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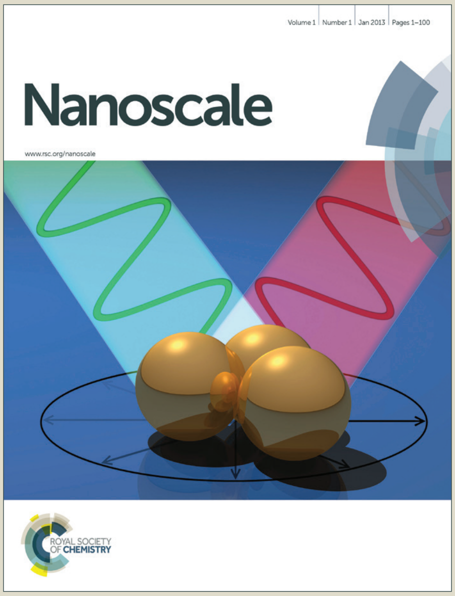

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Synthesis and Photo-darkening/Photo-brightening of Blue Emitting Doped Semiconductor Nanocrystals

Suresh Sarkar, Amit K. Guria, Biplab K. Patra and Narayan Pradhan*

Abstract: Programming the synthetic reaction chemistry, stable blue emitting Cu(I) or Ag(I) doped Al(III) co-doped ZnS(Al,Cu:ZnS or Al,Ag:ZnS) semiconductor nanocrystals are designed. Further, the photo-stability of the obtained intense blue-violet emission is studied, and the effects of doping/co-doping are correlated. Finally, it has been revealed that the strong binding surface ligand 1-dodacanethiol and Al(III) co-doping play pivotal role for achieving such a stable blue emitting doped nanocrystals.

Introduction

Light emitting doped semiconductor nanocrystals are known for their exclusive wide stokes shift and high thermal stability,[1] which enable them as one of the ideal materials for solid state lightening.[2] Wide varieties of such nanocrystals with various optically active dopants are already developed following different doping strategies.[1c-f,3] The emission of these doped nanocrystals is mostly tunable in visible window. But, the doped nanocrystals emitting intense high energy blue-violet light, a primary constituent of the white light, have not yet been widely explored. The existing such doped nanocrystals which are mostly synthesized in aqueous phase possess low intensity, and not comparable to the highly emitting leading doped nanocrystals.[4] Hence, synthesis of high energy emitting doped nanocrystals having intense and tunable emission with wide stokes shift remains challenging till date.

The ideal hosts for achieving such emission are the semiconductor nanocrystals with wide band gap such as ZnS, ZnSe etc. However, emission from these nanocrystals is strongly interfered with the generation of surface states which act as the competitive channel for the carrier relaxation that in turn quenches the dopant emission.[5] Further, doping induces additional dopant states,[1] and makes the recombination process more complicated for these nanocrystals. Hence, to obtain the high energy pure dopant emission, the formation of the unwanted surface states should be restricted or to be removed. To achieve this, both the synthetic as well as the interface chemistry are to be properly manipulated.

For ZnSe, the transition metal ion doping and the dopant induced new photo-physical properties have widely been studied,[1c,4g,h,6] but obtaining the intense dopant emission tunable in blue-violet window by restricting the size in smaller domain remains practically difficult. In this context, ZnS, a Cd and Se free greener material having bulk band gap ~3.6 eV (zinc blende), is an ideal choice. The Cu doped ZnS nanocrystals with tunable emission are already reported but the emission has poor intensity and mostly confined in blue-green window.[3a,b] Hence, the synthetic and doping protocol of ZnS need to be properly manipulated to obtain the emission in blue-violet window. Further, it has been observed that the tunable dopant emission obtained from different doped nanocrystals is strongly associated with photo-instability.[1c,6,7] Hence, not only the synthesis of high energy emitting doped nanocrystals but also the study of the photo-physics of the emission are critically important.

We adopt here the organic phase high temperature colloidal synthesis technique to obtain tunable high energy emitting (blue-violet) copper or silver doped ZnS nanocrystals. This has been achieved by employing suitable co-dopants and proper surface ligands which facilitate the doping process, stabilize the emission and also restrict the size. In addition, the chemistry of the photo-sensitivity of the dopant emission (photo-brightening and darkening) has also been studied herein detail in this communication.

