Study of Charge Transfer between CdSe/CdS core/shell and Vanadium(II) Doped ZnS Quantum Dots

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By

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Certificate

This is to certify that this dissertation entitled **"Study of Charge Transfer between CdSe/CdS core/shell and Vanadium(II) Doped ZnS Quantum Dots"** towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents the research carried out by **Reddy Pranavi** at Indian Institute of Science (IISc), Bangalore under the supervision of **Dr. Anshu Pandey**, Assistant Professor, Solid State and Structural Chemistry Unit (SSCU), IISc Bangalore during the academic year 2017-2018.

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Declaration

I hereby declare that the matter embodied in the report entitled "**Study of Charge Transfer between CdSe/CdS core/shell and Vandium(II) Doped ZnS Quantum Dots**" are the results of investigations carried out by me at SSCU Department, IISc Bangalore under the supervision of **Dr. Anshu Pandey** and the same has not been submitted elsewhere for any other degree.

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Abstract

Doping of charge (either electron or hole) into the bulk of semiconductor nanocrystals becomes extremely challenging as their surfaces are more prone to defects. Since the emergence of Quantum dots (QDs), major research was oriented towards the size dependent properties of these materials. Later advancements include the shape control, self assembly and various surface phenomena of these dots. Poor conductivity of QDs hampers their potential in making electronic devices. So, from last two decades, numerous efforts were made to enhance their conductivity. One of such techniques include injection of electron into the quantum confined state of QDs i.e., into the conduction band of QDs allowing flat flow of charges in the material and thereby improving conductivity in QDs films. Some of the attempts were made to dope an electron or hole into conduction or valence band respectively. For instance in electrochemical doping, a bias was applied across the film of QDs on an interdigitated electrode, and in some cases, alkali metal ions were used to inject electron into the conduction band of QDs. Nonetheless in these cases charge injection is reversible. When you stop applying bias in the former case or once the ions leave the surface of QD in the latter case, resulted in uncharged QDs. Electronic devices demand irreversible injection of charges into QDs. So, it is quite essential to find a method which injects charges irreversibly into the quantum confined state of QDs.

Here, we introduce a new strategy to dope charges into these QDs. This eliminates energetic disorder in assemblies. As a result these materials offer superior conductance. This is very important in making optoelectronic devices. The charge transfer between QDs can be done by using one QD having a high laying valence band, and another having a redox active dopant ion inside it.

V doped ZnS   **CdSe/CdS**
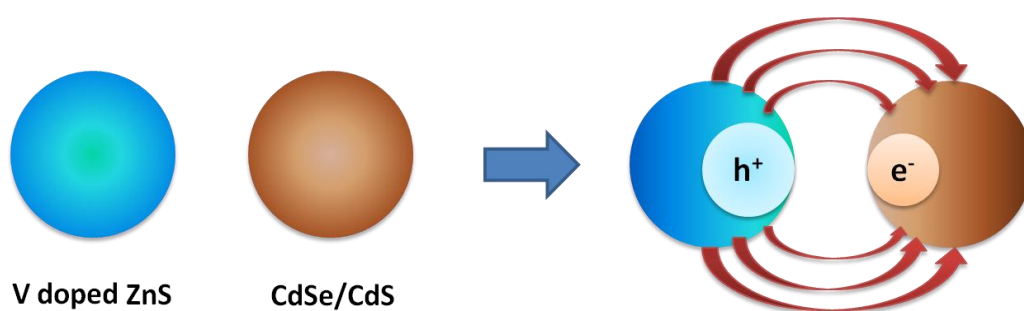
Figure1: Schematic representation of charge transfer between QDs

Once they are in proximity electrons flow from high laying valence band QD to the dopant level in the other dots. As a result there will be reduced electronic disorder in the system. The reduced electronic disorder can benefit optoelectronic devices as well as lead to the emergence of novel phenomena.

1.   Introduction:

Quantum dots (QDs) are semiconductor nanocrystals made up of ~1000 of atoms. In QDs, the electrons and holes are spatially confined in all three dimensions and as a consequence of confinement they have discrete energy levels like atoms.[1] Due to their size, a significant percentage of atoms are located on the surface. Atoms present on the surface of QDs are not completely bonded within the crystal lattice. This leaves "dangling" bond/s on the surface.[2]

When a photon of energy higher than E_g is absorbed, the excitation of the electron leaves an hole in the valence band.[3] Upon irradiation with light, this positively charged hole and the negatively charged electron form a bound to electron-hole pair, known as the **exciton**.[4] Formation of exciton is a quite common phenomenon in semiconductor nanocrystals, although in quantum dots, the average size of the exciton (the exciton Bohr radius[5]) is smaller than the size of dot, leading to a confinement energy as the exciton is squeezed into the material.[6]
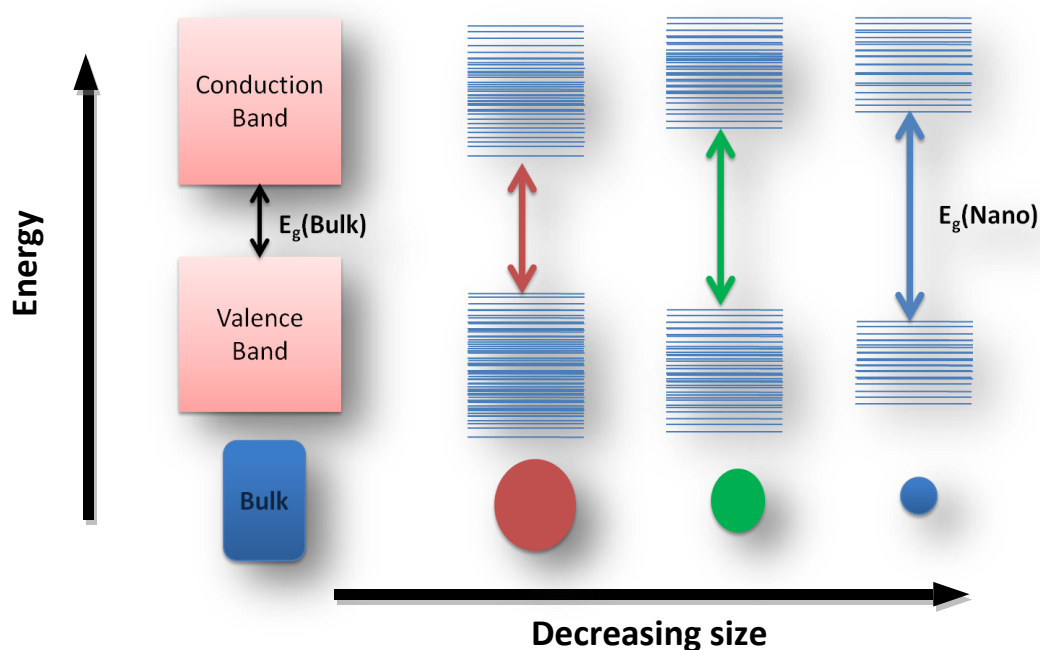
Figure 2: Schematic illustration of electronic band structure of quantum dots with varying size

