig. 5a, b which then attains a constant value in high frequency region. High value of ϵ' at low frequency shows conductivity nature of the QDs [30]. Higher dielectric constant in low frequencies (Fig. 5a) is attributed to two factors as well; lower electrostatic binding strength from space charge polarization near the grain boundary interface [31] and space charge polarization due to charged lattice defects [32]. When subjected to an electric field, the so called space charge polarizations are created with space charges delocalization and dipole moments. Space charge polarization is generally active at lower frequencies and indicates purity and perfection of the nanoparticles. It is also noticeable from Fig. 5a that, electric dipoles can follow the electric field at lower frequencies. Additionally, rotation polarization is created with

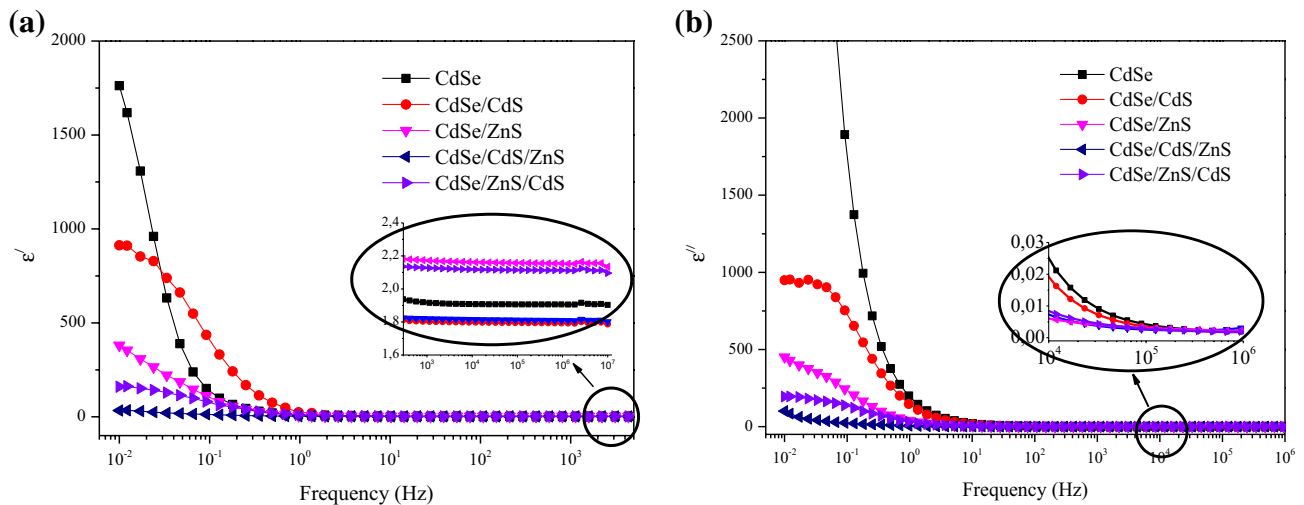


Fig. 5 Variation of the **a** real and **b** imaginary part of the effective permittivity at different frequencies

rotation of the dipole moments, showing contribution in high values of dielectric constant at lower frequencies [33].

Figure 5a shows higher value of ϵ' for bare CdSe core QDs in compare with capped ones. As it is depicted in Fig. 5a, capping bare core with shell or recapping core/shell with another layer of shell, decreases ϵ' amount. Same behavior is noticeable from Fig. 5b, that dielectric loss declines with capping core and core/shell structure. Thereby, electric loss tangent ($\tan \delta = \frac{\epsilon''}{\epsilon'}$) decreases with capping process. Loss tan decrease with capping process is also showed experimentally in next part. Meanwhile, author's attributes lower ϵ' in core/shell and core/multishell QDs to their heavier density in compare with bare core. This phenomenon is in agreement with what have been shown in scientific articles that surface and size play role in altering dielectric constant [34–37]. Negligible difference in ϵ' amount at higher frequency for all QDs is demonstrated in Fig. 5a-inset.

