

# RECENT DEVELOPMENTS FOR THE SYNTHESIS OF AIR STABLE QUANTUM DOTS

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**Abstract.** Inorganic semiconductor nanocrystals or quantum dots (QDs) show unique and size specific optical, photoluminescence (PL) and electronic properties, which make them very promising and demanding material for diverse applications. However, majority of QDs are susceptible towards surface oxidation when exposed to air, which modifies their functional behavior (e.g., PL quenching) and renders it useless for developing applications. Hence, synthesis, functionalization and fabrication of good quality QDs are performed under controlled inert atmosphere, which requires specific laboratory facilities, rendering it scientifically a tedious field and making it cost-sensitive. This review article focuses on recent developments in chemical synthesis and surface modification strategies for different QDs to make them stable under ambient conditions without compromising their opto-electronic properties. This article also includes the strategies adopted to regenerate the PL properties of already surface oxidized QDs.

## 1. INTRODUCTION

Quantum Dots (QDs) are fundamentally very small semiconductor nanoparticles exhibiting unique and size specific optical, photoluminescence and electronic properties [1-4]. Their unique features include size-controlled-tuneable emission, broad photo-excitation to narrow band-emission with strong fluorescence, high resistance to photo-bleaching and low degradation of their photoluminescence quantum yield (PLQY) over time [1-4]. All of these properties make them exciting as well as advantageous for various applications, e.g., in solar cells [5], light emitting diodes [6], lasers [7], emitters for color displays [8], optical fiber amplifier [9], high-speed signal-processing filters [10], bio-imaging [11], sensors [12], developer for latent fingerprint [13] and many more. Chemical synthesis strategies for QDs have seen tremendous progress throughout the last three

decades which has resulted their controlled size, shape and composition specific synthesis with proper ligand/stabilizer selection and easy integration/fabrication to make suitable devices and QD based functional materials. However, synthesis, functionalization, storage and fabrication of good quality QDs are performed under very controlled inert atmosphere due to following three reasons. Firstly, many precursors for QD synthesis are highly susceptible towards degradation by moisture and oxygen. Secondly, presence of oxygen during high temperature synthesis lowers the yield of desired QDs with concomitant formation of metal oxides as one side product as well as produce low quality QDs with many surface trap states. Thirdly, as prepared QDs are susceptible towards surface oxidation in presence of moisture, oxygen and light with generation of surface trap states and gradual decay of their luminescence intensity. It is to be mentioned

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**Table 1.** A list of major QD forming elements with their preferred oxidation states.

II	III	IV	V	VI
				O (-2)
	Al (+3)	Si(+4)	P (+5)	S (-2,+2, +4, +6)
Zn (+2)	Ga (+3)	Ge(+4)	As (+5, +3)	Se ( +2, +4, +6)
Cd (+2)	In (+3)	Sn(+4)		Te (+4, +6)
Hg (+2)		Pb (+2, +4)		

that, synthetic complexity and surface oxidation tendency for different QDs vary to a great extent. The problem has received considerable attention among the researchers throughout the globe and a handful of strategies have been developed for synthesizing QDs at ambient conditions with long term air stability. Due to economic and technological advancement in present era, most of the research laboratories in developed and developing nations are well equipped with advanced facilities and so synthesis, storage and processing is not a severe technical concern. But, as a scientific quest as well as for easy and cost effective utilization of QDs for various applications, it is necessary to develop strategies to make them stable under ambient condition. The present review article focuses on different synthetic and functionalization strategies adopted in recent years to protect QDs from oxidative degradation as well as the strategies adopted to regenerate the properties of already surface oxidized QDs. In the first part of this review, oxidative degradation phenomenon and consequent effect on QD's luminescence property is discussed. In second part, different strategies for making air stable and highly luminescent QD has been elaborated in detail, which includes i) core-shell QDs, where oxidatively susceptible core is protected by high band gap and air-stable shell material, ii) properly designed / selected organic ligand and small molecule protected QD, where ligands are densely packed on QD surface and restrict incoming O<sub>2</sub> to interact, and iii) different redox and photo induced brightening strategies, which can suppress the surface trap states and regenerate the photoluminescence of surface oxidized and weakly luminescent QDs. The last section depicts summary and future prospective of the work.

## 2. OXIDATIVE DEGRADATION OF QDS

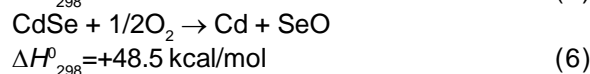
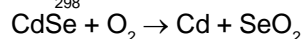
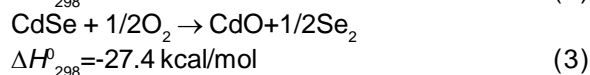
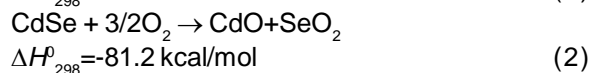
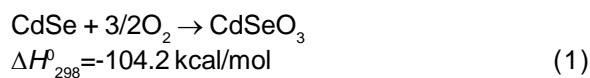
### 2.1. Surface oxidation

A large number of semiconductor nanocrystals with varying elemental compositions are available now which show size specific tunable band edge emission covering near UV to NIR region of the spectrum. Composition wise they could exist as single component [14] (Si, Ge), binary [15] [CdX, ZnX, InP (X = S, Se, Te) etc.], ternary [16] (CdSeS), Quarternary [17] (CuSnInP) as well as binary based core-shell [18] (e.g., CdSe/CdS) and in doped [19] (e.g., Mn<sup>2+</sup> doped ZnS) form. Among them, binary QDs have been studied widely and popularly classified according to their elementary position in periodic table. Hence, II-VI [CdX, ZnX, HgX (X=S, Se, Te.)], III-V (GaAs, InP) and IV-VI [PbX, (X=S, Se, Te, etc.)] based quantum dots are well known and proven as the most promising materials till date. Different synthetic strategies, excellent size specific opto-electronic properties and diverse range of applications of QDs are well documented and are not the focus of our present article. We will elaborate in brief about relative oxidative stability of different QDs, their probable oxidation pathways followed by different physico-chemical strategies to make them stable in air. Our discussion will exclusively evolve around photoluminescence properties of QDs as a measure of their quality for usefull applications.

Table 1 shows a list of elements according to the periodic table with their most stable oxidation states (in parenthesis), which forms bulk proportions of QDs. Oxidation states of constituent elements is a measure of the stability of their respective compounds and hence we could correlate it to the oxidative stability of different QDs. For example group II elements (Zn, Cd, Hg) prefer to adopt +2 oxidation states due to their full shell (d<sup>10</sup>) electronic configuration, thus stability of II-VI QDs, depends on the stability order of group VI elements in -2 oxi-

dition states. From Table 1, we can say, this stability order will be O>S>Se>Te, which in turn results the oxidative stability order as MO>MS>MSe>MTe (where M is Zn/Cd/Hg). Similar trend follows for IV-VI QDs, where mainly SnX and PbX (X= S, Se, Te) based semiconductor nanocrystals have been explored. Group IV based QD, (Si and Ge) are also prone towards oxidative degradation as their preferred oxidation state is +4, which they can attain by forming respective oxides (SiO<sub>2</sub>, GeO<sub>2</sub>) in presence of molecular oxygen and the process is further accelerated by high surface energy of small QD nanocrystals. Similarly all III-V based QDs are also prone towards oxidation as they could attain stable oxidation states by forming their respective oxide species. Thus, high surface energy and preference to attain more stable oxidation state promotes QDs to oxidize in presence of molecular oxygen and form corresponding oxides with different compositions.