EXPERIMENTAL SECTION

Synthesis of Al co-doped Cu:ZnS (Al,Cu:ZnS) and Ag:ZnS (Al,Ag:ZnS)

Nanocrystals

The Al,Cu:ZnS nanocrystals are synthesized following the modified method of our report.[3a] In a typical experiment, 0.1 mmol $ZnSt_2$, 0.1 mmol Al-oleate (1 ml from the stock, electronic supporting information, ESI), 5 ml octadecene, 0.5 ml tri-octylphosphine and 1 ml 1-dodecanethiol were loaded in a 100 ml round bottom flask and degassed for 30 minutes. In a separate vial, 0.3 mmol of elemental sulfur, 0.8 gm of octadecyl amine were dissolved with 1 ml of octadecene in inert atmosphere. This sulfur solution was quickly injected into the reaction flask at 270 ^{o}C. After cooling down the reaction to 180 ^{o}C, 0.05 ml of $CuSt_2$ stock solution (ESI) was added drop wise into the reaction flask. After 15 min of annealing, the temperature was raised to 220 ^{o}C. Then, after annealing for 45min at the same temperature, 3 ml of $ZnSt_2$ and stearic acid solution from the stock was added drop wise after 10 minutes of interval with 1 ml of each successive addition. Then, the reaction vessel was allowed to anneal for another 2 hrs. Finally, the reaction flask was cooled down to room temperature and the product was purified by acetone and ethanol mixture (1:1) as non-solvent with gentle heating. The Al,Ag:ZnS has been prepared following similar method only by replacing Cu stock solution with Ag stock.

Instrumentation

Optical absorption measurements have been carried out in Agilent 8453 spectrophotometer. Photoluminescence spectra were collected using a Horiba Jobin Yvon Fluromax-4 spectroflurometer. XRD of the nanocrystals is performed by Bruker D8 Advance powder diffractometer, using Cu K_{α} (λ= 1.54 Å) as the incident radiation. TEM images are collected on a JEOL-JEM 2010 electron microscopy using 200kV electron source. Specimens are prepared by dropping a drop of nanocrystal solution in chloroform on a carbon coated copper grid and the grid is dried under ambient condition. The dopant percentage and the composition of the doped nanocrystals are determined by ICP-AES using Perkin–Elmer Optima 2100 DV Instrument. At first, the doped nanocrystals have repeatedly been purified to remove excess precursors. Then the purified nanocrystals are dissolved in chloroform. The chloroform is then evaporated out and the dried nanocrystals are digested in concentrated HNO_3. The nitric acid solution of the samples is diluted with calculated amount of milli-Q water to perform the measurements. For time correlated single photon counting (TCSPC) measurement, the nanocrystals are excited at 295 nm using a picosecond diode laser (IBH Nanoled107) in an IBH Fluorocube apparatus (JY1IBH15000M). The fluorescence decays are collected on a Hamamatsu MCP photomultiplier. The fluorescence decays are analyzed using DAS6 software.

Result and discussion

For ZnS host, the major problem remains with its poor quantum confinement. To obtain tunable emission, the size of the host nanocrystals needs to be tuned and hence a proper control of the crystals growth is essential. Again, in ideal case of doping, relatively larger size host is required to compensate the dopant induced defects in the host lattice and hence doping in the smaller ZnS host nanocrystals is expected to be practically difficult. This is even more complicated when multiple dopants are introduced in single host nanocrystal. However, we have overcome these issues by programming the chemistry of synthesis and selecting appropriate surface ligands to restrict the size, minimize the

Ostwald ripening and facilitate the doping process.

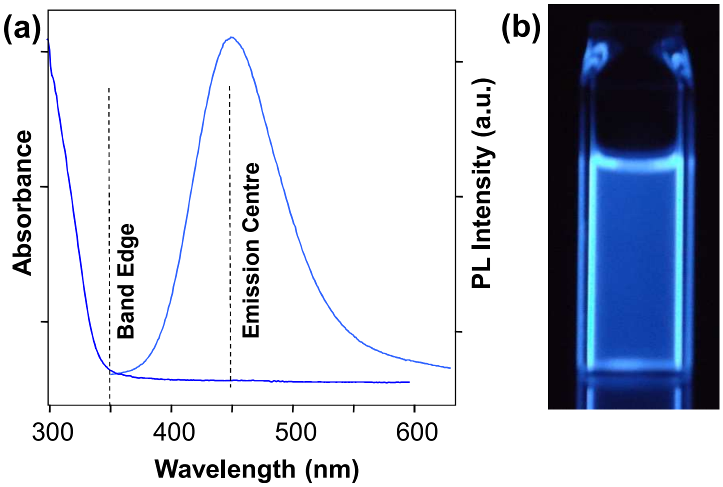

Fig. 1 (a) Presents the absorption and photoluminescence spectra of a typical sample of Al,Cu:ZnS nanocrystals. The spectral position suggests the nanocrystals have minimized self-absorption. (b) Shows the digital image of the solution of doped nanocrystals illuminated using 254 nm UV-lamp (6 mW).