Effective permittivity (ϵ'), decreases with increase of frequency (Fig. 5b) whereas at higher frequencies dipoles can no longer follow the field, as a result of which, effective permittivity decreases [11]. At higher frequencies, dipoles slowly fall off the electric field [30] which leads to decrease in dielectric amount [38, 39]. In higher frequencies, the space charge polarizations are dominated by the presence of ionic and electronic polarization [12].

Dielectric loss (ϵ'') is of vital importance in nonlinear optical materials applications [40]. Fluctuation of the dielectric loss (ϵ'') with frequency is depicted for the synthesized QDs, in Fig. 5b. It is evident that at low frequency, QDs exhibit high dielectric loss (highest in bare CdSe core QD). There is rather a sharp fall in ϵ'' amount with increase of frequency, and apparently becomes constant at high

frequency. The low value of the dielectric loss at high frequency proves high optical quality of the synthesized QDs. Inset of the Fig. 1b shows minimal fluctuation in ϵ'' at high frequency. Whereas, capping bare core and also recapping core/shell structure cause tangible differences in lower frequency. Trapped charge carriers in surface defects of QDs, increases loss factor in bare QDs, whilst capping process passivizes defects and declines loss factor (free charge carriers mobility) in the core/shell (multishell) QDs. This conclusion is in agreement with observation from loss tangent in next part (Fig. 6a).

Surface defects play trapping role for charge carriers and limits charge transfers. They can be passivized after capping bare core QDs. This additional step (second shell), eases charge carriers mobility in the matrix. Relatively lower ϵ'' in the core/multishell structure is an evidence for this phenomenon (see Fig. 5b). At the meantime, easier translocation of charge carriers promotes dielectric relaxation in the QDs. Delay in molecular polarization with respect to the applied electric field in dielectric medium is called dielectric relaxation [12]. Though bare CdSe QDs show better dielectric constant in compare with capped structure, higher losses in bare core is a substantial downside which should be taken to consideration in device fabrications.

Figure 6a illustrates dissipation factor ($\tan \delta$) versus frequency in the synthesized QDs. $\tan \delta$ is a current absorptive behavior in which charges consume current in order to be oriented along with the field propagation direction (higher in case of bare CdSe, see Fig. 6a). Capping core with shell and second shell shows less current dissipative behavior (Fig. 6a). Higher current is absorbed to overcome internal friction force and reorienting dipoles in the direction of applied electric field. Thereby, high