The detail study on oxidative degradation of bulk as well as nanocrystals of different semiconductors and subsequent effect on its optical properties has been carried out by using several spectroscopic and microscopic techniques [20-26]. In this respect Alivisatos et. al. work on oxidative degradation study of TOPO (tri-*n*-octylphosphine oxide) capped CdSe nanocrystals on gold surface is noteworthy and can be elaborated here in detail as an illustrative example [20]. X-ray Photoelectron Spectroscopy (XPS) study on fresh samples showed that core level peak positions of Se and Cd are identical with bulk CdSe material. It was also significant to observe that only surface Cd atoms were ligated (covered) with TOPO, whereas Se atoms were bare (unbounded) and on exposure to air, surface Se sites were oxidized to SeO<sub>2</sub>. However, after removal of TOPO ligands, both surface elements (Cd and Se) started to form oxides with different compositions. From thermodynamic viewpoint following oxidation/oxygenation reactions (Eqs. (1)-(6)) of bare CdSe nanocrystals are possible [27], which clearly indicate the most possible oxides to be formed are CdSeO<sub>3</sub>, SeO<sub>2</sub> and CdO and the experimental findings of the Alivisatos et. al.'s work was in agreement as all three compositions were confirmed from XPS results.



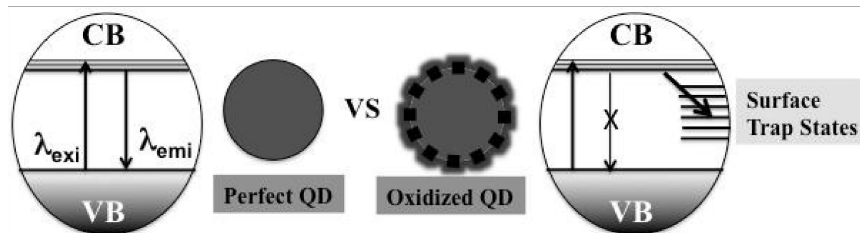
Thus, how does the surface oxidation of QDs takes place on their exposure to air? By reviewing the above work, we can arrange the sequence of events as follows: The available oxygen molecules first forms a layer over nanocrystal surface through physisorption. Due to high electronegativity of oxygen molecules, electron density from almost bare Se<sup>2-</sup> is transferred to oxygen and SeO<sub>2</sub> started to form. Also after removal of TOPO ligands, Cd-chalcogen back-bonds are replaced and cadmium oxide (CdO) or mixed cadmium-chalcogen oxides (CdSeO<sub>3</sub>) are generated. The as formed oxide species are initially physisorbed on to the surface of the nanocrystal but the lack of (chemical) bonding leads to slow dispersion (displacement) of these oxides from the surface. Afterwards, newly exposed surface is attacked by oxygen and the process continues.

## 2.2. PL of surface oxidized QDs

Surface oxidation of QDs strongly influences its PL properties and following four events are observed. (i) Due to surface oxidation, the effective core size of the nanocrystal decreases, which results a blue shift in its emission peak, although it is observed for a short period of time and soon suppressed by other processes [25]. (ii) The surface oxidation can also results a red shift of the emission peak which was attributed to the emergence of the localised energy levels in the band gap providing lower energy pathways [21]. (iii) Surface oxidation generates many surface trap states (discussed in next session), where excitonic electron is trapped non radiatively with the result of drastic PL quenching, thus abandoning the synthesized QDs useless for applications [20-26]. (iv) Lastly, a phenomenon called blinking behavior is observed at single particle level, where fluorescence intensity of QDs show fluctuation, although this can be observed even in QDs with out surface oxidation [28].

## 2.3. Generation of surface trap-states

Trap states are energy states which are present in nanocrystals surface (hence called surface trap states) or sometimes in bulk (carried by line/surface defects) which trap or occupy the charge carriers from their relaxation path by providing either low



**Scheme 1.** Schematic diagram showing energy states in non-oxidized and oxidized QDs; the occurrence of trap states in oxidized QDs leads to PL quenching.

charge density region or by absorbing their energy (Scheme 1). This results in the immobility of the charge carriers (electrons) and render them localised in these states for significant amount of time to disable them of a single continuous radiative transition path [29-31]. Thus, surface trap state mediated non-radiative recombination of charge carriers is the most prevalent explanation for quenched luminescence of oxidized QDs. Apart from surface oxidation, non-uniform aggregation of nanocrystals may also lead to formation of trap states on the surface. These may arise mostly in materials of higher or lower energy levels with different/same energy band-gap coming in direct contact with each other (eg: core-shell, non-uniform nucleation of same material). These materials may include shell coating over core material, surface oxides, functional groups attached as coatings and organic ligands attached for redispersibility or phase exchange of as prepared QDs [29-31]. The occurrence of trap states in an ideally synthesised nanoparticle may be due the one of following reasons; a) Extreme small size of crystal than to allow the crystal structure binding energy, b) Ostwald ripening taking place in nucleation c) surface tension of nanocrystals d) Unbalanced reactants leading to the vacancy sites in crystal lattice e) trap states may also arise due to difference in energy levels of the HOMO/LUMO of these surface functional groups f) Inefficient energy band gaps (extreme high electron capturing LUMO or extreme low hole capturing HOMO) their molecules or fluorophores may contain [32-34].

## 2.4. Enhancement of surface defects

The surface defects of QDs form as a part of crystallization process mainly due to difference of lattice energy in different unit cells upon extended crystallization, which leads to breakage of some lattice surfaces called surface defects [32]. These defect sites are highly reactive, show presence of free electrons, provide sites for nucleation, enhance growth

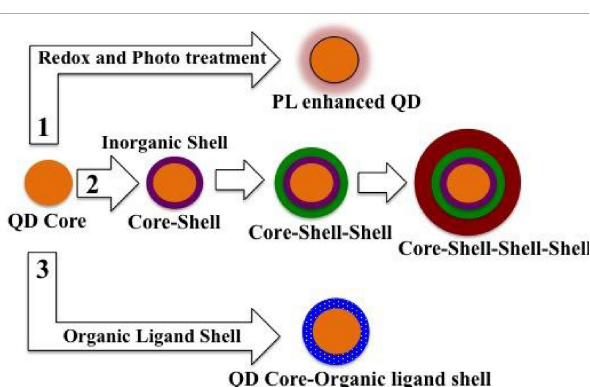
factor of the crystal, have a tendency to create extended lengths of defect lines and defect planes and act as trap states for relaxation of electrons. All the above factors contribute to the formation of additional crystal layers which contribute in quenching of luminescence due to non-uniform crystallization and reacting with dissolved oxygen species [33,34].

