

## Supporting Information

### **Influence of doping on semiconductor nanocrystals mediated charge transfer and photocatalytic organic reaction**

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#### **Materials:**

Zinc stearate ( $\text{Zn}(\text{St})_2$ , tech), Stearic acid (SA, 95%), octadecylamine (ODA, 97%), 1-octadecene (ODE, tech.), oleylamine (OA, tech, 70%), oleic acid (tech, 90%), cadmium oxide ( $\text{CdO}$ , 99.99%), trioctylphosphine oxide (TOPO, tech, 90%), S powder (99.9%), mercaptopropionic acid (MPA), mercaptoundecanoic acid (MUA), tributylphosphine (TBP tech), trioctylphosphine (TOP, tech, 90%), copper(II) chloride (99.99%), manganese(II) chloride (99.99%) and 4-nitrophenol (p-NP,  $\geq 99.5$ ) were purchased from Aldrich. Se powder (99.9%) was purchased from Alfa Aesar. Sodium borohydride ( $\text{NaBH}_4$ ) was purchased from Merck chemicals. Te powder (99.99%) was purchased from Plasmaterials. All chemicals were used without further purification.

#### **Methods:**

**Synthesis of  $\text{Cu}(\text{St})_2$ :** 2.84 gm of Stearic acid was dissolved in 50 ml of methanol at 70 °C. 2.93 gm of TMAH in 5 ml methanol was added into the stearic acid solution. 0.67 gm of  $\text{CuCl}_2$  dissolved in 5 ml of methanol was added drop wise to the stearic

acid mixture solution with vigorous stirring. The sky blue coloured precipitates of Cu(II)stearate were washed with hot methanol and dried in air for the further use.

**Synthesis of Mn(St)<sub>2</sub>:** 2.84 gm of Stearic acid was dissolved in 50 ml of methanol at 70 °C. 2.93 gm of TMAH in 5 ml methanol was added into the stearic acid solution. 0.62 gm of MnCl<sub>2</sub> dissolved in 5 ml of methanol was added drop wise to the stearic acid mixture solution with vigorous stirring. The white coloured precipitates of Mn(II)stearate were washed with hot methanol and dried in air for the further use.

### **Synthesis of semiconductor nanocrystals:**

**ZnS:** ZnS nanocrystals were synthesized in a modified literature procedure.<sup>1</sup>

In brief, 0.003 gm S powder, 0.063 gm Zn(St)<sub>2</sub> and 5 ml ODE were loaded in a 50 ml three necked flask. The reaction mixture was degassed for 15 minutes by purging Argon. The reaction flask was heated to 290 °C. In another vial, 0.008 gm of S powder and 0.8 gm of ODA along with 1 ml of ODE were taken in inert atmosphere. Then, the sulphur solution was injected into the reaction flask at 290 °C and the reaction mixture was cooled to 220 °C. In a separate vial, a stock of 0.632 gm Zn(St)<sub>2</sub>, 0.14 gm Stearic acid and 4 ml ODE were prepared and degassed by purging Argon. After annealing the reaction mixture for 5 minutes at 220 °C, 2 ml of the Zn stock solution was injected to the reaction mixture after 5 min of interval with 1 ml of each addition. Further, it was annealed for another 10 minutes at the same temperature and cooled down to room temperature. These synthesized nanocrystals were precipitated by using excess of acetone from ODE. Finally, these were precipitated using methanol as non-solvent and then dispersed in chloroform.

**Mn doped ZnS:** The Mn doped ZnS nanocrystals were also synthesized in a modified literature procedure.<sup>2</sup> In brief, 0.006 gm S powder, 0.063 gm Zn(St)<sub>2</sub> and 0.8 gm ODA and 0.08 gm of Mn(St)<sub>2</sub> in 5 ml ODE were loaded in a 50 ml three necked flask. The reaction mixture was degassed for 15 minutes by purging Argon. Then the reaction flask was heated to 270 °C and annealed for 5 minutes. In a separate vial, a stock solution of 0.632 gm Zn(St)<sub>2</sub>, 0.284 gm Stearic acid and 4 ml ODE were prepared and degassed by purging Argon. After annealing for 2 minutes at 270 °C, the temperature of the reaction flask was reduced to 250 °C and 1 ml of

stock solution was added slowly. Further, it was annealed at 220 °C for 15 min and then cooled down to room temperature. These synthesized nanocrystals were precipitated by using excess of acetone from ODE. Finally, these were precipitated using methanol as non-solvent and then dispersed in chloroform.

