Ag (I) and Cu (II) Doped Colloidal CdSe Nanocrystals: Partial Cation Exchange and Effect on Photoluminescence

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Certificate

This is to certify that this dissertation entitled " **Ag (I) and Cu (II) doped colloidal CdSe nanocrystals: Partial cation exchange and effect on photoluminescence**." towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by Bala Gopal Maddala at IISER Pune under the supervision of "Dr. Angshuman Nag, Ramanujan Fellow, Department of Chemistry, IISER Pune" during the academic year 2014-2015.

Date: 25-03-2015

Place: PUNE

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Declaration

I hereby declare that the matter embodied in the report entitled "**Ag (I) and Cu (II) doped colloidal CdSe nanocrystals: Partial cation exchange and effect on photoluminescence** " are the results of the investigations carried out by me at the Department of Chemistry, IISER Pune under the supervision of Dr. Angshuman Nag and the same has not been submitted elsewhere for any other degree.

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Place: PUNE

Maddala Bala Gopal

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Abstract:

Optical properties of the silver and copper doped CdSe nanocrystals has been investigated. Partial cation exchange with impurity ions is done using trioctylphosphine (TOP) to facilitate the controlled doping levels. Doping is as low as few impurity ions per nanocrystal. Finally, the role of dopant ions at very low concentrations and effect of TOP on photoluminescence of the CdSe nanocrystals is explained.
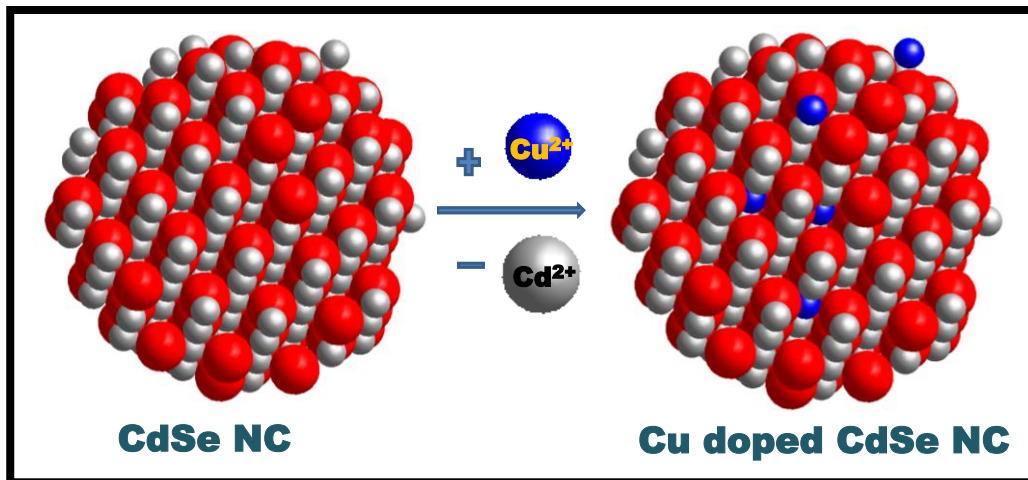
1. Introduction

1.1. Quantum Dot

Quantum dots (QDs) are the tiny semiconducting crystalline materials of sizes typically ranging from 2-20 nanometres (nm). They consists of few hundreds of atoms. As the size of the nanocrystal increases coupling between the molecular HOMO and LUMO levels increases and slowly the discrete energy levels near the band edges disappear with the decrease in band gap (shown in figure 1).[1] Addition of more atoms leads to increased coupling between HOMO-LUMO levels forming continuous band in bulk materials. Thus quantum dots displays unique properties intermediate to discrete molecules and bulk materials.

Quantum dot upon excitation leaves behind a hole in the valence band and an electron in the conduction band. Since these charge carriers (electrons and holes) are confined in very small volumes, they are bound to each other. This bound state of an electron and hole is called an exciton. Precisely, the electron wave function is bound in all 3 dimensions in a quantum dot. Conversely, if the wave functions are confined in 2D and 1D then they are called quantum wire and quantum well respectively. So the charge carrier in the quantum dot can qualitatively be considered as a particle in a 3D box. Therefore the energy needed to excite a charge carrier from highest valence band to lowest conduction band increases as the size of the nanoparticle decreases. Thus this confinement (known as quantum confinement effect) of charge carriers in very small volumes effects the exciton wave function, which in turn effects the density of electronic states and band gap as shown in figure 1. So charge carrier upon exciting emits lights of different wavelengths corresponding to the band gap of the material. In other words, the semiconductor nanocrystals (NCs) emits different wavelengths of lights based on their size. The size tunable electronic and optical properties of QDs have tremendous applications in Light Emitting Diodes (LEDs), solar cells, detectors etc. In addition, when the size of particles decreases, surface area increases gradually and making them suitable for catalytic applications and also in solar cells.
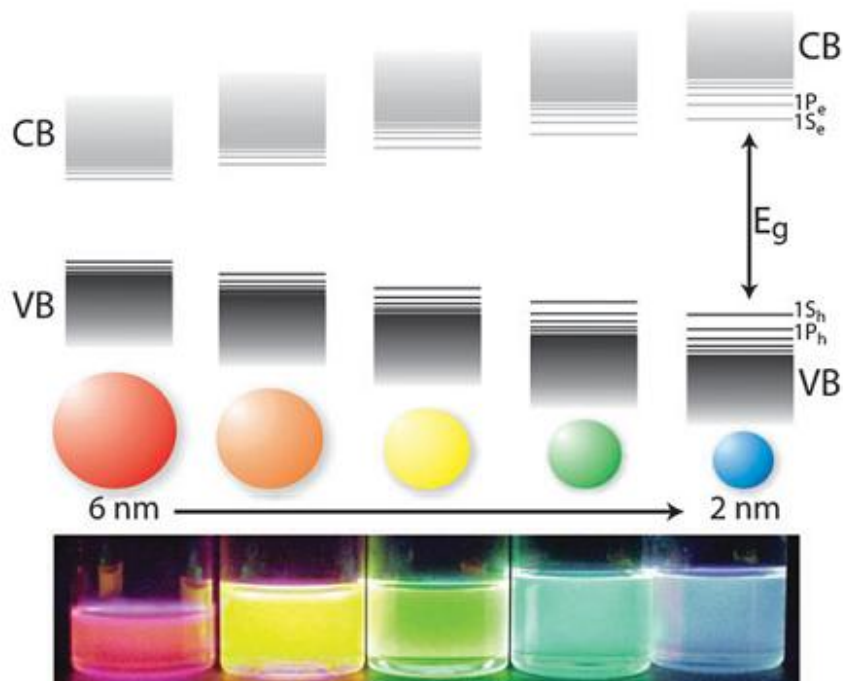
Figure 1. Pictorial illustration of the quantum confinement effect in colloidal CdSe NCs of sizes ranging from 2nm to 6nm. (Adapted from ref.[1] with permission of the Royal Society of Chemistry).