## 3. STRATEGIES FOR MAKING AIR STABLE QDS

Numerous efforts have been made to protect these precious materials from oxidation during exposure to air as well as regeneration of photoluminescence of surface oxidized QDs as described in the following sections (Scheme 2).

### 3.1. Inorganic shell growth

The process involves surface encapsulation of another material considered "Shell" over the principal product primarily called "Core"; hence the name, core-shell is derived. The growth of a shell has led



**Scheme 2.** A Schematic depiction of different strategies for making QD air stable or regenerating their PL property. Route 1 shows redox and photo treatment can be used to regenerate their PL property, route 2 shows inorganic shell growth strategy and route 3 shows organic ligand encapsulation strategy.

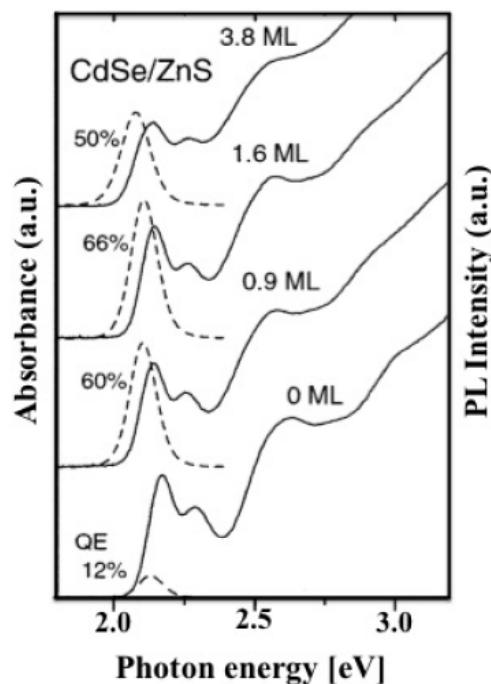
to a vast new exposure in creating high-class desired semiconductor nanocrystal products, which earlier seemed impossible. These new groups of materials offer many interesting and tunable physico-chemical properties compared to core or shell material alone, like absorption and emission profile, PL quantum yield, PL decay profile, redox potential, chemical reactivity, and so on. Thus the core-shell semiconductor QD synthesis has occupied a major interest of the research community due to the promises they hold and such has been the effectiveness of this strategy that seemingly unpopular and not-so-useful materials are now handy tools as shell materials. From air stability point of view, an inert (stable in air) shell on an air sensitive core material is the art of designing air stable core-shell QDs. Shell coating can passivate the surface trap states of core nanocrystal, thus results high PL quantum yield as well as makes the material robust against oxygen and moisture. The growth of a suitable shell is another science in its own, as a set of parameters need to be satisfied for successful synthesis of a core-shell QDs: a) Crystal lattice matching, b) Wider band gap value for shell than core material, c) More stability in given synthetic environment, d) Less reactivity with core materials, e) Bond-length matching, f) Similar synthetic approach, and g) Prevention of shell nucleation. The resultant good quality core shell materials show many interesting characteristics along with much improved air stability, e.g., higher optical absorption coefficient, high PL quantum yield, photostability with respect to photobleaching, decreased fluorescence lifetimes and reduced blinking behavior. The work, which gave conceptual input towards core-shell semiconductor nanocrystal synthesis, needs to be mentioned here before we proceed further and Rossetti and Brus reported it in 1982 [35]. In this work, they found that treating CdS nanoparticles with  $Zn^{2+}$  ions results PL intensity enhancement up to 35%, which was amazing at that time. They hypothesized that  $Zn^{2+}$  ions do not create any impurity surface site for such intense emission, rather they passivate the surface trap states and restrict nonradiative recombination pathway. Later, several core/shell QDs were synthesized and their detail photo physical studies supported the above-hypothesized mechanism behind PL enhancement and stability. These initial syntheses of core-shell QDs were carried out by Brus [36-38], Henglein [39], Bawendi [40-44], Alivisatos [45,46], Guyot-Sionnest [47], Weller [48], and Fendler [49,50] who developed strategies for making several core-shell QDs, like CdS-Cd(OH)<sub>2</sub>, CdSe-CdS, CdSe-ZnS, CdS-ZnS,

CdSe-ZnSe, CdS-HgS-CdS, and Si-SiO<sub>2</sub> with much improved air stability, higher PL quantum yield and decreased fluorescence lifetimes.

### 3.2. CdS and ZnS as inorganic shell

From air stability point of view, CdS and ZnS have come out as the preferred shell material and have been widely used to coat a variety of nanocrystals. Brus, Weller and Bawendi's group had successfully shown how the selection of a shell material influences so many of the above-mentioned properties at once. In a first of such studies, they have used ZnS shell over CdSe core, which results passivation of surface trap states, enhanced air stability, high absorption coefficient and enhanced luminescence QY (Fig. 1) [36,41,43,44,48].

Another significant set of contributions in core-shell synthesis starting from those early days are from Alivisatos's group who had shown practically many of the properties for core-shell structures. They have shown the use of CdS as shell for CdSe cores with increased stability of holes since they



**Fig. 1.** Absorption and emission spectra of CdSe core and CdSe/ZnS core-shell QDs with different ZnS thickness (in monolayers, ML) measured at room temperature along with the PL QY values. The sharp rise of emission intensity of CdSe/ZnS core-shell QD compared to bare CdSe is clearly evident from this figure. Reprinted with permission from H. Weller et. al., *Nano Lett.*, 2001, 1, 207. Copyright 2001 American Chemical Society.

have a decreased probability of leaving the surface when a shell is present. Confinement of the charge carriers of core consistently produces very high luminescence quantum yields [45,46].

From the beginning of this century, more common, commercially available and air-stable precursors for the synthesis of high quality II-VI QDs were established with most notable contribution from Peng et.al [51]. It was followed by the introduction of successive ion layer adsorption and reaction (SILAR) method for the synthesis of core-shell QDs by Peng et. al. in 2003 [52], which is still the most favored strategy for the synthesis of a variety of core-shell semiconductor NCs. Initially SILAR method was developed for the deposition of several QDs on wide band gap semiconductor thin films by Weller et. al. to modify their electronic property [53]. Here shell precursors are added sequentially to the reaction environment in presence of core nanocrystal with the result of layer-by-layer growth of shell material over core. The effectiveness, reproducibility and simplicity of this method has made it the most favored strategy for the synthesis of a variety of core-shell semiconductor NCs [52,54-56]. Using SILAR approach Hollingsworth's group recently synthesized very thick (18 to 19 monolayers of CdS, ZnS and  $Cd_xZn_{1-x}S$ ) shells over CdSe core with high chemical robustness, suppressed blinking behavior and enhanced photostability with respect to photobleaching [55].