For doping, optically active Cu(I) or Ag(I) ions and for co-doping the trivalent Al(III) ions are chosen to obtain the tunable blue-violet emission. Fig. 1a shows a representative UV-visible and photoluminescence (PL) spectra of Al,Cu:ZnS nanocrystals, which exhibit the emission at far lower energy than the band edge absorption. Fig. 1b presents the digital image of the illuminated nanocrystals under UV excitation. These doped nanocrystals are synthesized following the modification of our previously reported protocol for ZnS.[3a] Here, additionally, 1-dodecanethiol and tri-octylphosphine (TOP) ligands are introduced along with 1-octadecylamine in the reaction system to control the crystal growth and particle size. The dopant Cu(I) or Ag(I) is introduced during the growth of the nanocrystals, and Al(III) ion is introduced at the beginning during the ZnS formation. Fig. 2a and 2b show the successive PL spectra of Al,Cu:ZnS and Al,Ag: ZnS respectively, collected at different time interval from a typical reaction. Both these doped nanocrystals show the tunable emission in blue-violet window. Fig. 2c and 2d present the excited state decay lifetime for both the doped nanocrystals(Al,Cu:ZnS and Al,Ag,ZnS) at 460 nm emission, and accordingly the average excited state life time of 279 ns and 187 ns suggests that these emissions are emanated from the involvement of the respective dopant states of the nanocrystals.[1e,f,3d] For comparison, we have also carried out the excited state lifetime measurement for the Cu:ZnS and Ag:ZnS presented in the ESI Fig S1. Further, we have analyzed the crystal phase for both sets of nanocrystals which has found to be zinc blende. The particles size is mostly tuned within 3-4 nm (Fig. 3). Energy dispersive X-ray analysis (EDX) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) show the presence of both Al and Cu (or Ag) in respective doped nanocrystals (Fig. S2, and table S1and S2 in ESI).