1.2. Synthesis of colloidal quantum dots

Colloidal nanocrystal synthesis has gained importance because of the ease with which various morphologies (size, shape) can be altered just by changing reaction temperature, time and changing the precursor concentration. In this thesis, nanocrystal synthesis is done using hot injection method.[2] Hot injection method is a common technique to obtain monodisperse particles. In this method one of the precursor (usually organometallic compounds) dissolved in organic solvent is kept at high temperature, followed by quick injection of the other precursor (elemental) which is at room temperature. This quick injection leads to supersaturated solution followed by nucleation of small crystallites. Quick injection of the solution at room temperature into the solution at high temperature leads to sudden temperature drop, which separates the nucleation and growth processes forming monodisperse quantum dots. The obtained nanocrystals are passivated with organic solvent molecules resulting in highly luminescent nanoparticles.

1.3. Surface states

The atoms present on the surface of the nanocrystal are not perfectly bonded or coordinated as compared to the atoms which are present in the interior of the nanocrystal. Therefore these surface atoms will have unsatisfied chemical bonds which are known as dangling bonds. These dangling bonds leaves energy levels within the bandgap of NC, which is a setback for quantum yield (QY) of the NCs. When an electron occupies these localized surface states, the overlap between the electron and hole wave function reduces. This results in poor radiative recombination rates. Eventually, exciton relaxes via nonradiative pathways through heat dissipation by phonons (crystal vibrations). So it is very important to take care of surface states to obtain highly luminescent particles.

1.4. Motivation

Colloidal QDs have gained lot of attention due to potential optoelectronic applications.[3-8] The unique property of monodisperse QDs, which is narrow emission spectral bandwidth allows us to attain sharp colour emitting quantum-dot light emitting devices (QLEDs). Emission wavelengths can be tuned controllably by just changing the size of the same nanocrystal due to quantum confinement effect.[9-13] Since the light emitters in these devices are quantum dots, it is highly desirable to synthesize high quantum yield particles. Since the first report on QLEDs by Colvin et al [3] back in 1994, there are several attempts to enhance the quantum yield of the particles. Surface defect states of quantum dots are detrimental to the quantum yield (QY%) of NCs. Due to these defects, charge carries gets trapped resulting in decreased QY.[14] Core shell quantum dots offered solution to this problem. These kinds of surface modifications to the quantum dots lead to confinement of exciton and passivation of surface defect states. This results in decreasing the non radiative decay channels and leads to improvement of QY.[15-18] CdSe/CdS, CdSe/ZnS and CdSe/CdS/ZnS core shell systems have shown considerable improvement in QY.[5,18] Kyung-Sang Cho et al. have shown high performance QLEDs based on CdSe/CdS/ZnS core shell structures.[8] However, this QLEDs operate by electroluminescence phenomenon. Electroluminescence is the phenomenon, where electrons and holes are injected into

the quantum dot layer which is sandwiched between electron and hole transport layers. It is highly desirable that the injected charge carriers are transported easily through several layers of QDs. But, in the core shell NC systems, the shell formed on the NC acts as a barrier for the efficient charge transport. Spatial confinement of excitons in core shell particles can also lead to carrier-carrier interactions which further leads to high non-radiative auger recombination rates of the core.[19] Charge accumulation and poor charge transport, strong quenching of luminescence QY under electric fields in these core shell quantum dots restricting us to achieve high efficient QD based LEDs.[20] At this stage it is highly desirable to look for an alternative for these core shell QDs to achieve comparable QYs.

Recently, Norris et al [21] reported that doping of Ag (I) impurity ions at very low concentrations in colloidal CdSe nanocrystals leads to enhancement in the photoluminescence comparable to core shell particles. Here the doping is as low as 1 Ag ion to 20 ions per NC. However, the exact reason behind these enhancements is not discussed in the paper. Alternatively, the presence of charge on the QDs would result in improving auger recombination's which decreases the QY. However, this kind of unusual enhancement in the PL due to impurity ions is very much unexpected and motivated us to study the lightly doped systems.

Partial cation exchange is a method which allows us to dope impurity atoms at very low concentrations into nanocrystals. But, these kinds of studies on nanocrystals are limited in literature.[22-27] Cation exchange phenomenon offers great tunabilities to the nanocrystal systems. Full cation exchange or partial cation exchange in a system can be exploited. Since, the cation exchange is done after synthesis, it offers great control over maintaining the shape, quality and uniform size distributions of the nanocrystals as compared to other methods where impurities are added during the reaction. In this post synthesis modification of NCs, anion sublattice remains intact, whereas cations get exchanged with other cations of our interest based on the application we are looking for. By this way we can obtain NCs of new material without changing the morphology of the initial NCs. This allows us to compare easily different properties of the NCs. In fact, using this method, materials of specific crystal phase can be achieved where the same cannot be obtained using direct synthesis. However, there are very few publications on post synthesis lightly doped semiconductor nanocrystals. Robert et al. have shown light copper doping into CdSe nanocrystal where copper precursor

is added at the start of the reaction.[28]   Here, in the thesis we describe the post synthesis partial cation exchange of copper (II) ions in CdSe nanocrystals. There are no prior articles on post synthesis lightly doped CdSe nanocrystals with copper ion to the best of our knowledge. In addition, we are discussing the effect of lightly doped copper ion on the PL and also comparing the results with previously reported silver ion doping.[21]

2. Methods

2.1. Experimental Section

2.1.1. Chemicals

Cadmium oxide (99.99%, Aldrich), silver nitrate (99%, Aldrich), Copper nitrate trihydrate (Merck chemicals), selenium (99.99%, Aldrich), trioctylphosphine (TOP, Aldrich), tetradecylphosphonic acid (TDPA)(Aldrich), trioctyl phosphine oxide (TOPO) (ReCuent plus, 99%, Aldrich) and oleylamine (technical grade, 70 %, Aldrich) , toluene (99.5%, Rankem), ethanol (99.9% AR, S D Fine chem. Ltd).