Another recently developed strategy for the synthesis of CdS-ZnS and CdSe-ZnS core-shell QDs is called single source precursor method, where a zinc complex, zinc ethylxanthate  $\{Zn(ex)_2\}$  [57] or zinc diethyldithiocarbamate  $\{Zn(DDTC)_2\}$  [58-60] is used as a single source precursor for the shell growth. These Thio-Zinc complexes decompose at relatively low temperature (150 to 200 deg C) and produce small ZnS seeds, which started depositing over core and finally results core-shell QDs and hence makes the synthetic process simpler than traditional SILAR based approaches. Zhong et. al. also recently developed a non injection based method for gram scale synthesis of air-stable CdSe/ZnS core shell multipod nanocrystals [60]. In this strategy CdO and Se powder were directly added in paraffin liquid in presence of TOP and oleic acid as ligands at high temperature to form the initial CdSe multipod nanocrystals, which was later encapsulated with ZnS shell using single source precursor  $\{Zn(DDTC)_2\}$  for making them air-stable [60].

Doped semiconductor nanocrystals are an important variant of QDs, where a second metal (mostly

transition metals, e.g., Cu, Mn, Ag, Cr, etc) is doped in a host semiconductor nanocrystal with emergence of unique photoluminescence properties due to the involvement of doped metals 'd' orbital in photo excitation and/or emission process [19]. As we have already discussed, 'S' based group II-VI QDs (e.g., CdS, ZnS) are oxidatively stable and hence they are used as a shell on oxidatively sensitive QDs to develop stable core shell QD system. But due to crystal lattice mismatch and / or synthetic complexity this strategy has not been successful for all systems. Cu doped ZnSe QD is a very interesting system with tunable blue-green emitting behavior but very prone towards surface oxidation in presence of light and oxygen [61]. Unfortunately CdS or ZnS shell growth on Cu doped ZnSe have not yet been successful. Pradhan's group developed a synthetic method, where a small amount of 'S' (< 10% with respect to Se) was introduced during growth process of QD, thus diluting the surface 'Se' percentage and form an alloy type surface with  $ZnSe_{1-x}S_x$  composition [62]. The strategy is different from core-shell system, as the amount of 'S' is too small to form even a single shell layer of ZnS. The obtained QD is very resistant towards oxidative quenching and showed stable photoluminescence with 40% quantum yield in both water and organic solvents.

Most of the core-shell materials we discussed in above section were synthesized using high boiling organic solvents at relatively high temperature conditions. Instead of using high boiling organic solvents, aqueous based synthetic approaches have also been developed recently for the synthesis of air stable core-shell and core-shell-shell nanocrystals [63-67]. Zhang et. al., reported the synthesis of 3-mercaptopropionic acid (MPA) stabilized CdTe/CdS core-shell QDs by following SILAR route under microwave heating conditions with much improved luminescence quantum yield (40%) compared to the initially synthesized only core (CdTe) nanocrystals (8%) [63]. A prototype aqueous based synthetic strategy under hydrothermal conditions [64] and normal heating condition at 90 deg C was also reported [65]. Microwave irradiation based strategy was also utilized by Wang et. al., for the synthesis of core-shell-shell MPA-capped CdTe/CdS/ZnS NCs in water [66]. The synthesis is comprised of three steps, where first CdTe core was synthesized followed by coating this core with CdS shell and finally formation of a ZnS shell over CdS. The purpose of using CdS in the middle layer was to reduce the large lattice mismatch (16.6%) between CdTe and ZnS as CdS has comparable lattice con-

stant with CdTe (6%). Apart from microwave irradiation based aqueous synthetic approach, CdTe/CdS core-shell NCs was also synthesized by ultrasonic treatment [67].

Infrared-emitting (IR) quantum dots (NQDs) are also very promising material with possible application in diverse areas, like lasers, high-speed circuits, sensors, detectors and as biological labels. Few notable examples, with prominent emission profile in this spectral range are CdTe/CdSe core shell QD, and PbSe, InAs, InP QDs. As we can anticipate that all of them are air sensitive and hence, to improve their air stability and PL property, they were encapsulated with a suitable high band gap inorganic shell [68-71]. ZnS encapsulated core shell or core-shell-shell type InP/ZnS [69], CdTe/CdSe/ZnS [68] and PbSe/CdSe/ZnS [71] are most notable examples. Similarly, CdS was used to synthesize IR emitting PbSe/CdSe/CdS [70] core-shell-shell QD with good stability and long career lifetimes.

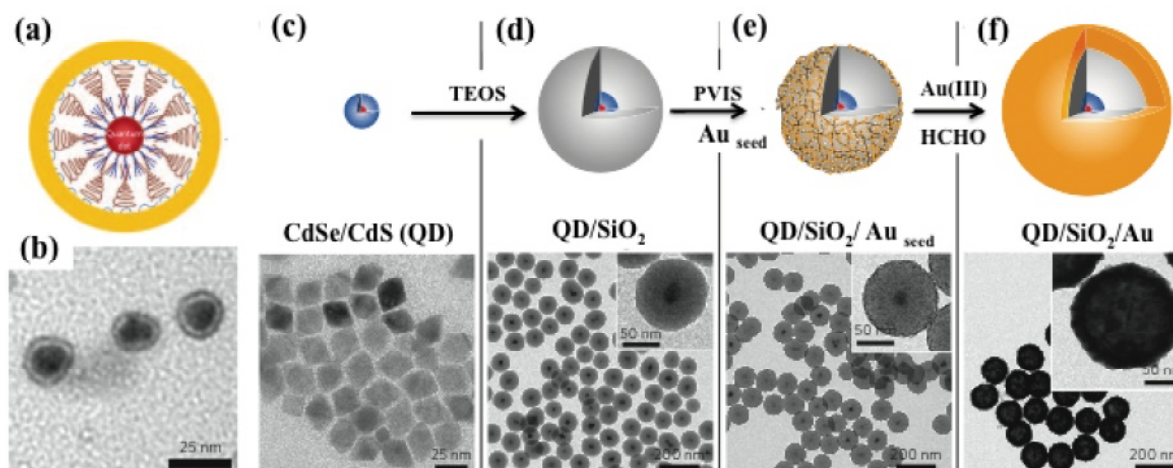
### 3.3. Silica (SiO<sub>2</sub>) as inorganic shell

Apart from the use of CdS and ZnS as air-stable inorganic shell coating for the synthesis of core-shell NCs, SiO<sub>2</sub> is another choice as air-stable shell material and proven successful for a variety of QDs. Silica as a shell coating is advantageous due to its exceedingly high stability with respect to moisture and oxygen, chemical inertness, optical transparency, desired porosity and simple synthetic routes [72]. Silica coating of a wide variety of nanostructures including QDs, metal nanostructures and even organic dyes are now widely studied with a major goal of their use in biological applications [72]. The efficacy and optoelectronic characteristics of silica as a shell was carried out first by Brus et. al. for Si-SiO<sub>2</sub> core shell system which showed much improved air stability with resistance towards photo bleaching and quantum confinement effect [37,38]. Other notable studies include SiO<sub>2</sub> coated CdSe/ZnS, CdTe, CdSe/CdS QDs [73-78] which are highly robust, stable in water at ambient conditions with good luminescence characteristics. Generally it is observed that, silica coating imparts good air stability and hence, maintains the original PL behavior of core nanocrystals, but does not much influence (enhance) the PL intensity and position ( $\lambda_{\text{emi}}$ ) as observed by CdS and ZnS as shell. The majority of silica coated QDs were synthesized by using water-in-oil microemulsion (known as W/O microemulsions, where water droplets are dispersed in bulk oil) technique. Both hydrophobic and hydrophilic QDs with amine/Phosphine oxide/phosphine/

fatty acid or even thiol as capping ligands are introduced in the W/O micremulsions in presence of TEOS (tetraethylorthosilicate) as silica source. Hydrolyzed TEOS replaces the original ligands from QD surface and finally through more hydrolysis and condensation, a silica shell is formed surrounding the QD core.