This energy can be modeled as particle in a box as given in equation 1,

$$E_{confinement} = \frac{\hbar^2 \pi^2}{2a^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) = \frac{\hbar^2 \pi^2}{2\mu a^2} \qquad \text{----------} \quad (1)$$

Where m_e is effective mass of the electron, m_h is the effective mass of hole, μ is the reduced mass of the exciton and *a* is the radius of QD.

If the exciton size is comparable to the Bohr exciton radius, it is then said to be in "weak confinement regime". Strong confinement regime, where the size of exciton is much smaller than the Bohr exciton radius, is of more interest. In this regime, confinement effects dominate, resulting in tunable optical and electronic properties.[7] An additional energy is also present which is associated with the coulomb attraction between the electron and hole as given below in equation 2,

$$E_{exciton} = -\frac{1}{\varepsilon_r^2}\frac{\mu}{m_e}R_y \qquad \text{----------} \quad (2)$$

ε_r is the dielectric constant (size dependent) of the QD, R_y is the Rydberg constant
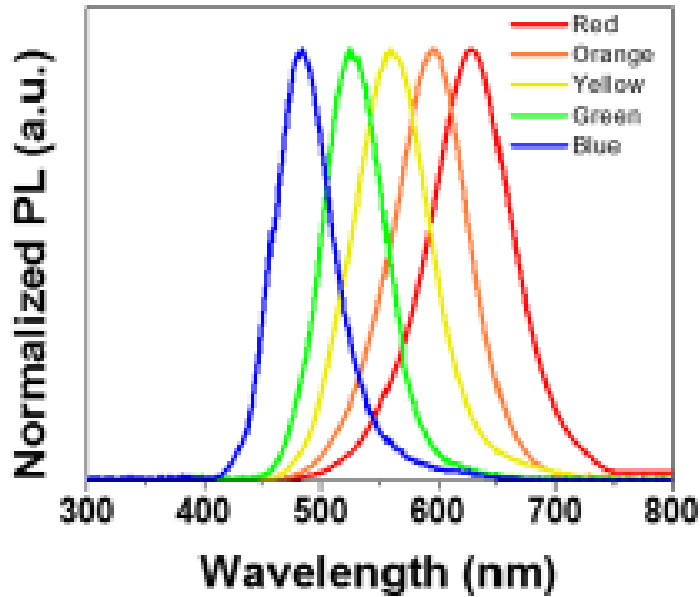
Figure 3: Red shift in emission spectra of InP quantum dots with increasing size (Ref: 26)

Therefore, the total energy is the sum of band gap, the confinement energy and the energy of bound exciton and is as follows

$$E_{total} = E_{band\ gap} + E_{confinement} + E_{exciton} = E_{band\ gap} + \frac{\hbar^2 \pi^2}{2\mu a^2} - \frac{1}{\varepsilon_r^2}\frac{\mu}{m_e}R_y$$

This excited electron relaxes back to the valence band annihilating the exciton and is accompanied by emission of light, a process called *fluorescence.*[8] As shown in fig. 3, the bigger the dot is, the lower (redder) it's absorption onset and fluorescence emission is, in terms of energy. Similarly, smaller dots have blue or higher absorption and emission.

About CdSe/CdS Core-Shell QDs:

Depending on the band off-set positions of QDs different types of core-shell QDs exist.[9]

If the conduction band and valence band of core lie within the band gap of the shell, it is known as *Type I* core-shell QDs i.e., Examples include CdSe/CdS, ZnS/CdSe, CdSe/InAs etc. Vice-versa is *Inverse Type I* (Eg: CdS/HgS, CdS/CdSe). On the other hand, the conduction band and valence band of the core are both higher or lower than the band edge of the shell, such QDs are known as *Type II* (Eg: CdTe/CdSe, CdSe/ZnTe) (Fig. 4, adapted from Reference 9)

Figure 4: Schematic of electronic band structure and band off-sets of core- shell quantum dots

CdSe/CdS, the QD we synthesized and used here, is an example of Type I core-shell QDs. Dangling bonds on the surface of the QDs are responsible for their low fluorescence quantum yields.[10] Encapsulation of QDs with a material that has a larger band gap helps in surface passivation, thereby enhancing the quantum yield.[11]