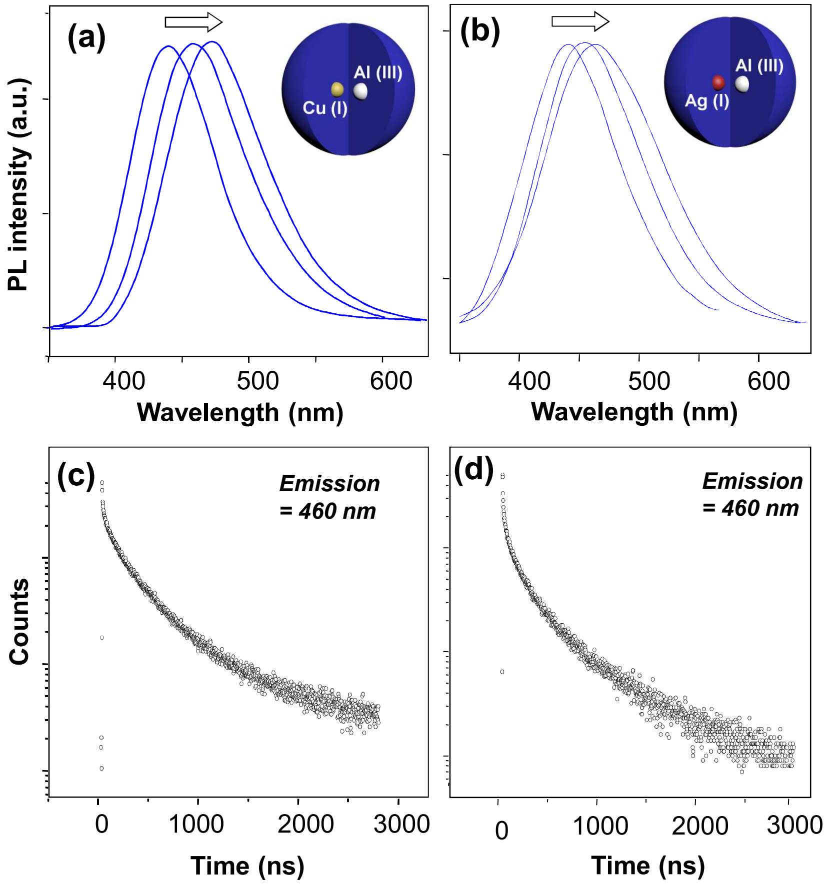

Fig. 2 (a) and (b) present successive PL spectra of Al,Cu:ZnS and Al,Ag:ZnS nanocrystals. The excitation wavelength is 320 nm. UV-visible spectra corresponds to both PL spectra are provided in ESI (Fig. S3). (c) and (d) Show the excited state decay lifetime plots of Al,Cu:ZnS and Al,Ag:ZnS respectively at 460 nm emission position.

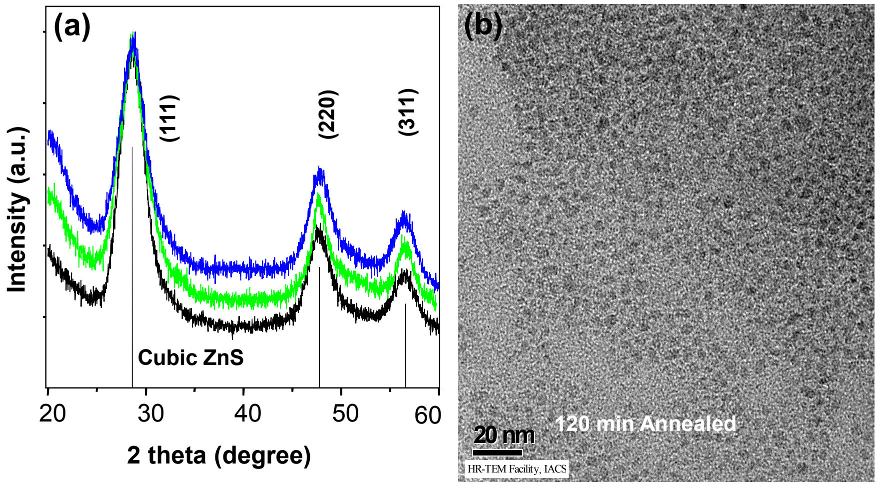

Fig. 3 (a) Presents successive XRD patterns of the blue emitting nanocrystals obtained from the reaction system at 30, 90 and 180 minutes (bottom to top). (b) Shows the TEM image of Al,Cu:ZnS nanocrystals. The monodispersity is lost to some extent because of long time annealing.

Next, when we have analyzed the spectroscopic results, it has been observed that the most striking feature is the intense blue emission which is achieved mostly due to restriction of growth of the ZnS nanocrystals by proper manipulation of reaction parameters. The sulfides of Al(III), Cu(I) and Ag(I) have differences in their formation constants and lattice constants than the ZnS. Hence, insertion of multiple dopants in one nanocrystal has the practical difficulties. Moreover, the size of the nanocrystals has to be retained relatively smaller to obtain the high energy emission. This has been overcome by long time annealing (>1 hr) under slow growth process which enables the dopant insertion efficiently. The strong binding ligands such as 1-dodecanethiol and TOP help for slow growth. Without these capping ligands the nanocrystals grow relatively larger, and undergo Ostwald ripening, turning the reaction solution turbid within 30 minutes of annealing at the identical reaction conditions.

Further, it is reported that the 1-dodecanethiol ligand also helps in reducing the reactivity of the Cu-precursor which in turn effectively controls the efficiency of doping.[8] Hence, the slow adsorption of the dopants onto the nanocrystals surface and subsequent overgrowth remain the ideal for the doping of Cu and Al in the same nanocrystals here in this case. But, to understand whether the co-doping of Al indeed helps in intensifying or stabilizing the emission, a detail study has been carried out.

Fig. 4 Shows stability plot of Cu(I) dopant emission under air exposure of the nanocrystals synthesized in different reaction conditions. The blue line corresponds to the Cu:ZnS nanocrystals synthesized in absence of 1-dodecanethiol ligand. Red line corresponds to Cu:ZnS nanocrystals synthesized in presence of 1-dodecanethiol without Al(III) co-dopant precursor. The black line corresponds to the Al,Cu:ZnS nanocrystals synthesized in presence of 1-dodecanethiol.