2.1.2. Synthesis of colloidal CdSe nanocrystals

Colloidal CdSe nanocrystals were synthesised by adding cadmium oxide (0.64 mmol), tetradecylphosphonic acid (TDPA)(1.28 mmol), trioctyl phosphine oxide (TOPO) (4.2 mmol) and oleylamine (5 mL) in a 3 neck round bottomed flask following modified procedure.[29] The reaction mixture was kept at 100 $^{\circ}$C followed by purging with nitrogen for 10 minutes and then under vacuum for 30 minutes with continuous stirring. This process was repeated for 3 times to ensure all the moisture and O_2 are removed. Then the temperature was raised to 320 $^{\circ}$C. After the solution turned colourless, the temperature was lowered to 270 $^{\circ}$C. A 4 ml TOPSe (Selenium dissolved in TOP) (0.2M) solution prepared in glove box was added and kept at that temperature for 10 min till the solution became dark red in colour. The solution was cooled to 90 $^{\circ}$C followed by addition of 10ml toluene to prevent solidification of reaction mixture. The nanocrystals were separated by the addition of ethanol followed by centrifugation at 7000 rpm for 10 minutes. This washing was done 2-3 times to remove unreacted precursors. Finally CdSe nanocrystals were redispersed in toluene.

2.1.3. Partial cation exchange

For partial cation exchange, 5 mg/ml CdSe solution was stirred at 60 °C.The concentration of the CdSe solution was found from the method following previously reported literature.[30] Stock solution of silver(I) and copper(II) were prepared by adding 1 ml of 0.1 M ethanolic solution of $AgNO_3$ and $Cu(NO_3)_2$ respectively with 1.5 ml TOP and then rapidly stirred for 30 minutes at 45 °C. Silver doping is done by adding small amounts of stock solutions were added to 250 microlitres of CdSe solutions based on the number of dopant atoms per nanocrystal as described by a reported protocol.[21] For example, 104 µl of dopant solution was added to 250 µl of 5 mg/ml CdSe solution to achieve 1 dopant atom per nanocrystal. Total volume of cationic solution was kept constant (260 µl) by adding solution of TOP (3 vol%) and ethanol (2 vol%) in order to maintain a fixed concentration of TOP and ethanol for all reactions. Partial cation exchange of copper ion was done by adding 34, 67 and 208 µL of stock solution with 250 µL of CdSe NC dispersion (5 mg/ml) which yielded 1.3, 3.8 and 7.5 Cu/NC. Partial cation exchange reactions were done in glove box under inert atmosphere.

2.2 Instrumentation

UV-visible absorption and photoluminescence (PL) spectra of all the doped and undoped CdSe NCs dispersed in toluene were recorded using a Perkin Elmer, Lambda-45 UV/Vis spectrometer and FLS-980 (Edinburgh instruments), respectively. Powder XRD patterns of the NCs were obtained using Bruker D8 Advance X-ray diffractometer using Cu Kα as X-ray source. EPR measurements of the copper doped particles were done using JEOL JES - FA200 ESR Spectrometer, Japan (IIT, Bombay.). ICP-OES (Inductively Coupled Plasma-Optical) analysis of the doped samples were done using ARCOS M/s. Spectrophotometer, Germany (IIT, Bombay).

3. Results and Discussion

Highly luminescent colloidal CdSe NCs were synthesized using hot injection method.[2] In our case, TOPSe solution at room temperature was injected to cadmium precursor solution at 280 °C. This lead to the formation of several CdSe nuclei along with sudden drop in temperature. The drop in temperature prevents the formation of new nuclei. Further, precursors will add to the existing nuclei forming particles of uniform size

distribution. The surface of the nanocrystals were stabilized with TDPA and TOP/TOPO. The XRD plot of the synthesized CdSe nanocrystals (figure 2) suggests that the particles were obtained in their pure phase. Clearly, XRD pattern of CdSe NCs
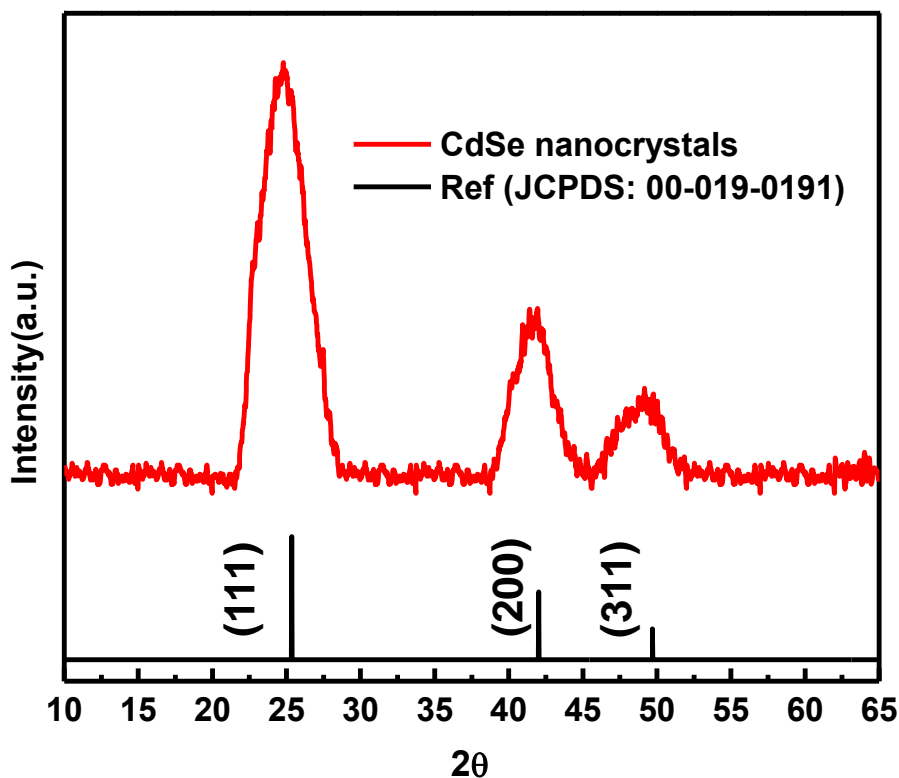