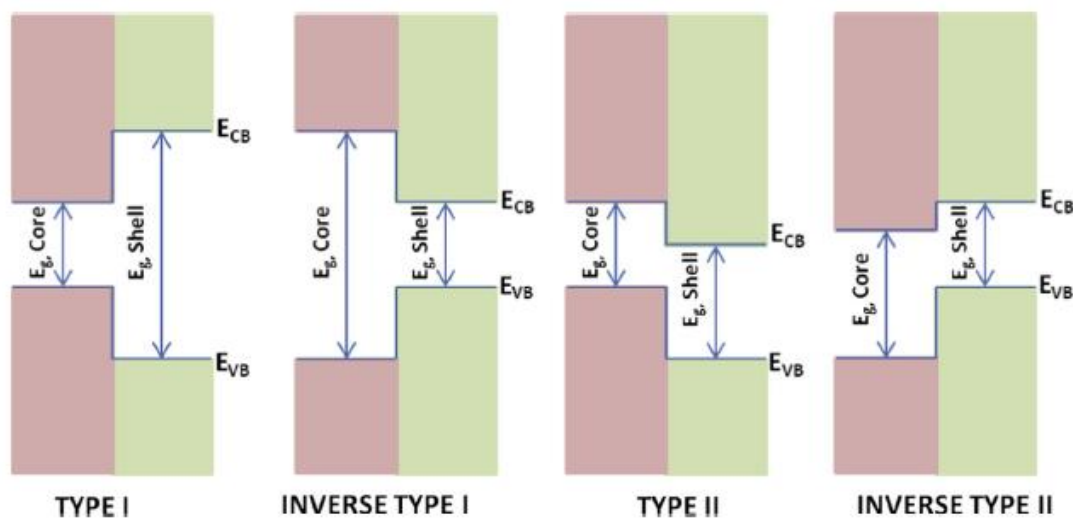ZnS, on the other hand, is a wide band gap material[12-13] and is apt for our study. Doping is a process of intentional insertion of foreign (impurity) atoms into the crystal.
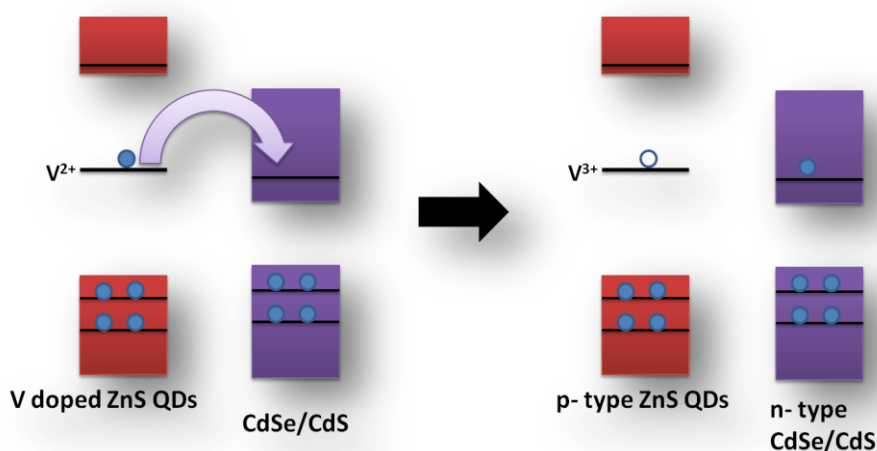
Figure 5: Schematic of charge transfer between quantum dots

Introducing impurity atoms into QDs, which has only a few hundreds of atoms, may lead to their expulsion to the surface.[14-15] Hence, it is not an easy job to dope either atoms or charge into the confined states of QDs. Based on the previous reports on irreversible hole injection into the quantum confined states,[13, 16-17] we followed similar methods to achieve electron injection. Doping Vanadium(II) into ZnS QDs can result in the donation of electron into the low laying conduction band of the CdSe/CdS QDs (Fig. 5) upon mixing.

2.   Methods:

2.1.   Chemicals used:

Cadmium(II) acetate dihydrate ($Cd(CH_3COO)_2.2H_2O$, purity 98%, Sigma-Aldrich), Myristic acid ($CH_3(CH_2)_{12}COOH$, purity 98%, Sigma-Aldrich), Selenium (Se, 99.99%, Sigma-Aldrich), Cadmium Oxide (CdO,), Zinc(II) acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, purity 98%, Sigma-Aldrich), Vanadium(II) chloride (VCl_2), purity 85%, Sigma-Aldrich), Sulphur powder (S, <99.5%), Sodium Borohydride ($NaBH_4$, 98%, Sigma-Aldrich), 1,4 butanediol ($HO(CH_2)_4OH$, 90% AR), Butyraldehyde, Octadecene (ODE, technical grade 90%, Alfa Aesar), Oelylamine (OLA, Sigma-Aldrich), Oleic acid (OA), Trioctylphosphine (TOP, Sigma-Aldrich)

2.2. CdSe/CdS QDs synthesis:

Colloidal CdSe QDs were synthesized by using Cadmium acetate and Selenium powder as respective precursors. 0.1 mmol (26.6 mg) of $Cd(ac)_2.2H_2O$ was transferred into a 25 mL RB along with 70 mg of Myristic acid and 4 mL Octadecene (ODE) as solvent. This mixture was heated to 220°C under Argon atmosphere, after thorough degassing at 100°C. A clear solution was seen at 220°C after about 5 min, which upon cooling down to room temperature using a water bath, formed a white precipitate indicating the formation of Cadmium Myristate. 5 mg of Selenium powder and 2 mL ODE was transferred into this solution and degassed at 100°C. At around 210°C, the solution turns from yellow to orange indicating the initiation of CdSe QDs nucleation. Then 1 mL of oleylamine was injected gently into the flask allowing the growth to begin. After a minute or two at 220°C, CdS shell was grown on CdSe using 1 mL each of 0.1M Cadmium oleate and 0.1M Sulphur in ODE. The shell growth was done by injecting the precursors dropwise to prevent side nucleation of CdS.

2.3. 0.1 M Cadmium Oleate synthesis:

0.32 gm of CdO is taken in a 25mL round bottom flask and 3 mL of OA, 5mL of ODE were added. This solution was heated to 230°C under argon after proper degassing at 100°C. Once the solution becomes clear, 5mL+10mL+1mL of ODE was added stepwise. After the addition of ODE, 1mL of OLA was added and the reaction mixture was cooled to room temperature, yielding cadmium oleate.