**Cu doped ZnS:** The Cu doped ZnS nanocrystals were also synthesized in a modified literature procedure.<sup>1</sup> In brief, 0.063 gm of Zn(St)<sub>2</sub> in 5 ml of ODE was taken in a 50 ml three necked flask and degassed with Argon flow. The temperature was increased to 280<sup>0</sup>C. In a separate vial, 0.05 gm of elemental Sulphur with 0.8gm of ODA with 1 ml of ODE was taken and degassed at mild temperature. Then, this entire sulphur stock was swiftly injected to the reaction flask and sharply cooled down to 200<sup>0</sup>C. Then, 0.05 ml of Cu-stock (1 mmol of Cu(st)<sub>2</sub> in 10 ml of ODE under inert atmosphere) solution was added drop wise. In a separate vial, a stock solution of 0.632 gm Zn(St)<sub>2</sub>, 0.14 gm Stearic acid and 4 ml ODE were mixed together and degassed by purging Argon. After annealing the reaction mixture in flask for an hour at 200 °C, 2 ml of Zn-stock solution was slowly added twice in 10 min of interval with 1 ml of each addition. Further, it was annealed at the same temperature for another 1 hour and then cooled down to room temperature. These synthesized nanocrystals were precipitated by using excess of acetone from ODE. Finally, these were precipitated using methanol as non-solvent and then dispersed in chloroform.

**ZnSe:** ZnSe nanocrystals were synthesized following literature procedure.<sup>3</sup>

In brief, 0.063 gm Zn(St)<sub>2</sub> and 5 ml ODE were loaded in a 50 ml three necked flask. After degassing for 15 minutes by purging Argon, the temperature of the reaction flask was increased to 290 °C. In a separate vial, a stock solution of 0.039 gm of Se in 0.5 ml TBP was prepared in glove box and 0.5 gm ODA were mixed together and degassed by purging Argon. Then as soon as the temperature of reaction flask reached to 290 °C, the prepared stock solution was injected swiftly at a time and the temperature was reduced to 260 °C, annealing for another 5 minutes. Then the reaction mixture was cooled down to room temperature and precipitated by using excess of acetone from ODE once. Several rounds of washings were carried

out by dissolving in chloroform and precipitating with methanol before used for ligand exchange.

**Mn doped ZnSe:** Mn doped ZnSe nanocrystals has been prepared following the literature methods.<sup>4</sup> In brief, 0.05 gm Mn(St)<sub>2</sub> and 8 ml ODE were loaded in a 50 ml three necked flask. After degassing for 15 minutes by purging Argon, the temperature of the reaction flask was increased to 290 °C. In a separate vial, a stock solution of 1.83 gm of Se in 10 ml TBP was prepared in glove box. Then, the 0.5 ml TBP-Se from the stock and 0.8 gm ODA (molten through gentle heating in inert atmosphere) were mixed together in inert atmosphere which was injected swiftly to the reaction flask at 290 °C and cooled down to 250 °C. In a separate vial, a stock solution of 0.632 gm Zn(St)<sub>2</sub>, 0.14 gm Stearic acid and 4 ml ODE were mixed together and degassed by purging Argon. After annealing for 30 minutes at 250 °C, the temperature of the reaction flask was raised to 280 °C and 2 ml of Zn-stock solution was added swiftly. Further, it was annealed for another 5 min lowering the temperature to 250 °C and rest 2 ml of Zn-stock was added slowly at 250 °C and further annealed for 15 min at the same temperature and then cooled down to room temperature. These synthesized nanocrystals were precipitated by using excess of acetone from ODE. Finally, these were precipitated using methanol as non-solvent and then dispersed in chloroform.