Figure 2. Powder XRD pattern of CdSe NCs (Red colour). JCPDS (00-019-0191,space group F-43m (216)) data for bulk CdSe is shown as reference.

match with the cubic zinc blende of bulk CdSe (JCPDS no: 00-019-0191) with symmetry group F-43m (216). The diffraction pattern shows three different peaks. The peak at $2\theta = 25^0$ correspond to the reflection of (111) plane. The peaks at $2\theta = 42^0$, 50^0 correspond to the reflection of (220) and (311) plane respectively. The size of the CdSe NCs and extinction coefficient of CdSe NCs is obtained from UV-VIS spectrum using Peng's method.[30] The diameter (D) of the particles is obtained using equation 1.

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + (41.57) \quad \textbf{(1)}$$

Where λ is the wavelength at which nanocrystals show absorbance maximum for lowest energy excitonic transition. Further, the extinction coefficient for CdSe nanocrystals is calculated using equation 2. From the extinction coefficient value, concentration of the NCs is calculated using beer lamberts law.

$$\varepsilon = 5857 \, (D)^{2.65} \qquad \textbf{(2)}$$

An absorbance and PL plot of the synthesised CdSe NCs is shown in figure 3. Absorbance maximum for CdSe NCs is shown at 530 nm corresponding to the low energy excitonic transition of nanocrystals and PL maximum at 542 nm.
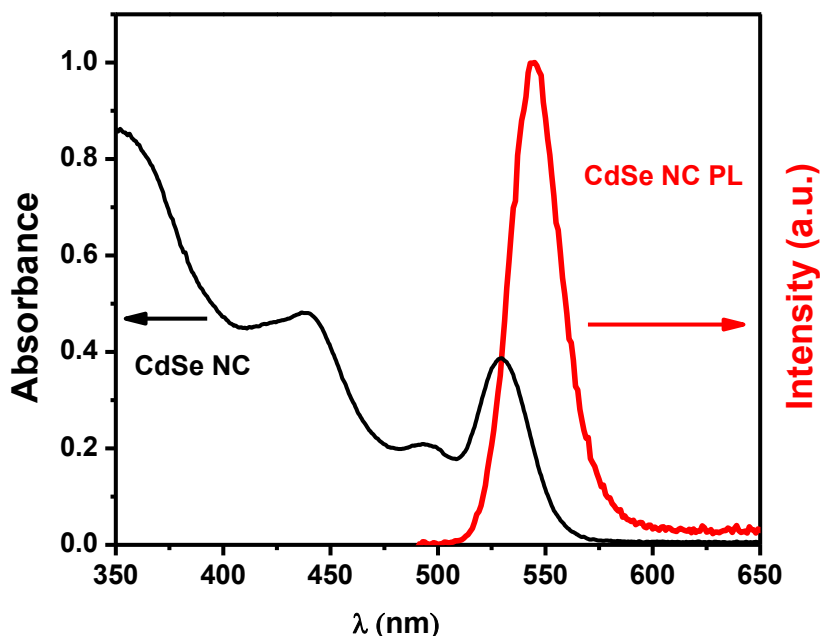

Figure 3. Absorbance and photoluminescence spectra of 3 nm diameter CdSe nanocrystals showing absorption maximum at 530 nm and PL maximum at 542 nm.

To prevent complete cation exchange of CdSe nanocrystals with dopant ions, copper nitrate and silver nitrate were treated with TOP along with ethanol. TOP being the soft base, binds to Ag^+ (soft acid) and Cu^{2+} (Intermediate soft acid) which makes these dopant ions unavailable for the complete cation exchange. Here TOP plays the major role in partial cation exchange. Without TOP, selenium being the softer anion tries to bind with softer Ag^+ and Cu^{2+} ions than with Cd^{2+} ion which will result in complete cation exchange. So, in our case TOP is making dopant ions unavailable. Even though, there will be some amount of free ions in the solution which facilitates the controllable doping levels. Here Ag^+ and Cu^{2+} ions being small ions diffuse easily through the crystal lattice. Partial cation exchange has been done with mild heating at 50-60 °C to facilitate the cation diffusion process. The diffused ions either occupy interstitial position or replace some of the Cd^{2+} ions from the crystal lattice. Ethanol present in the stock solution helps to extract these Cd^{2+} ions, thus favouring the

reaction towards forward direction which makes the reaction thermodynamically more favourable.

3.1. Partial cation exchange with Ag (I) ion:

Absorbance plots of various doping concentrations of silver (I) ion is shown in figure 4. The number of Ag ions per NC mentioned here are based on prior report.[21] The absorption maximum for all the dopant concentrations remain at approximately 530 nm. This suggests that NC size and shape remains intact upon doping. PL measurements were done at the excitation wavelength of 470 nm. PL plots shown in figure 5 are absorbance normalized. Partial cation exchange with Ag (I) in CdSe was
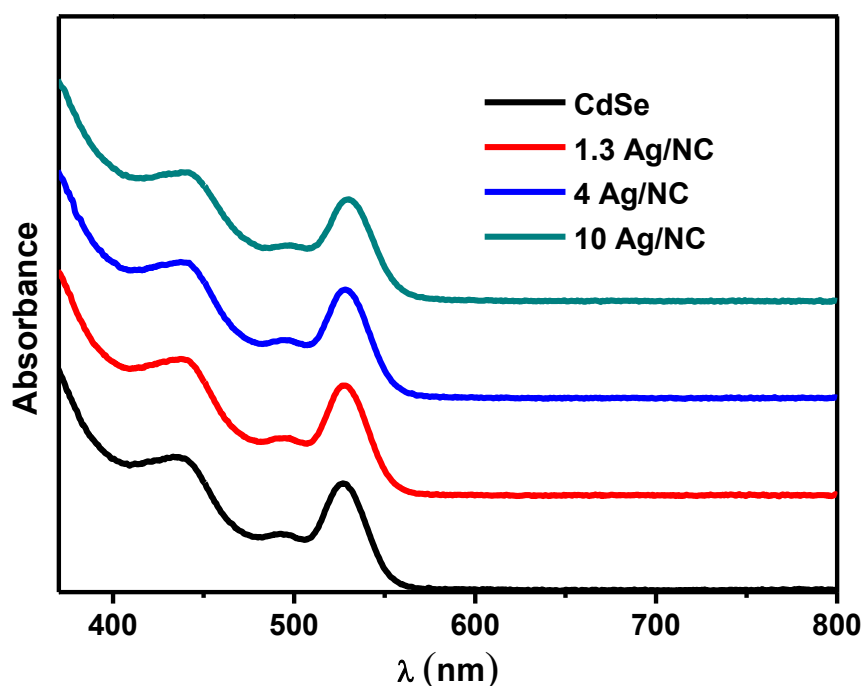