### 3.4. Noble metal (Au) as inorganic shell

Noble metal coating over QDs is an excellent idea as it can impart high air stability and make it easy to functionalize with a variety of organic ligands as per the need thanks to the well-developed field of ligand protected gold clusters [79]. But direct QD-Metal core shell nanomaterial synthesis is difficult to achieve due to their crystal structure mismatch as noble metals adopt FCC structure whereas QDs mostly exist in wurtzite, zinc blende and diamond structures. Also it is proven that direct contact between luminescent QD and gold nanostructure results complete luminescence quenching of QD. Thus, special reaction design and careful synthetic execution is required for successful synthesis of good quality QD-Metal core shell material with novel optical properties. Gao et. al., have synthesized a hybrid plasmonic gold shell encapsulated CdSe/ZnS nanostructures with a middle layer of organic ligands and ionic polymers (Fig. 2) [80]. This middle layer creates a precise separation between QD and Au as well as its amphiphilic character makes the synthesis feasible between hydrophobic QDs and hydrophilic Au precursors. The material is stable enough at ambient atmosphere as well as in aqueous solution with PL quantum yield of 39%. In another very recent study Dubertret et. al., have synthesized a hybrid quantum dot/silica/gold core-shell-shell system which is comprised of CdSe/CdS/SiO<sub>2</sub>/Au structures with high chemical robustness due to outer gold shell along with high PL quantum yield, strong resistance towards high-power photoexcitation and non blinking fluorescence behavior [81]. The synthesis involves four steps; first hydrophobic TOPO capped CdSe/CdS was synthesized using SILAR based approach. Then water-in-oil micro-emulsion process was utilized using TEOS as silylating reagent to grow the SiO<sub>2</sub> shell over QD. In third step, QD/SiO<sub>2</sub> was functionalized with poly (1-vinylimidazole-co-vinyltrimethoxysilane) followed by deposition of small (3 nm) gold particles. In last stage, more HAuCl<sub>4</sub> was added along with mild reducing agent formaldehyde to deposit Au(0)



**Fig. 2.** Figure (a) and (b) depicts respectively the schematic diagram and TEM image of CdSe/ZnS QD encapsulated with a gold shell along with a middle layer of organic ligands and ionic polymers. Figure (c) to (f) depicts the synthetic scheme (top) and respective TEM images (bottom) of CdSe/CdS (QD), QD/SiO<sub>2</sub>, QD/SiO<sub>2</sub>/Au<sub>seed</sub> and QD/SiO<sub>2</sub>/Au nanoparticles respectively. For (a) and (b); Reprinted with permission from X. Gao et. al., *Nature Nanotechnology*, 2009, 4, 571. Copyright 2009 Nature Publishing Group. For (c) to (f); Reprinted with permission from B. Dubertret et. al., *Nature Nanotechnology*, 2015, 10, 170. Copyright 2015 Nature Publishing Group.

on the outer gold surface to get the final CdSe/CdS/SiO<sub>2</sub>/Au hybrid core-shell nanostructures (Figure 2).

### 3.5. Organic ligand shell

Organic ligands are some specific molecules containing neutral or ionic coordinating atoms with high bonding affinity to electrophilic sites. Bare QDs are very susceptible towards coalescence due to high surface to volume ratio and surface energy and hence are stabilized with suitable organic ligands, macromolecules or ions. Ligands form bonds with surface atoms of QD and have found to perform three major roles; passivation, functionalization, and steric spacing. From air stability point of view, effective passivation of QD surface by organic ligands is the most important part so that the material is non-reactive to its environment with most notable concern from oxygen and moisture in air. Ligands also play crucial role as a redox mediator and can act in either way towards PL behavior of QDs. Selected category of ligands can provide necessary charge ( $e^-$ ) to trap states, thus non-radiative recombination pathway is restricted which results PL enhancement. On the other hand ligands can also quench the PL by providing intermediate energy states that act as trap states and capture the excitonic electrons. Surface encapsulation of QDs with a variety of ligands has been explored and it has come out that aliphatic amines and organic thiols provide ef-

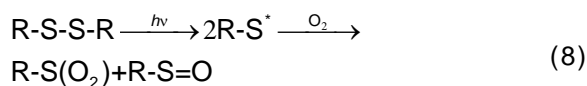
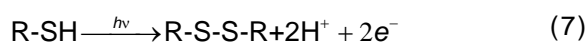
fective stability as well as PL enhancement for certain category of QDs. It is also reported that thiols can regenerate the PL of already surface oxidized and hence non-luminescent QDs through surface cleaning, trap state passivation and strong adsorption on surface atoms.

The earliest study on positive influence of aliphatic amines on PL enhancement of QDs was reported by McLendon et. al., for CdS and Cd<sub>3</sub>As<sub>2</sub> QDs, which showed 450% increase of PL quantum yield when treated with certain tertiary amines (NEt<sub>3</sub>, NMe<sub>3</sub>, DABCO) [82]. Similar observation was authenticated in later studies also using other aliphatic amines and detail spectroscopic analysis confirmed that, these amines actually fill surface trap states by donating its electron pair (partially) and can suppress the non-radiative recombination pathway and facilitates radiative recombination from band-edge states [83-85]. Its was also very interesting finding that aromatic amines (e.g., pyridine) were not able to show such PL enhancement, possibly due to their weaker basic character. However, aliphatic amines are not suitable ligands for long-term stability of QDs due to their weak (labile) bond strength and tendency towards photo degradation.