Fig. 4 shows the plots for time dependent change in the emission intensity of the doped and co-doped nanocrystals under air flow in room light. This suggests that the emission intensity remains almost unchanged for both the thiol ligand capped doped (without Al(III)) and Al(III) co-doped nanocrystals. On the other hand, when the reaction is carried out in absence of thiol, the dopant emission is photo-bleached within few minutes of air exposure (Fig. 4). This suggests that thiol mostly stabilizes the emission under ambient condition even without Al(III) ion. However, the emission position with or without Al(III) as co-dopant remains identical. This further suggests that the photo-recombination process mostly follow similar to that of Cu doped nanocrystals which are widely reported in several hosts.[1c,1e,6,7] But, to understand more about the effect of co-doping we have further studied the photo-oxidation process under irradiation for both thiol capped doped nanocrystals with or without co-dopant.

Fig. 5 shows the time dependent change in intensity of both Al,Cu:ZnS and Al,Ag:ZnS thiol capped nanocrystals under UV irradiation. Interestingly, it has been observed that in both cases the doped nanocrystals show photo-darkening and the Al co-doped nanocrystals show photo-brightening. This result indeed suggests that co-doping resist the fast formation of non-radiative channels as observed for only Cu or Ag doped ZnS nanocrystals. Room light under ambient condition is not enough to oxidize the surface of these thiol capped nanocrystals. But, for the intentional irradiation with high energy in presence of air, thiol capped Cu^+ (or Ag^+) doped nanocrystals cannot protect the surface well enough where Al as co-dopant helps in minimizing the induction of unwanted surface states and hence protects the dopant emission for longer time.

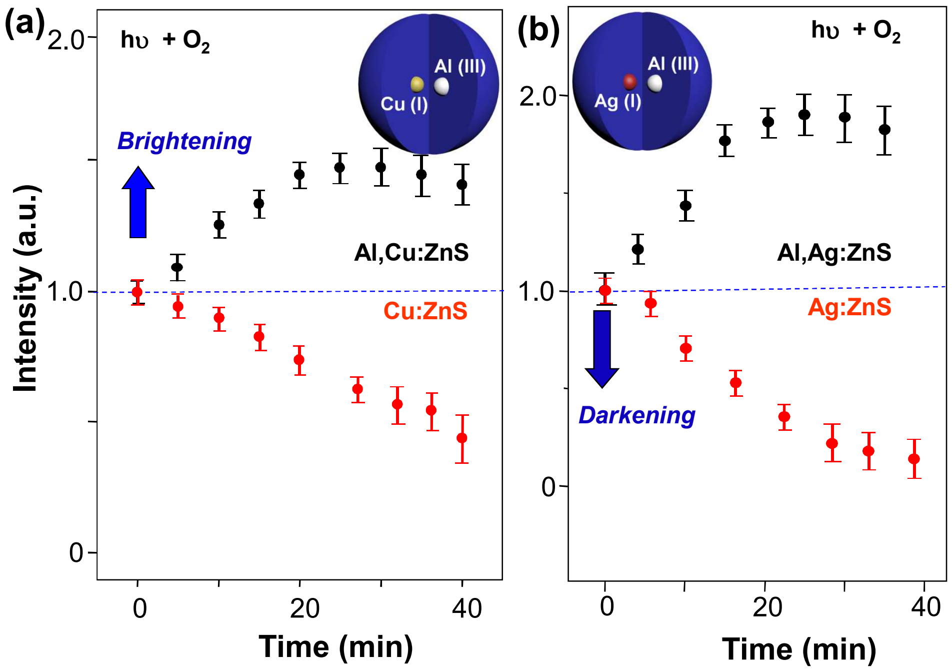

Fig. 5 (a) and (b) show the plot of change of photoluminescence intensity with time during irradiation of Al,Cu:ZnS and Al,Ag:ZnS nanocrystals. Bottom panels show the change of intensity of Cu doped and Ag doped ZnS nanocrystals only. The emission centre for both cases is ~460 nm and the irradiation has been carried out with 254 nm irradiation source (UV-lamp) taking the purified sample solution in chloroform in a screw cap cuvette. Here, to mention that that the severe purification of the sample is avoided for this UV-irradiation process. The maximum quantum yield obtained for Al,Cu:ZnS and Al,Ag:ZnS remained 16% and 12% respectively.