2.4. V doped ZnS QDs synthesis :

ZnS QDs were first synthesized and Vanadium was then doped into ZnS. Sulphur anion (S^{2-}) was synthesized first by reducing Sulphur powder using $NaBH_4$. 20 mg of Sulphur powder was transferred to the flask along with 1 mg of $NaBH_4$. One to two drops of 1,4-butanediol is added and the temperature is increased to 100°C under argon which allows the reduction of Sulphur from S^0 to S^{2-}. 1 mL ODE is added to the flask to dissolve this mixture. And 0.5 mL of Butyraldehyde was injected so that the unreacted $NaBH_4$ will be taken up and butyraldehyde is converted to butanediol. In another flask, 20.8 mg of Zinc acetate was kept along with 4 mL of ODE and 1 mL of Olelyamine and heated to 180°C. The reduced sulphur from first flask was injected into the second flask at 180°C and a pale yellow solution was obtained indicating the formation of ZnS QDs. After a minute or two, 2 mg Vanadium dichloride dissolved in

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oleylamine was injected into ZnS QDs. To ensure the incorporation of Vanadium inside the ZnS QDs, 0.5mL each of Zinc oleate and S in oleylamine were injected dropwise.

Note: Vanadium(II) chloride is highly susceptible for oxidation in the presence of air. Hence, it is weighed and dissolved in oleylamine inside the glovebox and is taken out with proper sealing.

2.5.　0.1 M Zinc oleate synthesis:

0.55 gm of $Zn(acetate)_2$ was taken in a 25mL round bottom flask and 3mL of OA, 5mL of ODE were added. This solution was heated to 230°C under argon after proper degassing at 100°C. Once the solution becomes clear, 5mL+10mL+1mL of ODE was added stepwise. After the addition of ODE, 1mL of OLA was added and the reaction mixture was cooled to room temperature, yielding zinc oleate.

2.6.　Cleaning of QDs:

Both the QDs were extracted by centrifuging them firstly in 3:1 ratio of methanol to ethanol solvents for about 2 minutes at 4000 revolutions per minute (rpm). After centrifugation, the supernatant is disposed and the precipitate is retained. Second step was same as that of the first except that the ratio used is now 1:3 of methanol to ethanol. Next step includes addition of few drops of Isopropanol. 1-Butanol was also used to clean V doped ZnS QDs.

2.7.　Mixing procedure:

2.5mL of cleaned CdSe/CdS dots in hexane with S exciton optical density (OD) at 0.1 are taken in a vial. 2.5mL of cleaned V doped ZnS QDs in hexane OD slightly higher than 0.1 is transferred to the vial containing CdSe/CdS dots. After soft sonication, the solvent is evaporated using vacuum. After evaporation, the mixture is dissolved again in 2.5mL of hexane for absorption and PL measurements.

3. Characterization:

3.1. Experimental Characterization:

UV-Visible absorption spectra were recorded using Ocean optics USB4000 spectrometer. Detector is Toshiba TCD1304AP covering 200 – 1100 nm.

Transmission Electron Microscopy(TEM) images were taken by a JEM 2100F TEM machine at a 200kV accelerating voltage.

X-Ray Diffraction analysis was done using Phillips PAN analytic X-Ray Diffractometer using Cu Kα radiation.

PL Decay curves were obtained using Edinburg Instruments FLS920 Series Flourescence Spectrometer with a 450W continuous Xe arc lamp as an excitation source.

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) was done on perkin elmer.

I vs V plots were recorded using keithley model 6485 picoammeter. Specifications of interdigitated platinum electrode used are as follows: Ref: DRP-G-IDEPT10

Dimensions of bands or gaps is 10 μm

Glass substrate dimensions: L = 22.8 mm, W = 7.6 mm and Thickness = 0.7 mm

Cell constant for 10 μm IDE = 0.0118 cm^{-1}

Number of digits: 125*2

Optical and Structural Characterization of CdSe/CdS QDs:
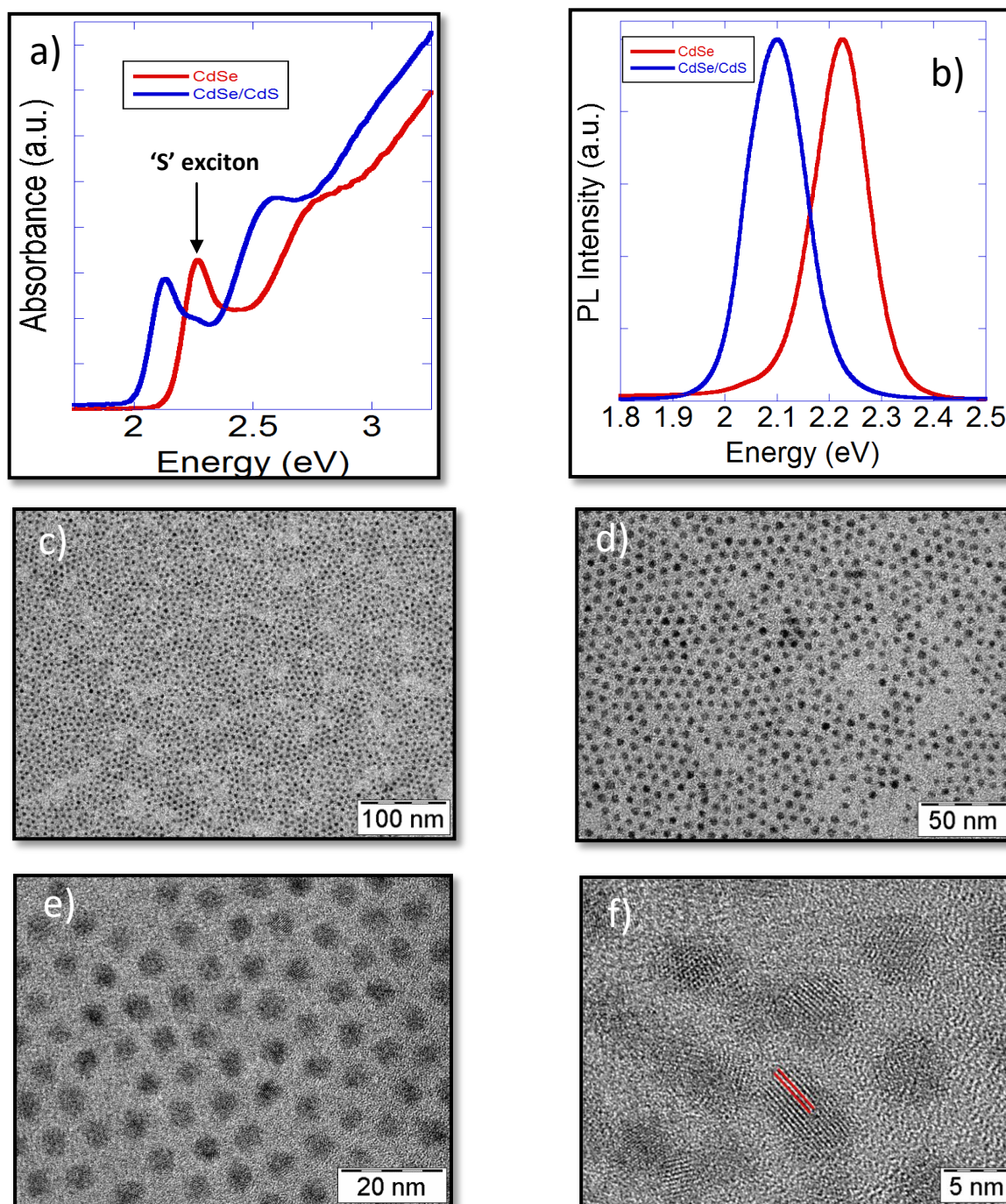
Figure 6: a) Absorption spectrum of CdSe/CdS QDs b) PL spectrum of the same c) and d) TEM image of cleaned CdSe/CdS QDs e) and f) HRTEM image of the same