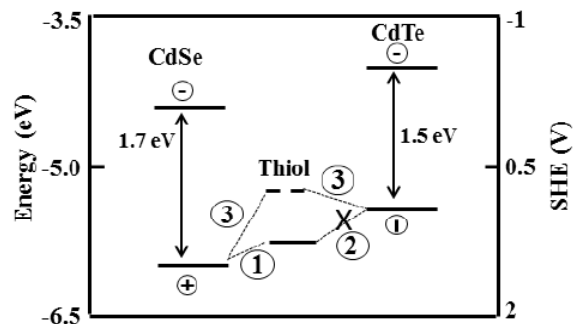
Organic thiols are better ligand in terms of bond strength and provide much efficient encapsulation of nanocrystal surface, thus provide long term air stability, although they are also prone towards photo degradation on prolong exposure to light specially



in presence of oxygen (Eqs. (7) and (8)) [86]. Both hydrophobic and hydrophilic thiols have been utilized as passivating ligands for a wide variety of QDs to make them stable under ambient conditions in a desired solvent or in solid form. In case of CdX series ( $X = S, Se, Te$ ), it was observed that thiol form very strong bonds and passivate all three QDs but only CdTe retain good (enhanced) PL property where as CdS and CdSe lacks it, particularly CdSe becomes completely quenched. Wuister et. al., reported a detail account on this strikingly distinct paradox of PL behavior of thiol encapsulated CdSe and CdTe QDs. CdTe and CdSe have different energy levels, and in particular the position of top of their valence band (HOMO). The redox energy level of most of the thiol molecules remains above the valence band of CdSe, but below that of CdTe (Fig. 3) [87]. This cause photo generated hole trapping on the thiol molecule for CdSe and quenching of its luminescence, but hole trapping by thiol in CdTe does not happen, which results high PL-QY, partly also due to protection from oxidative degradation due to efficient passivation. Several examples on synthesis of thiol encapsulated luminescent CdTe QDs and their application has been reported [88,89]. Although bare CdSe cannot be passivated by thiol for the above-mentioned reason, but after their encapsulation with a wide band gap shell, thiol could be utilized for passivation with retention of PL intensity, much improved air-stability and desired solubility. Hence, organic thiol passivated CdSe/ZnS [90-92] core shell QDs have become a popular choice for robust and highly luminescent QDs and specially important are such type of materials possible application in bio-imaging, as biological labels and in sensing [93,94].



Apart from CdX series ( $X=S, Se, Te$ ), other QDs also have been successfully passivated with thiol ligand with good PL property and high air stability. In a recent study Ning et. al. demonstrated an effective approach to eliminate surface trap states in InAs nanowires (NWs) of both zinc-blende (ZB) and wurtzite (WZ) structures with the recovery of band edge emission by using octadecyl thiol as passivating ligand. The thiol passivated NWs are stable in air for several months implying the efficacy of this surface modification strategy [95]. In another recent article, Pradhan et. al., showed that, thiol treatment

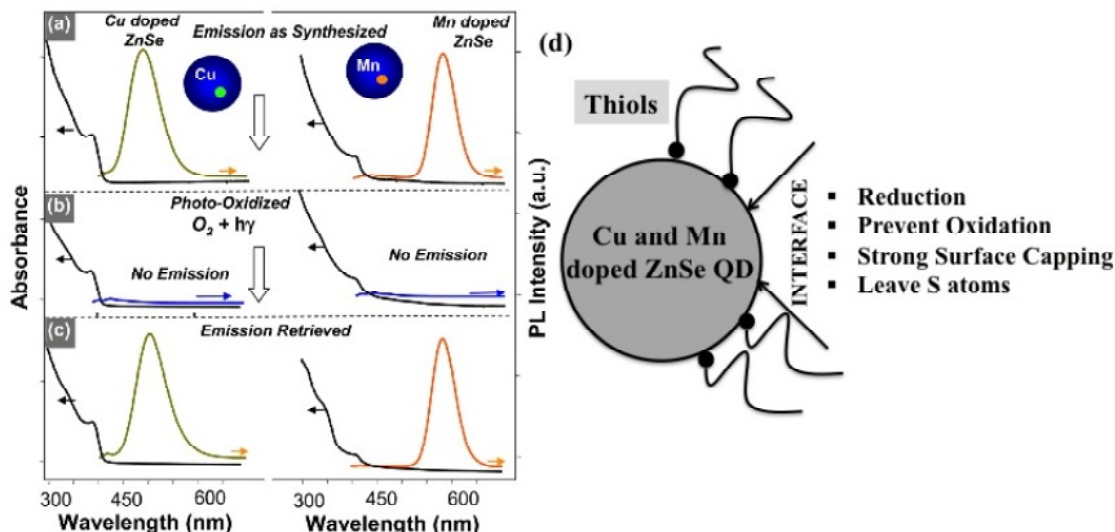


**Fig. 3.** Vacuum scale energy and standard potential energy diagram for bulk CdTe and CdSe. The standard potential for thiol resides below the valence band of CdTe and thus hole trapping can not occur (process 2) but it resides above the valence band of CdSe, which result hole trapping (process 1) and cause PL quenching. If thiol could have little higher standard potential (dashed lines) then it could quench the PL of both CdSe and CdTe (process 3). Reprinted with permission from S. F. Wuister et. al., *J. Phys. Chem. B*, 2004, 108, 17393. Copyright 2004 American Chemical Society.

is an effective strategy to clean, stabilize and regenerate the photoluminescence properties of months old doped semiconductor nanocrystals [96]. Air exposed, months old and completely quenched amine capped Cu-doped and Mn-doped ZnSe nanocrystals were treated with selected organic thiol ligands, which remove the surface oxidative states as well as resist further oxidation of the nanocrystals with the result of complete recovery of PL emission. The role of thiol ligand here are many fold: Firstly through its strong adsorption property it cleans the surface and removes some oxidized quencher species, secondly it acts as a mild reducing agent in presence of light (see Eq. (7)), and reduces the surface oxidized species, thirdly being a strong ligand it replaces weak amine groups with the formation of strong bonds and gives long time stability (Fig. 4) [96]. Further, the authors also successfully tested this strategy for retrieving the PL of oxidized CdTe nanocrystals [96]. Last but a very significant and recent addition in this category is the use of phosphonic acid ( $R-PO_3$ ) as ligand by Jeong et. al. for obtaining air stable PbSe QDs [97].

### 3.6. Small molecule/ion adsorption

Small molecule adsorption on QD surface can be an effective strategy for their stability, however the selection of proper adsorbent is very crucial, as it



**Fig. 4.** (a) Absorption and emission profile of the initially formed Cu-doped and Mn-doped ZnSe QDs showing their good PL behavior. (b) Absorption and emission spectra of the same samples after surface oxidation show no emission at all. (c) Absorption and emission spectra of these surface oxidized QDs after treatment with MPA. (d) Schematic figure showing multiple roles of thiol ligands on retrieving the emission of above QDs. Reprinted with permission from N. Pradhan et. al., *J. Phys. Chem. Let.*, 2013, 4, 2084. Copyright 2013 American Chemical Society.