Next, to understand this unique behavior of the co-doping we further investigate the mechanism of this photo-brightening and darkening of both the doped and co-doped nanocrystals. Even though, we have used Cu-precursor as Cu(II), but in presence of fatty amine, it is reported to be reduced to Cu(I).[1e,9] For either case of Cu(I) or Ag(I) doping, when it is inserted in the host lattice, creates a hole excess which in turn generates anion vacancy.[10] This indeed facilitates the surface oxidation. In absence of thiol at the interface, the amine capped doped nanocrystals show instantaneous loss of the emission under irradiation (within a minute). But, thiol ligands at the interface restrict the photo-oxidation process to a certain extent, and also clean the oxidized surface. In case of ZnSe, we have recently shown that thiol ligands at the interface can introduce a ZnS atomic layer, and intensifies the dopant emission under irradiation.[7] But, here in the case of ZnS, a surface layer of sulfide does not have significant impact to protect the emission as the material itself is ZnS, and the surface cleaning as well as the reducing character of thiol are not enough to stop the surface oxidation during continuous irradiation. Hence, the case here is different than that of the ZnSe. Rather, the co-dopant trivalent Al(III) ion helps in protecting the emission. This suggests that the hole excess or anion vacancy induced in the lattice by substitution of Zn(II) with Cu(I) or Ag(I) is compensated by the presence of trivalent ion, and that actually resist the propagation of surface oxidation for a particular time frame and hence, initially, the co-doped nanocrystals show photo-brightening which is assumed to be due to surface cleaning by thiol ligand.

The above assumption is further supported with the results obtained from the irradiation of these co-doped nanocrystals under inert atmosphere. In absence of air, the thiol ligands capped Cu or Ag doped nanocrystals (without Al) show photo-brightening to a certain extent rather than the photo-darkening. This clearly suggests that both the thiol ligand and the incorporation of the co-dopant Al(III) ion in the same host reduce the possibility of surface oxidation and formation of unnecessary surface states as well. As a result, the obtained emission is found to be stable even under irradiation for certain time frame.

Further, the question arise, why Al(III) has been selected as co-dopant. It is well established that introduction of Cu(I) (or Ag(I)) and In(III) ions inside the lattice of ZnS, results the CuInZnS (CIZS) or AgInZnS (AIZS) ternary nanocrystals.[11] But, introduction of Indium(In) in our reaction system leads to the formation of separate ZnS and CIZS nanocrystals as In(III) ions are more reactive than Al(III). Hence, Al(III) as co-dopant, which is the same group III element and less reactive to form the ternary nanocrystals is preferred for this case.

Conclusion

In summary, we address here few practical and fundamental issues related to Al(III) co-doping in the Cu or Ag doped high band gap ZnS semiconductor nanocrystals and obtain intense stable high energy emission. The wide blue-violet window tunability has been achieved by proper chemical and synthetic strategy manipulation. The doping has been carried out with slow growth over long time of annealing with proper choice of capping ligands and co-dopant. Finally, one of the technologically important high energy emitting with wide stokes shift nontoxic nanomaterials has been achieved. In addition, the photo-physical aspects of the dopant emission and the effect of co-doping on the emission intensity and stability are investigated.

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Notes and references

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Electronic Supplementary Information available: detail of synthesis and supporting figures.

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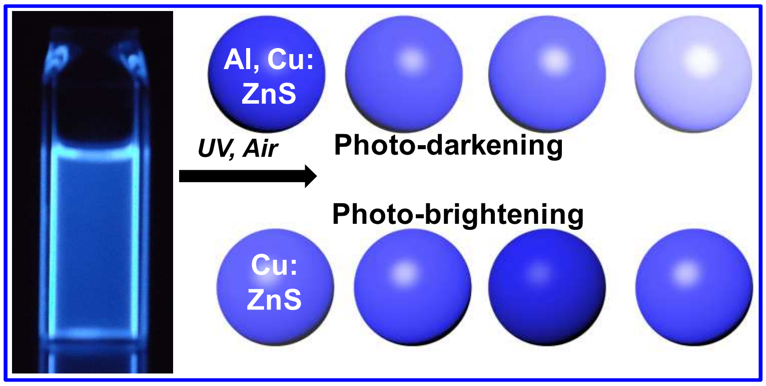

Keywords: Doping, co-doping, Blue emission, Photo brightening, Photo darkening

Sort abstract demonstrating the novelty:

Blue emitting Cu(I) or Ag(I) doped Al(III) co-doped thiol capped ZnS semiconductor nanocrystals are found to be more stable under UV-irradiation than the corresponding doped nanocrystals.