The shift in S exciton of CdSe to lower energy was seen upon growth of CdS shell on it[18] accompanied by red shift in PL emission spectra. The reason for the same is explained in fig. 7. Growth of CdS shell also enhances stability towards photo-oxidation.
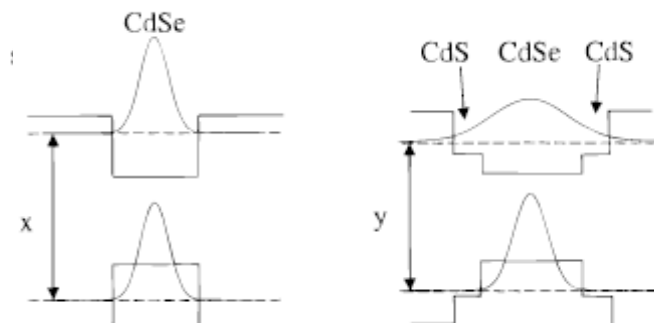
Figure 7: Schematic core and core/shell potentials (dotted lines) and electronic energy levels (solid lines) as given by particle in a box model. (Adapted from Reference 12)

The TEM images show that the QDs obtained are spherical and are homogenously dispersed. Size distribution of the QDs was very narrow as shown in fig. 8. The average size of the QDs was close to 4.8 nm with a standard deviation of $\pm$ 0.2 nm.
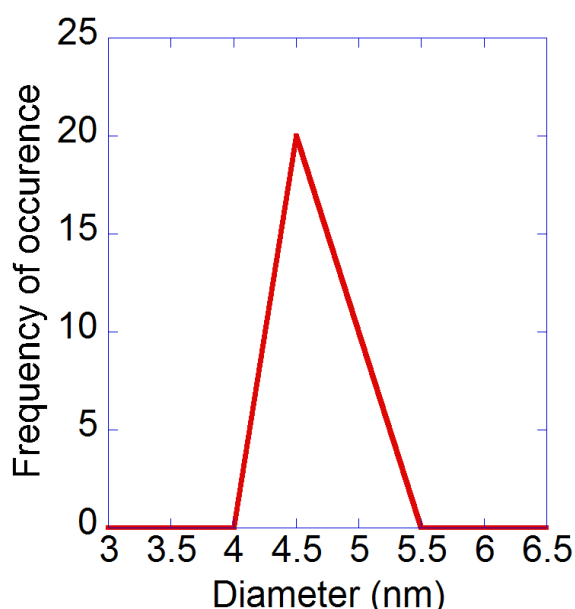
Figure 8: Analysis of TEM data for the calculation of QD diameter