needs to satisfy many parameters. (i) It should adsorb strongly on QD surface and hence will form an outer monolayer shell with specific chemical composition. (ii) The resultant surface monolayer shouldn't drastically affect the opto-electronic properties of the inner material. (iii) The packing geometry of surface monolayer should be very compact to restrict the incoming  $O_2 / H_2O$  molecule to react with the QD surface. The use of small molecule or ion over the traditional bulky organic ligands has the advantage of reaching every possible surface sites and passivating surface trap states, if possible, so that non-radiative recombination and surface oxidation both processes are restricted. The use of halide ions for this purpose has been proven successful for few selected QDs. In a recent work Pietryga et. al. showed that treating PbSe QDs with chlorine results some displacement of surface Se atoms with immediate formation of a thin layer of lead chloride ( $PbCl_x$ ) (Fig. 5 and Table 2) [98]. The resultant QD is stable in air up to six months without any significant change in its emission property due to efficient blockage of oxygen to PbSe surface by the surface layer of  $PbCl_x$ . Sargent et. al. did a comprehensive study on the stability of NIR emitting PbS colloidal quantum dots which are very useful material for opto-electronic device fabrication including solar cell. They were in search of a suitable ligand with smaller dimension, which could efficiently pas-

sivate the surface trap states along with high packing density and good intra-particle (in thin film form) charge transport property. Treating the as synthesized PbS with chloride ions ( $Cl^-$ ) by introducing oleylamine solution of  $CdCl_2$ , they were able to achieve much-improved air stability [99]. In further continuation of their search for a better passivant, Sargent's group showed that adsorption of iodide ion ( $I^-$ ) on PbS QD resulted a highly robust material with strong resistivity towards areal oxidation [100]. Theoretical modeling using density functional theory showed the compact surface layer of iodide compared to other halide ions, which came out as the best ion to completely shield incoming oxygen molecule. Experimental result was completely in agreement with the calculation, which showed iodide adsorption resulted complete resistivity towards oxidation of PbS QD while other halide ions and other anions (acetate) yielded inefficient packing geometry on PbS surface hence showed poor resistivity towards surface oxidation. This iodide stabilized PbS QD was utilized to fabricate solar cell with high stability and consistent solar power conversion efficiency up to 8% [100].

**Table 2.** A summary of procedures adapted for synthesizing air-stable QD's.

Method	Advantages	Reference
Inorganic Shell Growth: Capping with a outer CdS/ZnS layer	Enhanced air stability, Passivate surface trap states, High absorption coefficient, Enhanced Luminescence QY	[36,41-44,48, 51-60]
Inorganic Shell Growth: Capping with a Silica (SiO <sub>2</sub> ) layer	Air Stable, Inert to variety of chemicals, Silica is optically transparent, Long shelf-life, Ease of further surface functionalization	[37-38,72-78]
Inorganic Shell Growth: Capping with a outer metal (Au) layer	Impart high air-stability, Functionalization with variety of organic ligands, Reduced non blinking behaviour	[80,81]
Organic Shell Growth: Capping with a suitable organic ligand	Moderate air stability, Functionalization easy for QD's further use	[82-85,87]
Surface Passivation with Small Molecule/ion	Small Molecules reaching every possible surface site, Most of the trap states are passivated at molecular level, Suitable for device fabrication	[98-100]

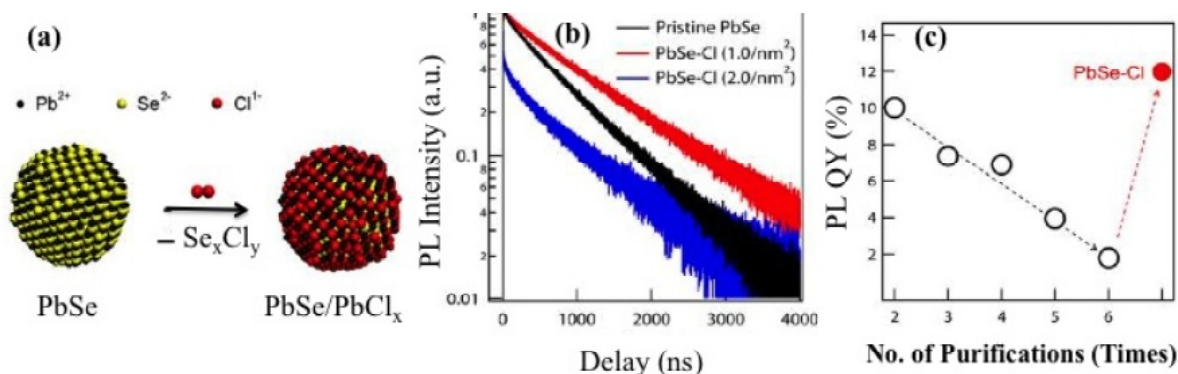
### 3.7. Redox brightening of QD emission

PL intensity of QDs gradually decreases with time especially when exposed to air and light, due to surface oxidation and generation of surface trap states. So, it can be anticipated that in reverse treatment, i.e., by applying controlled reduction at QD surface, their luminescence could be retrieved due to trap state passivation by injected electrons. Researchers using different source of electrons have studied this surface reduction strategy to regenerate the PL properties of already surface oxidized QDs and those can be classified in two ways: i) using a suitable chemical (reducing agent), ii) using electrochemical reduction.

### 3.8. Chemical reduction method

Borohydride based reducing agents (BH<sub>4</sub><sup>-</sup>) are most common for synthesis of metal and semiconductor nanostructures. Pradhan et. al., has studied the effect of borohydride (BH<sub>4</sub><sup>-</sup>) treatment on surface oxidized Mn<sup>2+</sup> and Cu<sup>+</sup> doped ZnSe nanocrystals, which resulted immediate PL enhancement due to surface state passivation. Further study showed that organic thiols are better molecular reductants and stabilizers for retrieving PL of the above-oxidized QDs in presence of light or heat [96]. The similar

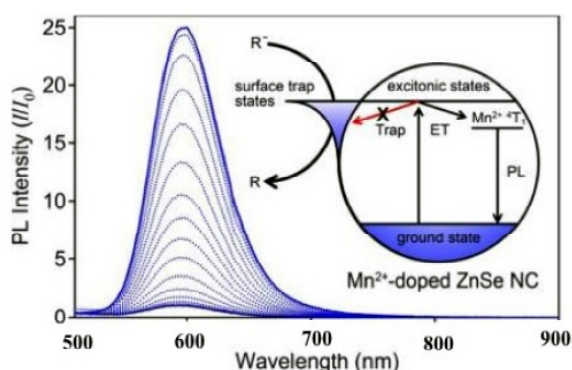
PL enhancement was observed for oxidized CdTe QDs using MPA as reductant as well as a stabilizer [96]. Thiol molecule here Acts as a reducing agent (in presence of light /heat), provides electron for passivation of surface trap states, act as a strong ligand and resists further photo-oxidation by strong adsorption onto QD surface as well as by capturing reactive oxygen species (Eqs. (7) and (8)). Park et. al., also demonstrated similar methodology where dithiothreitol (DDT) was used as reducing agent as well as ligand in presence of light to induce PL enhancement of silica coated CdSe/ZnS [101]. Hence, selection of reducing agent is crucial and that should depend on electron potential of trap states and reduction potential of oxidized species. Gamelin's group have studied redox brightening of colloidal Mn<sup>2+</sup> doped ZnSe NCs via the addition of sodium-potassium alloy (NaK<sub>2</sub>) as reductant and achieved up to 48% enhancement of PL intensity (Fig. 6) [102]. They used a variety of molecular reductants (with different redox potential values) and found varying degree of PL enhancement, which implies that trap states are of wide energy range. Further to this, precise redox titration showed that the PL enhancement is associated with multiple reducing equivalents per NC. However this redox brightening is temporary phenomenon as upon exposure to air the obtained luminescence gradually disappears due to surface re-oxidation.