Figure 4. Absorption spectra of CdSe nanocrystals with different silver doping concentrations showing absorption maximum at 530 nm. NCs are dispersed in toluene (Absorbance plots are shifted vertically for clear representation.).

done using the procedure described by ref 21. Figure 5 shows the intensity of band edge emission at 542 nm in the 1.3 Ag/NC (red) is 4.5 times compared to undoped CdSe nanocrystal (black). Further doping results in PL intensity drop to 1.1 in 10 Ag/NC sample. Figure 6 shows normalized PL plot where dopant related peak of silver (I) ion at 648 nm is seen clearly at higher doping concentrations. Figure 7 shows

intensity of dopant related defect state emission at 648 nm is steadily increasing from 0.01 in undoped CdSe nanocrystal (black) to 0.28 in 10 Ag/NC. Ref[21] suggested that the dopant related emission originates through recombination of photo-generated electron in the conduction band of host with Ag-bound hole residing in a mid-gap state.
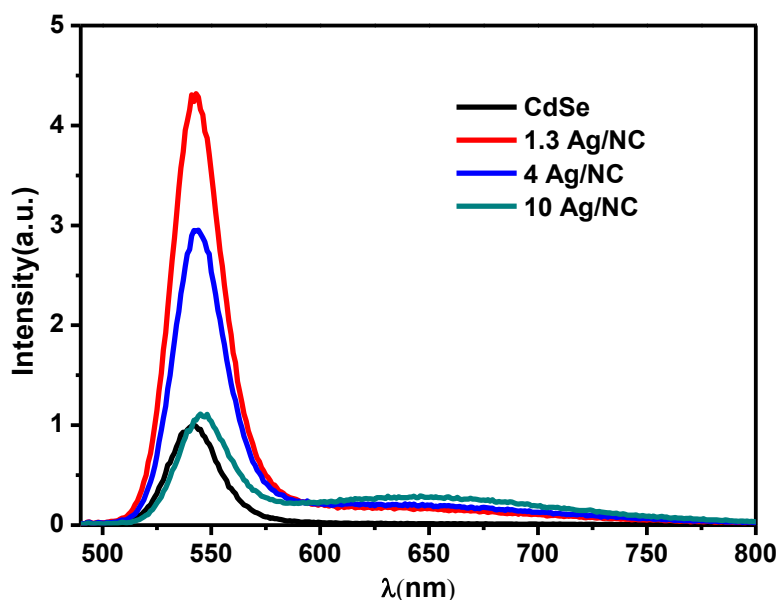

Figure 5: PL spectra of silver doped CdSe nanocrystals with different dopant concentrations. Spectra is normalized with corresponding absorbance at excitation wavelength 470nm.
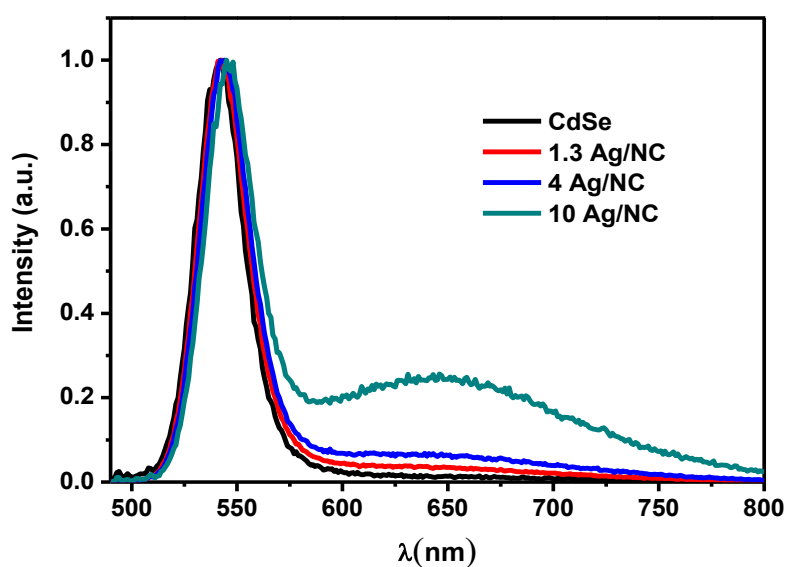