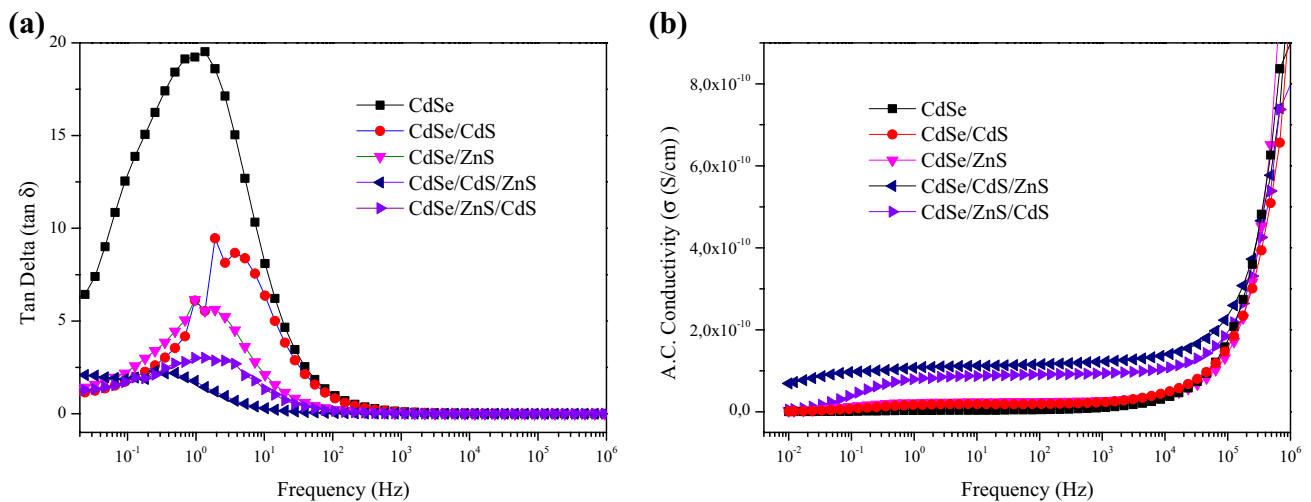


Fig. 6 Frequency dependent of $\tan \delta$ **(a)** and conductivity versus **b** for the CdSe based QDs

value of dissipation factor at low frequency is extracted in bare QD. Rotation of dipolar molecules and other kinds of molecular transfer to different positions is also current absorptive [28]. In reports [11, 12], it has been shown that higher temperature reduces relaxation time and shifts $\tan \delta$ peak toward high frequencies, whereas in our case this phenomena took place after introducing shell layer to core and core/shell QDs. Depicted shift in peak position of CdSe toward high frequency after capping process might be corresponded to lower relaxation time. It is noticeable from Fig. 6a, that capping CdSe with shell of CdS/ZnS semiconductors reduces loss-rate factor in low frequencies.

To the best of writer's knowledge, the AC electrical conductivity of nanoparticles or nanocomposites depends on frequency and temperature [9, 33, 41]. Electrical conductivity is a prominent factor revealing information about charge transport phenomenon in matrix. Considering QDs in solvent, due to nanocrystals small size, charge carriers reach surface of the QD easily, enabling transfer of electrons by thermionic emission or tunneling which enhances the conductivity of the mixture [42]. Figure 6b illustrates AC conductivity of the QDs with the reciprocal of frequency. Noticeably, AC conductivity of each sample enhances with increasing of the applied frequency. Exponential change in conductivity, confirms semiconducting nature of CdSe based QDs [43]. There is a small but noticeable difference in AC conductivity of bare CdSe in regard with the capped ones (Fig. 6b). It can be noticed that, capping and recapping bare QDs, eases tunneling of charge carriers to the surface that are in contact with matrix. Higher, yet not tangible conductivity of the core/shell and multishell structures in lower frequencies are in regard with this reason. Meanwhile, it has been approved in studies that the mixture of QDs with polymers, composite films

[11, 13] and liquid crystals [9], alters conductivity of the matrix due to the ion exchange or ion hopping, the tunneling or the jump over energy barrier [11].

Up until now, it has been proved that the conductivity nature of polymeric matrix enhances with addition of QDs. But understanding the interaction mechanism between different structures of the impregnated QDs (core, core/shell, multishell) in polymeric chains is of outmost importance to be considered in device fabrications. Here, we solely showed dielectric and conduction changes in QDs with distinct structural arrangement in hexane. Their implementation impact on conductivity mismatch in polymeric matrices are highly advised [44, 45].

4 Conclusion

Nano-composite matrices with CdSe based QDs are attracting considerable attention in fabricating electronic devices and nano circuits. In order to design much efficient device, it is critically important to study QDs dielectric properties to find the best candidate in matrix. Temperature effect on dielectric properties of QDs has been shown in many studies. In this work, we studied the effect of surface defect passivation with different shell structures on dielectric and conductivity of CdSe QDs. Dielectric permittivity and loss, dissipation factor ($\tan \delta$) and AC conductivity of QDs are investigated after introducing first and second layer of shells on CdSe. It is shown that surface passivation plays an important role in dielectric, conductivity enhancement and consequently suppresses dielectric losses and dissipation factor through better charge tunneling to outer layers and less trapping of charge carriers is the outcome of defect passivation. Considering

applications of nano device in industries, the bare CdSe core showed higher dielectric permittivity in compare with core/shell (multishell) QDs whereas, addition of shell layer declines $\tan \delta$ and loss factor in core/shell (multishell).

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest.

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