**Fig. 5.** (a) Schematic diagram showing the effect of chlorine treatment on PbSe QDs. (b) PL decay profile of PbSe QDs with varying chlorine concentration. (c) PL QY of oleic acid capped PbSe QDs show gradual decay with increasing number of purifications, whereas PL QY regained and enhanced by chlorine treatment. Reprinted with permission from J. M. Pietryga, et. al., *J. Am. Chem. Soc.* 2012, 134, 20160. Copyright 2012 American Chemical Society.

### 3.9. Electrochemical reduction method

Gamelin's group also studied the PL electro-brightening of oxidized QDs by applying a cathodic bias to ZnSe and Mn<sup>2+</sup> doped ZnSe QD films in electrochemical cells. The best result showed up to 40-fold enhancement of steady state PL of ZnSe QDs, which was ascribed due to reductive passivation of surface traps with positive potential value than conduction band potential [103]. Incorporation of Mn<sup>2+</sup> dopants into the ZnSe QDs introduces a well-

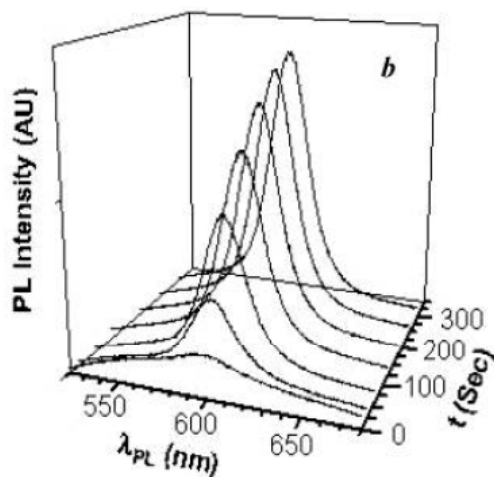


**Fig. 6.** Enhancement of PL intensity of oxidized form of Mn<sup>2+</sup> doped ZnSe QDs due to its trap states passivation by using sodium-potassium alloy (NaK<sub>2</sub>) as reductant. Inset: schematic diagram showing that trap states are filled with electrons from molecular reductants and this leads to PL enhancement. Reprinted with permission from D. R. Gamelin et. al., *J. Am. Chem. Soc.*, 2012, 134, 16175. Copyright 2012 American Chemical Society.

defined fast exciton deactivation pathway that allows the electron trap kinetics to be clocked. Analysis of the difference in PL electro-brightening magnitudes with and without Mn<sup>2+</sup> yields an effective electron trapping rate constant of  $<10^{11} \text{ s}^{-1}$ , comparable to that for energy transfer to Mn<sup>2+</sup>, and much greater than that for excitonic PL. These findings provide new insight into the roles of surface trap states on QD photo-luminescence. Similar study by other groups also demonstrated that electrochemical surface trap state electron filling could greatly accelerate the PL intensity [104,105].

### 3.10. Photo-induced enhancement of QD emission

Light (photo) induced PL enhancement has been observed by several groups for a number of binary as well as core-shell QD systems which are partially oxidized or have poor crystalline surface structure [23,106-115]. Exposure of these QDs with suitable energy light can trigger the reconstruction of surface atoms with the possible result of surface trap state passivation. Xiao et. al. have shown the time and radiation energy dependent PL intensity enhancement of CdSe films under vacuum (Fig. 7) [23]. The process suppresses nonradiative recombination to trap states and thus enhances emission intensities of QDs. Buratto et. al., have proposed this mechanism for photoinduced PL enhancement of CdSe nanocrystals [106]. Eychmuller group also reported similar photoinduced PL enhancement of alloy type ZnSe(S), Zn<sub>1-x</sub>Cd<sub>x</sub>Se nanocrystals and the possible mechanism was proposed to be chemical



**Fig. 7.** Enhancement of PL intensity of CdSe QDs as a function of time by using photoradiation under vacuum with an excitation intensity of  $80 \text{ kW/cm}^2$  at  $514.5 \text{ nm}$ . Reprinted with permission from M. Xiao et. al., *J. Phys. Chem. B.*, 2004, 108, 5507. Copyright 2004 American Chemical Society.

bond rearrangement and defect relocation at the QD [109,111,113]. The strategy has now become a standard protocol to enhance the luminescence quantum yield of several other semiconductor NCs and are used routinely as a post preparative treatment for obtaining good quality QDs.

#### 4. SUMMARY

The unique optical and electronic properties of semiconductor nanocrystals (QDs) have made them precious for various applications, but at the same time their intrinsic redox behavior makes them susceptible towards oxidation in presence of air. This surface oxidation process modifies their many functional behavior with most notable example of PL quenching and render them useless for developing applications. The strategies adopted for making QDs air stable involve a robust shell formation with either inorganic material or organic ligand based which are oxidatively stable and protect the inner core of QD from air. Apart from protection of inner core from outer atmosphere, the shell also can enhance the absorption coefficient, PL quantum yield and reduced decay time. The influence of inorganic shell and/or organic ligand shell on QD's electronic property is very crucial; hence proper selection of shell material is necessary. As inorganic shell, CdS, ZnS,  $\text{SiO}_2$ , and Au are mostly preferred due to their better stability in air and high band gap value, although due to synthetic complexity and crystal lattice mismatch,

their use is case specific and not universal. As organic ligand or small molecule/ion, thiols (R-SH) and halide ions ( $\text{Cl}^-$ ,  $\text{I}^-$ ) have been used with good air stability for a number of QDs. It should also be kept in mind that, oxidative stability of QDs should not come at the cost of their efficacy at major applications. To be more specific, the stabilizer should be short and compact, so that QDs electronic character is retained and useful. Thus, there is an urgency to find out more effective strategies for surface coating of air sensitive QDs with suitable inorganic or organic shell and more research is required in this direction. Also, the reported inorganic shell formation schemes require tricky synthetic work, which sometimes results poor reproducibility and hence need simpler synthetic strategies along with more precession. The effective synthesis of QD/Au core/shell nanoparticle is another promising arena due to robustness of outer Au shell and possibility of its functionalization with a variety of functional groups. Apart from the above discussion of making QDs air stable, there is another line of research where researchers are trying to regenerate the properties (e.g., PL property) of already surface oxidized QDs. The use of suitable reducing agent to clean the surface and fill up the trap states with sufficient number of electrons can result in brightening of QDs photoluminescence. Chemical reduction and electrochemical reduction methods have been tried to regenerate the photoluminescence of surface oxidized QDs. Photo induced emission brightening of semiconductor nanocrystals has also proved promising. Unfortunately, all of these PL brightening phenomenon of QDs is reversible in nature and hence again show luminescence quenching on exposure to air. But still their importance remains very significant, for example for light emitting semiconductor nanocrystals, these strategies can be implemented for easy and cost effective utilization before final device fabrication. With the recent advances in the wide application of semiconductor QDs, we expect more effort will be put forward for making them air stable and finding ways to make them perfect before their application.

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