Figure 6: Normalized PL spectra Ag-doped CdSe NCs with different dopant concentrations showing emergence of dopant related peak at 648nm.
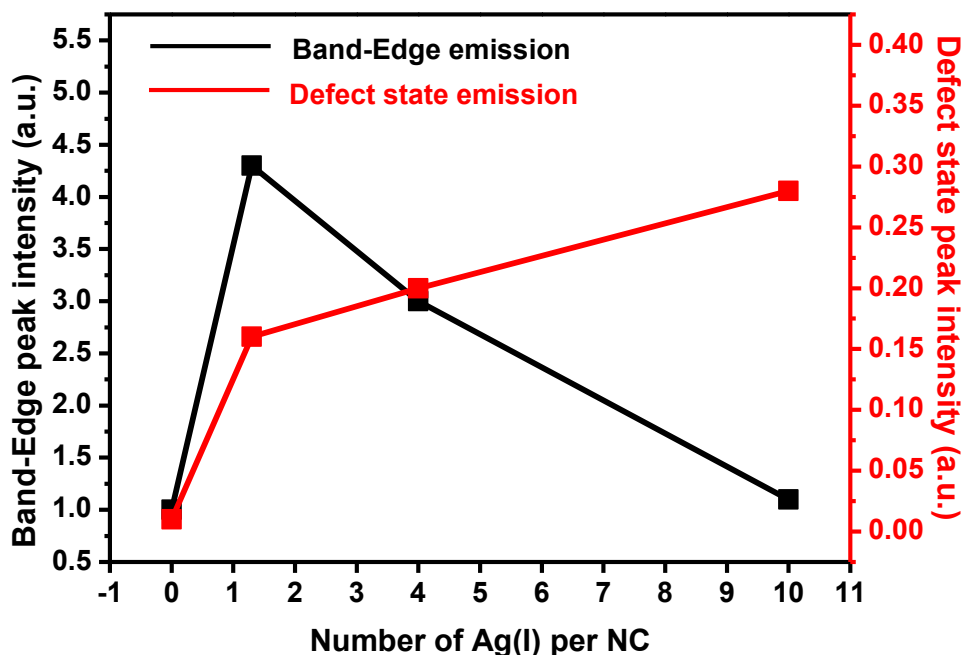
Figure 7: The variation of intensity of both excitonic PL near 542 nm and Ag-dopant related PL near 648 nm as a function of dopant concentration.

3.2. Partial cation exchange with Cu (II) ion:

ICP-OES analysis of the doped samples is shown in table 1. Number of CdSe units in a 3 nm CdSe NC are calculated using the method described by Angwafor et al. It is found from the absorbance maxima for the CdSe NC which is at 530 nm that each CdSe nanocrystal has 250 CdSe units. Further, using this information, number of copper ions doped in a single NC is calculated from ICP-OES measurements. Preliminary EPR data suggests that copper doped is in +2 oxidation state.

Absorbance plots of various doping concentrations of copper (II) ion is shown in figure 8. The absorption maximum for all the dopant concentrations remain at approximately 530 nm. This suggests that NC size and shape remains unchanged upon doping. PL measurements were done at the excitation wavelength of 470 nm sample. Similar trend is observed in copper doped particles. Figure 9 shows the enhancement in the PL intensity of band edge emission at 545 nm in the 1.3 Cu/NC (red) is 3.8 times compared to undoped CdSe nanocrystal (black). Further doping results in PL intensity drop to 1.1 in 7.5 Cu/NC sample as shown in figure 9. Figure 10 shows normalized PL plot where dopant related peak of copper (II) ion at 780 nm is seen clearly at higher

doping concentrations. Figure 11 shows intensity of dopant related defect state emission at 780 nm is steadily increasing from 0.06 in undoped CdSe nanocrystal (black) to 0.45 in 7.5 Cu/NC sample (green).

Sample	% of Cd	% of Cu	No. of Cu/NC
1	99.5	0.5	1.3 Cu/NC
2	98.5	1.5	3.8 Cu/NC
3	97.0	3.0	7.5 Cu/NC

Table 1. Cd and Cu concentration from ICP-OES analysis of the copper doped CdSe samples.
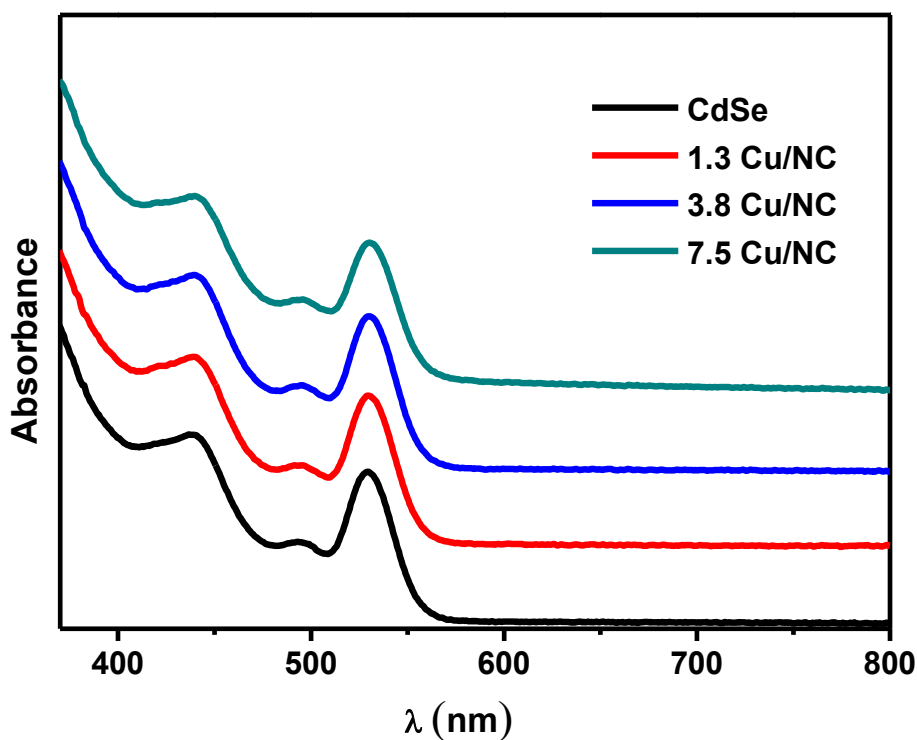