## 3.2.   Optical and Structural Characterization of V doped ZnS QDs
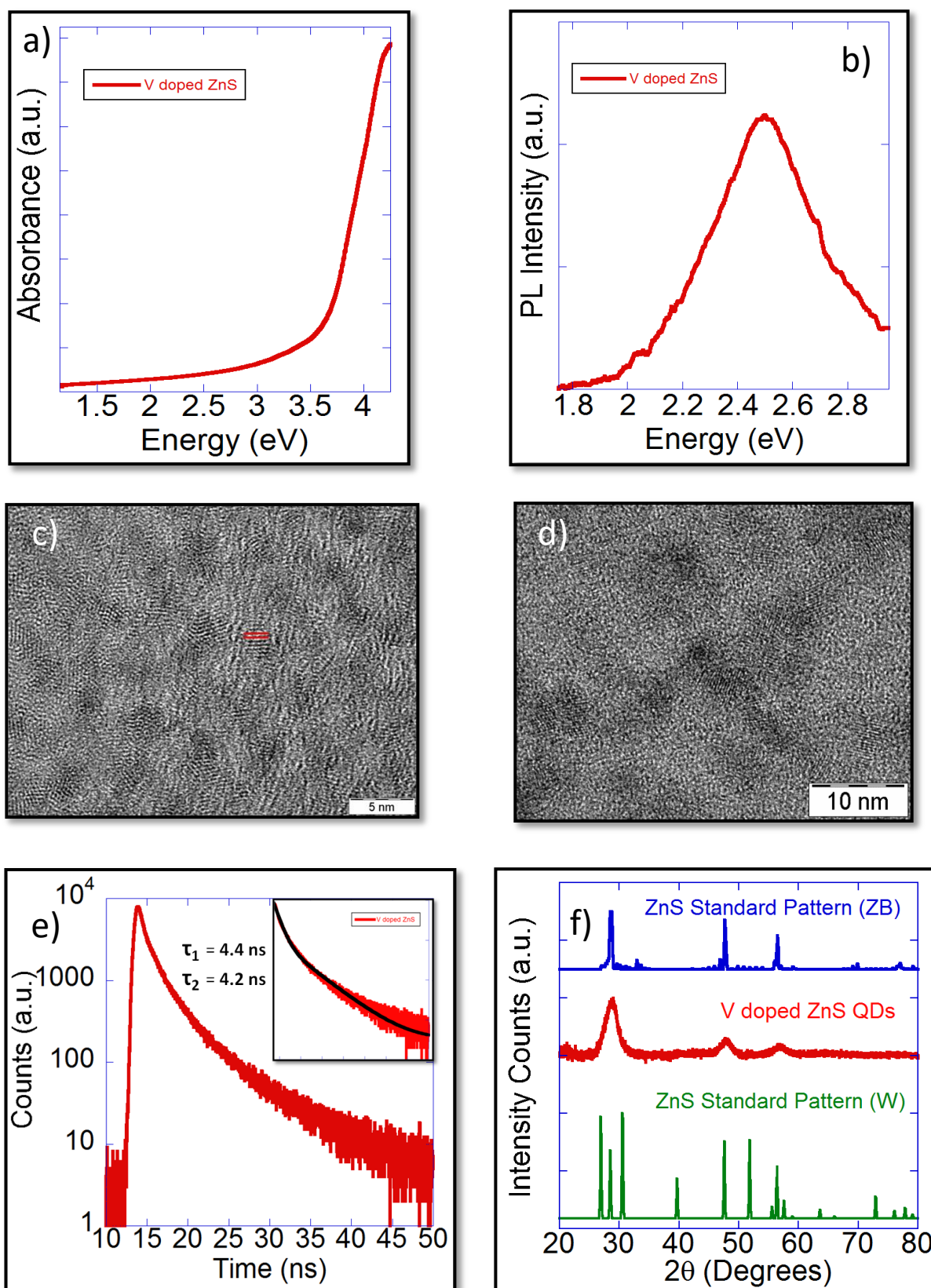
Figure 9: a) Absorption spectrum of V doped ZnS QDs b) PL spectrum of the same c) TEM image of cleaned V doped ZnS QDs d) HRTEM image of the same e) PL Decay kinetics(Inset: Black solid line is the curve fit) f) XRD patterns
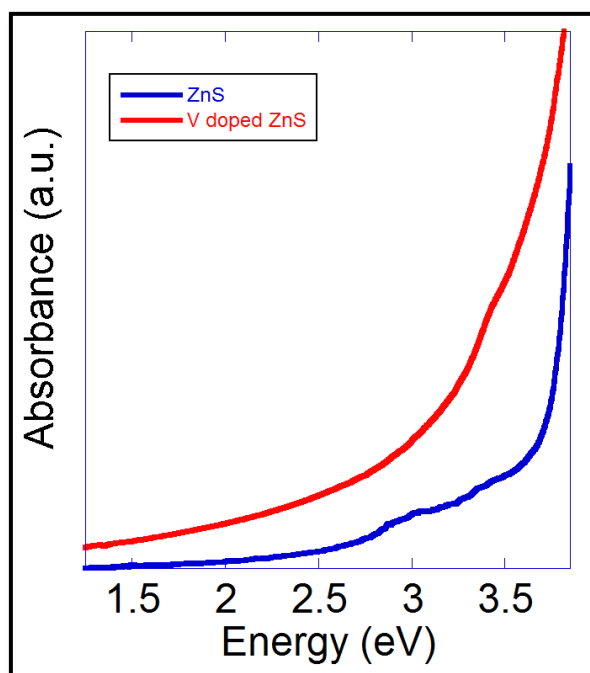
Figure 10: Absorption spectrum of ZnS (Bluesolid line) and V doped ZnS (Red solid line)

The absorption tail of the sample after V doping is extending upto 1.5 eV, which is below the bulk band gap of ZnS. This long tail implies the presence of states at the host band gap. The poor contrast seen in the TEM images of these QDs is because of the low electron densities associated with Zinc and Sulphur. QDs are of the size ~5 nm in diameter. Life time of the QDs was found to be 4.2 ns from the PL decay curve.

XRD patterns of these QDs match with that of Zinc Blende(ZB) crystal structure of Bulk ZnS.[19] No peaks corresponding to impurities were found implying that the QDs obtained are single phase and highly crystalline.

3.3. Elemental analysis:

ICP-OES analysis:

	Zn (mg/L)	V (mg/L)
Sample 1	22.85	0.16
Sample 2	44.01	0.43
Sample 3	187.70	2.22

Table 1: Concentrations of Zn and V ions in V doped ZnS QDs obtained from ICP-OES measurement

Consider Sample 2, Concentrations of Zn and V are 44.01 ppm and 0.43 ppm respectively. 1 ppm of V contains $0.12*10^{20}$ ions or atoms. That implies 0.43 ppm contains $0.052*10^{20}$ ions. Similarly calculating for Zn, 44.01 ppm contains $4.193*10^{20}$ ions of Zn. Ratio of V:Zn ions gives 1.24%. Repeating the same for Sample 1 and Sample 3 gives 0.92% and 1.52% respectively. On averaging the three sample percentages, we get 1.23%, indicating that the V doping is 1.23%.