Figure 8: Absorption spectra of doped CdSe nanocrystals with different copper doping concentrations showing absorption maximum at 530 nm. NCs are dispersed in toluene (Absorbance plots are shifted vertically for clear representation.).
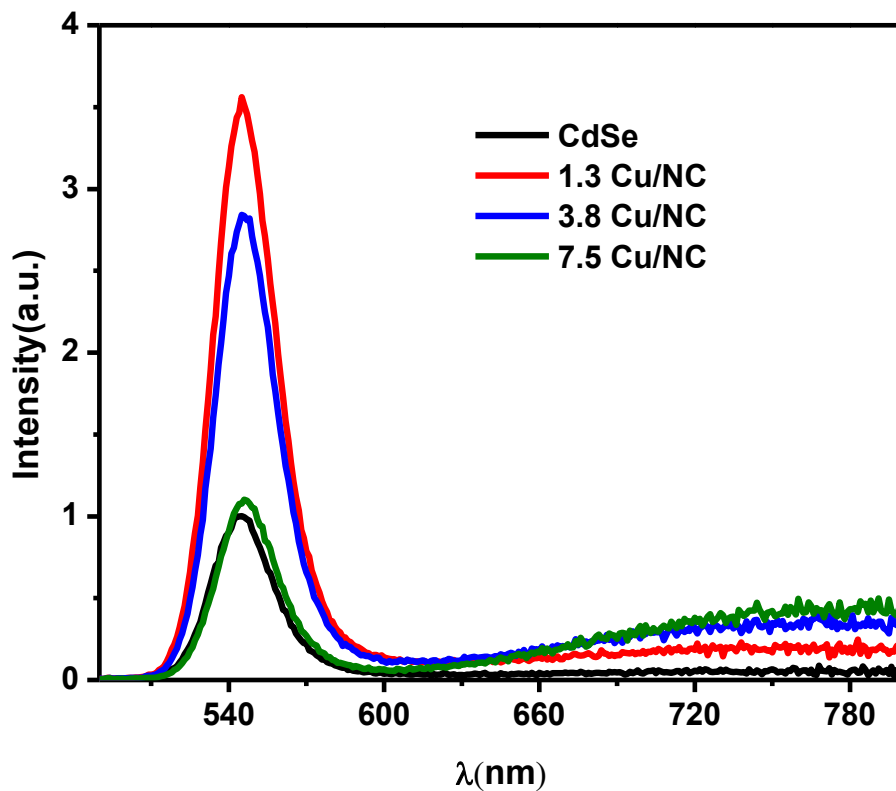
Figure 9 : PL spectra of copper doped CdSe nanocrystals with different dopant concentrations. Spectra is normalized with corresponding absorbance at excitation wavelength 470nm.
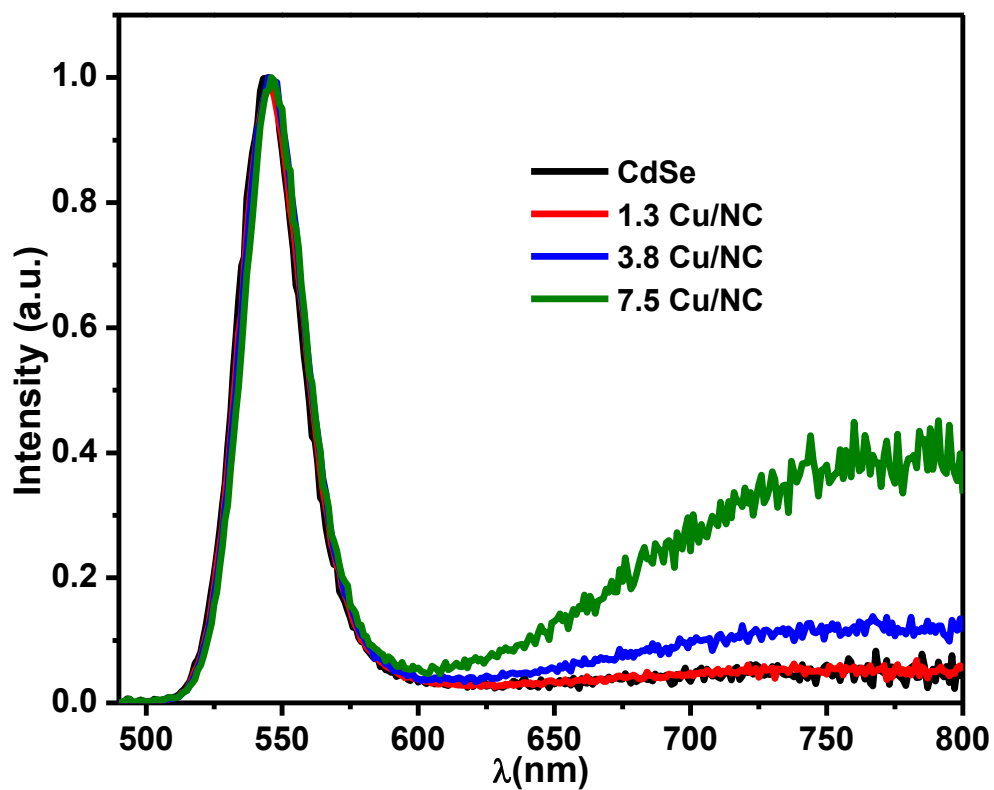

Figure 10: Normalized PL spectra Cu-doped CdSe NCs with different dopant concentrations showing emergence of dopant related peak at 780nm.
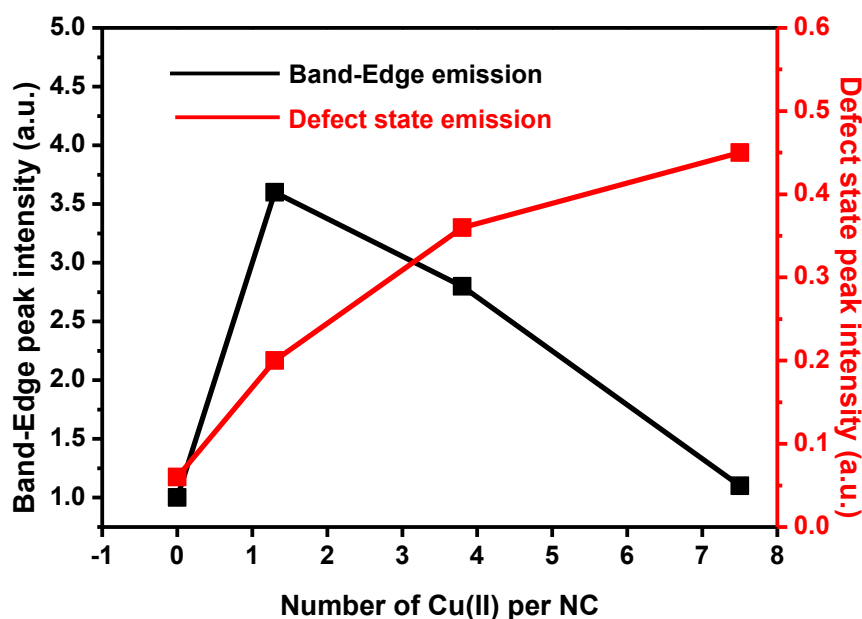
Figure 11: The variation of intensity of both excitonic PL near 542 nm and Ag-dopant related PL near 780 nm as a function of dopant concentration.