4.   **Results and Observations:**

After the mixing of two dots, bleach in the absorption and quench in the PL intensity is observed as shown in Figure 8a and b respectively.
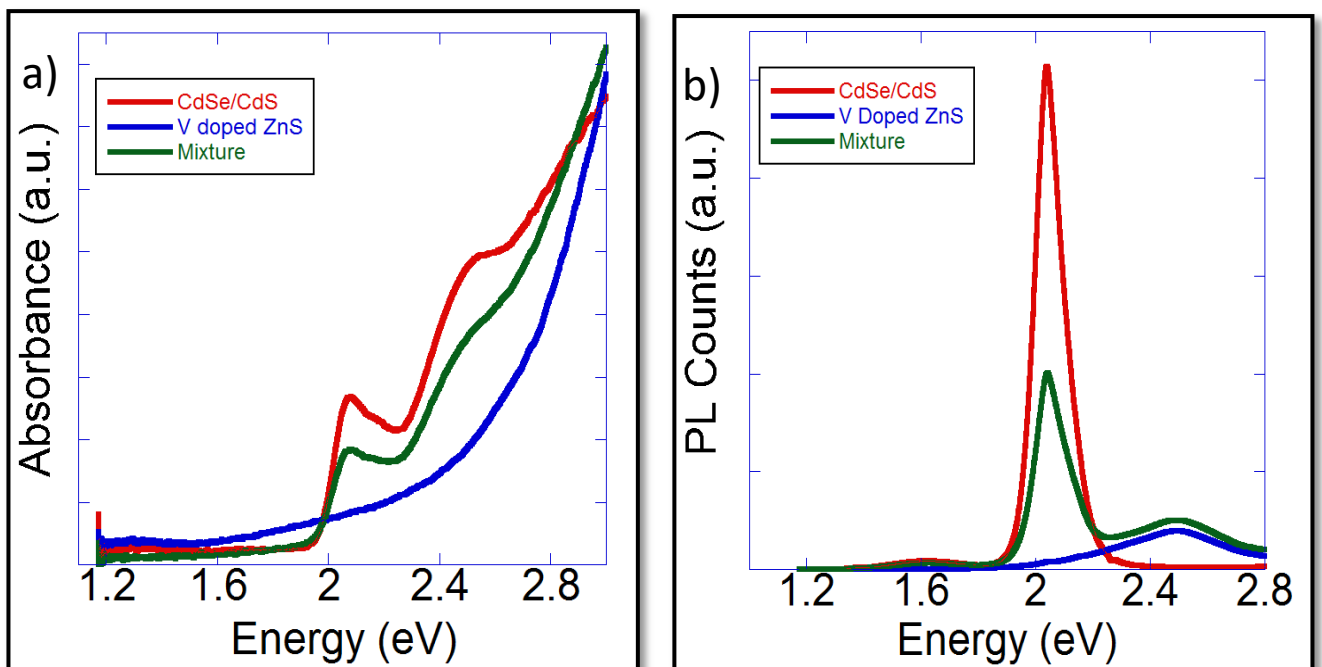

Figure 11: a) Absorption spectrum of Mixed QDs b) PL spectrum of the same

This mixture after being kept for one day, has shown complete quench in PL intensity (fig. 12).
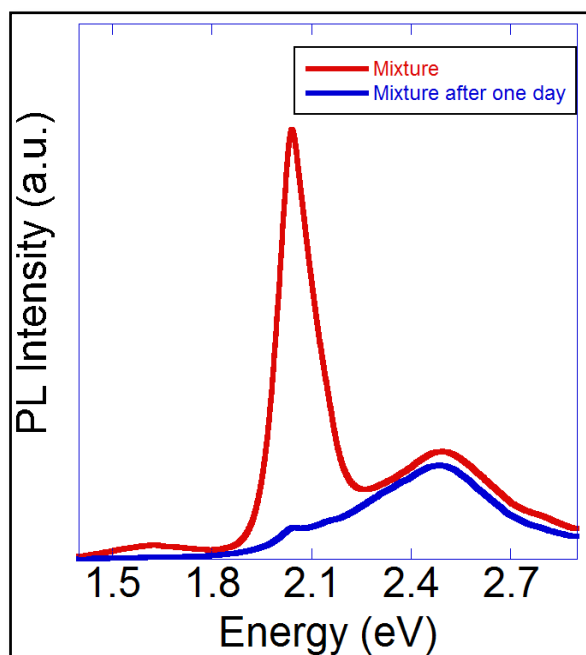
Figure 12: PL spectrum of mixture after one day

Band Edge Absorption Bleach:

The charge injection from V doped ZnS to CdSe/CdS was done by following the previous procedure used for hole doping. To mention briefly, the absorption spectra of cleaned CdSe/CdS was taken (figure 10 a green). Then, cleaned Vdoped ZnS QDs were added to and kept aside to evaporate solvent to achieve close contact between the dots. Once V doped ZnS QDs (Absorption spectra of V doped ZnS (figure 10 a blue line) meets and comes in contact with CdSe base QDs, electrons from vanadium(II) gets injected into the conduction band of CdSe. Due this electron transfer, the conduction band of CdSe based QDs will be partially filled, as a result we see less absorption at the band edge of CdSe based QDs in the mixture (figure 10a red).

PL quench:

This particular PL quench experiment was done by taking PL spectra of CdSe/CdS (figure 10 b red) and V doped ZnS (figure 10 b green) separately in 2.5 ml of hexane. The solutions were then mixed and dried by evaporation at RT. The QDs were then redispersed in 2.5 ml of hexane and PL spectrum of the mixture was recorded. We observed decrease in the intensity of PL spectra when compared to original spectrum (figure 10 b red) taken before mixing. Decrease in the intensity of PL

occurred because of enhanced non-radiative recombination in a trion[20-21] or a more highly charged exciton. This is attributed to auger decay,[22-23] whereby an interband transition recombination is coupled to an intraband excitation in the presence of extra hole or electron.[16]

4.1. *I vs V Characteristics:*

Conductivity measurements were performed by drop-casting the mixture (dissolved in hexane) on the interdigitated platinum electrode. 1:3 ratio of ammonia to isopropanol is used as a cross linker. Cross linker was drop casted on the mixture after the solvent was evaporated. Molecular cross linkers of different length and conjugation are known to reduce the gap between QDs and hence increase the conductivity significantly.[24] The film was washed with ethanol to remove extra cross linker. From figures 13 a,b,c and d, it is observed that upon treating the interdigitated platinum electrode, coated with the mixture, at different voltages yielded corresponding currents. The highest current obtained being 1.7 μA at 1.5 V.