The broad emission, extended up to near-infrared (NIR) region is red-shifted compared to excitonic emission and is assigned to emission arising from Cu dopant. Similar NIR emission was recently observed by Viswanatha and co-worker[31] from Cu-doped CdSe NCs, suggesting the success of our partial cation exchange reaction preparing Cu-doped CdSe NCs. This NIR PL has been attributed to transition from conduction band of host NC to the Cu d level in the mid-gap region.[32-34] Lower intensity of Cu-related emission compared to excitonic emission is probably because of better passivation of NC surface, since in the absence of hole traps excitonic emission with shorter lifetime can dominate over Cu emission with longer lifetime.

3.3 Effect of TOP on PL of CdSe NCs

Figure 12 demonstrates the PL spectra of CdSe NCs after treating with TOP and ethanol in similar way that was used during cation exchange reaction. Same protocol of cation exchange reaction was followed but without having the dissolved cations. NCs were treated with a mixture of ethanol and TOP. Figure 12 shows that the intensity of excitonic emission increases sharply after treating CdSe NCs with ethanol and TOP, similar to the enhancement of excitonic emission observed for low level of Ag and Cu
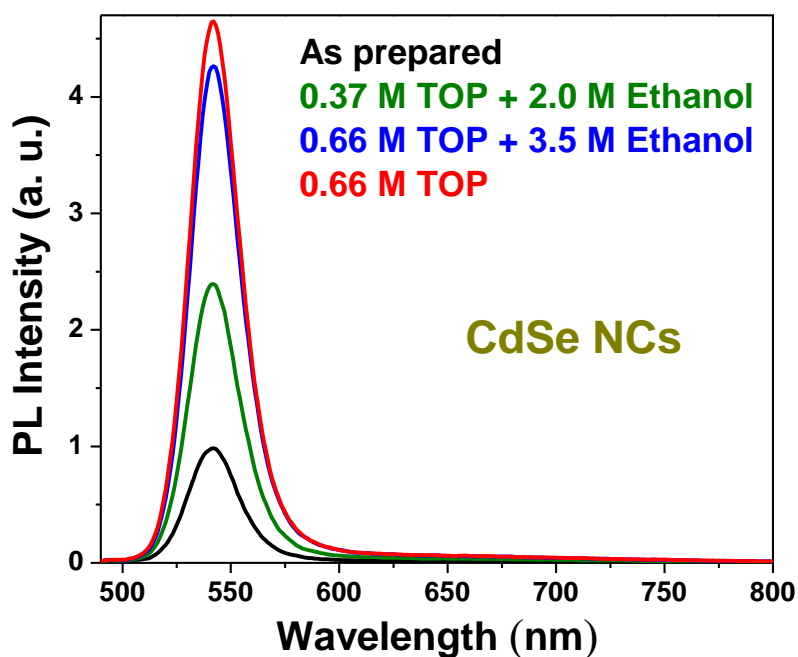
Figure 12: PL spectra of CdSe NCs after treating with TOP and ethanol in a way similar to that used during cation exchange reaction.

doping (Figure 5 and 9). In fact, a very similar result was also obtained after treating the CdSe NCs with only TOP in the absence of ethanol. These results suggest that the enhancement of excitonic PL at low level of doping is because of interaction of TOP with CdSe NC, and not because of added Cu^{2+} or Ag^+ ions. Figure 12 shows the 4.6 times enhancement of excitonic PL of CdSe NCs, after treating CdSe NCs with 0.66 M TOP. We note that the same amount of TOP (0.66 M) was also present in the partial cation exchange reaction for 1.3 dopant / NC showing enhancement excitonic PL by a factor 4.3 and 3.8 for Ag and Cu doped NCs respectively (Figure 5 and 9). These results, in fact, suggest that the intensity of excitonic PL slightly decreases even at 1.3 dopant per NC, compared to NCs treated with TOP. Further increase in TOP concentration does not change the PL intensity. It is very clear from the data that the initial rise in PL intensity is just due to TOP. TOP being the surfactant, initial addition results in passivizing the surface defect states to some extent and on further addition of TOP does not have any effect on PL intensity. However, higher doping levels of impurity atoms results in drop in the band edge emission and the impurity related peak is getting significant. This could be due to recombination of photo excited electrons in the conduction band of host NCs with the low lying levels of dopant atoms in the mid gap region, which results in appearance of dopant related peak at higher

wavelength compared to band edge peak. Further, the data confirms the negligible effect of dopant ions on enhancement in the PL intensity. Here the dopant related peaks are coming at wavelengths specific to the dopant ion, 648 nm for Ag ion and at 780 nm for Cu ion.

4. Conclusions

In conclusion, partial cation exchange of CdSe nanocrystal with Ag (I) and Cu (II) ions is successfully demonstrated using TOP as a medium for controllable doping levels. Doping leads to dopant specific PL peaks arising at 648 nm for Ag ion and at 780 nm for Cu ion. At higher concentrations of doping levels the dopant related peak is getting significant which could be due to recombination of photo excited electrons with the low lying levels of dopant ions, which results in appearance of dopant related peak at higher wavelength compared to band edge peak. Further, Ag ion doping results match with the previous reported literature. In addition, partial cation exchange with Cu ions in CdSe NCs was done for the first time. However, partial cation exchange with Cu and Ag ions in CdSe NCs shows that initial enhancements in the PL intensity is due to the cleaning of NC surface i.e. passivation of dangling bonds and trap states present on NC surface by TOP. TOP here acting as a coordinating ligand on the surface of the NC passivates the surface defects thus reducing the non radiative decay channels for the charge carriers. So, the enhancement of PL intensity is solely due to TOP and dopant ions have negligible role in the PL enhancements.

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