Implications of this PL quench were studied using Fourier Transform Infra-Red (FTIR) spectroscopy.[25] FTIR needs the sample to be very clean and free off all the organic ligands. It was very difficult to clean V doped ZnS dots. Due to low temperature synthesis, the precipitate obtained was oily even after several rounds of cleaning. Due to insufficient signal to noise ratio, intraband spectrum could not be observed.

I vs V curves in the presence of an external light source were also recorded. They show an enhancement in the current obtained compared to that of the current in the absence of light (dark). More importantly, the high value of observed current in QD mixtures is consistent with the occurrence of a small density of free carriers in the system.
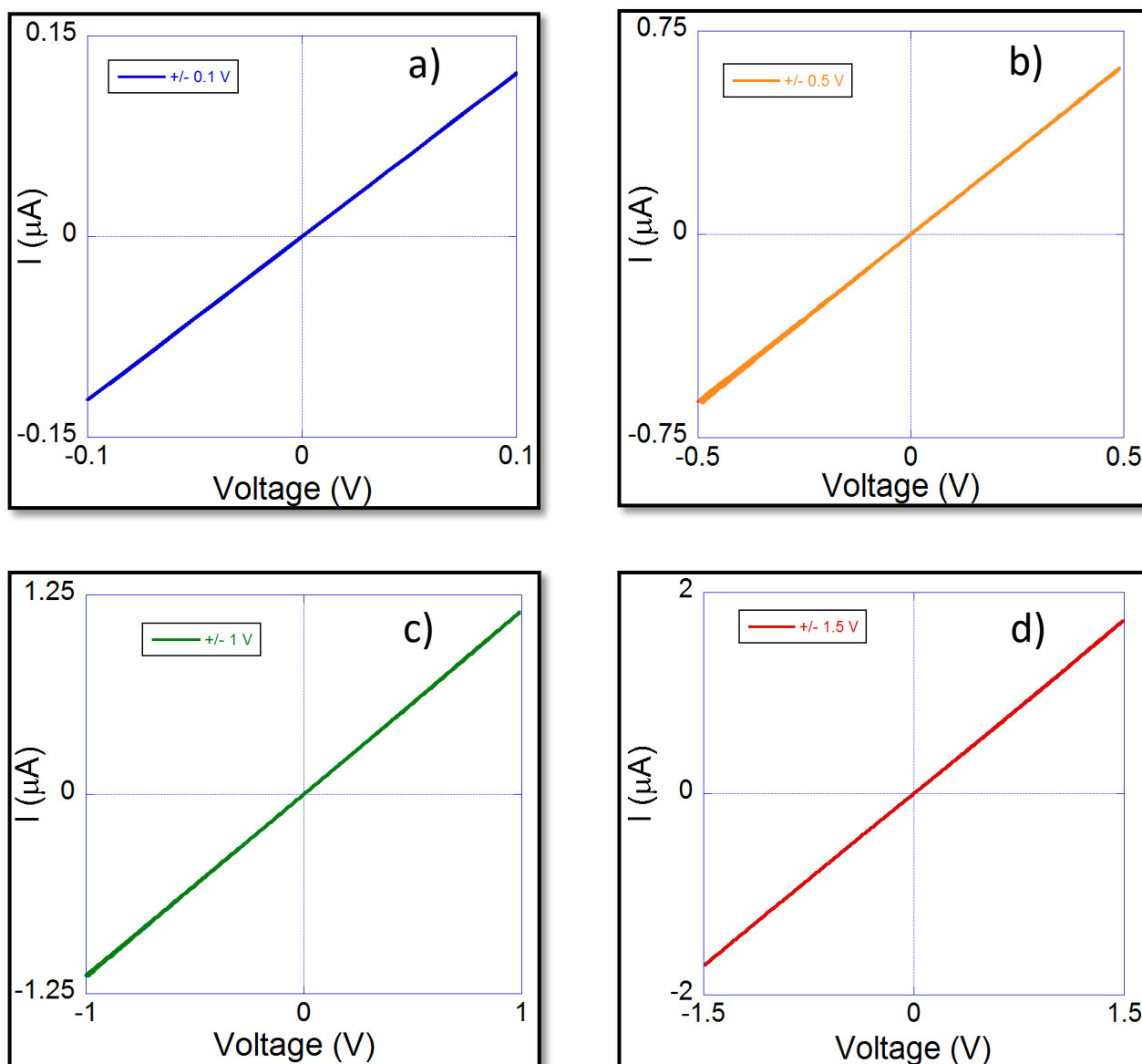
I vs V plots of the mixture:

Figure 13: a) I vs V of mixed QDs with voltage ranging from -0.1 V to +0.1 V b) -0.5 V to +0.5 V c) -1 V to +1 V d) -1.5 V to +1.5 V

5. Conclusions:

Successful synthesis of colloidal V doped ZnS QDs was reported. Absorption band edge of V doped ZnS extended to 1.5 eV, which is much below the bulk band gap of ZnS, as a result of V doping. TEM images show that the size of QDs obtained was 5 nm. XRD patterns show no peaks corresponding to impurities and match with Zinc Blende patterns of bulk ZnS. PL decay curve suggests a life time of 4.2 ns. ICP-OES data indicate Vanadium doping percentage of 1.23 with respect to Zn.

Mixing of CdSe/CdS and V doped ZnS QDs was done and quench in PL intensity of CdSe/CdS QDs was observed indicating electron transfer from V doped ZnS QDs to CdSe/CdS QDs. Current obtained from conductivity measurements was of the order of µA in magnitude. Photoresponse of the assemblies was found to be consistent with the charge transfer hypothesis.

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