**Cu doped ZnSe:** Cu doped ZnSe nanocrystals has been prepared following the literature methods.<sup>4</sup> In brief, 0.063 gm Zn(St)<sub>2</sub> and 8 ml ODE were loaded in a 50 ml three necked flask. After degassing for 15 minutes by purging Argon, the temperature of the reaction flask was increased to 290 °C. In a separate vial, a stock solution of 1.83 gm of Se in 10 ml TBP was prepared in glove box. Then, the 0.5 ml TBP-Se from the stock and 0.8 gm ODA (molten through gentle heating in inert atmosphere) were mixed together in inert atmosphere which was injected swiftly to the reaction flask at 290 °C and cooled down to 220 °C. Then, 0.05 ml of Cu-stock (1 mmol of Cu(St)<sub>2</sub> in 10 ml ODE in inert atmosphere) was added dropwise and annealed at the same temperature. In a separate vial, a stock solution of 0.632 gm Zn(St)<sub>2</sub>, 0.14 gm Stearic acid and 4 ml ODE were mixed together and degassed by purging Argon. After annealing for 45 min at 220 °C, 2 ml of Zn-stock solution was added drop wise in two successive session of 1 ml of each addition with 10 min

interval. Further, it was annealed for another 45 min then cooled down to room temperature. These synthesized nanocrystals were precipitated by using excess of acetone from ODE. Finally, these were precipitated using methanol as non-solvent and then dispersed in chloroform.

**ZnTe:** ZnTe was synthesized following similar procedure as ZnSe but TOP-Te has been used instead of TBP-Se.

**(g) CdS:** CdS nanocrystals were prepared following the modified literature method.<sup>5</sup> In brief, 0.024 gm CdO and 8 ml ODE and 0.56 gm of oleic acid were loaded in a 50 ml three necked flask. After degassing for 15 minutes by purging Argon, the temperature of the reaction flask was increased to 180 °C. In a separate vial, a stock solution of 0.03 gm of S in 2 ml ODE prepared in inert atmosphere and injected swiftly to the reaction flask at 180 °C. The reaction mixture was annealed for a while to get the CdS nanocrystals of desired size. These synthesized nanocrystals were precipitated by using excess of acetone from ODE. Finally, these were precipitated using methanol as non-solvent and then dispersed in chloroform.

**(g) CdSe:** CdSe nanocrystals were prepared following the modified literature method.<sup>6</sup> In brief, 0.012 gm CdO and 8 ml ODE and 0.28 gm of stearic acid were loaded in a 50 ml three necked flask. After degassing for 15 minutes by purging Argon, the temperature of the reaction flask was increased to 250 °C and cooled down to room temperature. Then again, 1 gm of ODA and 1 gm of TOPO were added to the reaction flask and degassed for 20 min at 100 °C. In a separate vial, a stock solution of 1.83 gm of Se in 10 ml TOP was prepared in glove box. Then the 0.5 ml of the TOP-Se solution was injected into the reaction mixture raising the temperature at 280 °C. Then, it was cooled to 250 °C and annealed for a while to get the CdSe nanocrystals of desired size. These synthesized nanocrystals were precipitated by using excess of acetone from ODE. Finally, these were precipitated using methanol as non-solvent and then dispersed in chloroform.

### **Surface modification of the synthesized nanocrystals:**

The surface ligands of the synthesized nanocrystals were exchanged with MPA or MUA as required to carry out the charge transfer reaction in aqueous medium. In a typical procedure, MPA was added to the chloroform solution of the nanocrystals with vigorous shaking under warming condition (50 °C) till the complete precipitation of these nanocrystals. Then after several rounds of washings with ethanol and chloroform, these were dispersed in mili-Q water with the aid of NaOH base. Similarly, we carried out the MUA ligand exchange using saturated solution of MUA in ethanol instead of MPA.

### **Reaction procedure:**

The MPA (or MUA) capped desired nanocrystals were dispersed in mili-Q water with the help of NaOH and the pH of the solution was adjusted at pH ~ 8. Then the solution was centrifuged to get a clear solution of dispersed nanocrystals in water. Concentrated aqueous solution of p-NP of same pH was prepared. 2 ml of freshly prepared aqueous solution of ZnS nanocrystals (desired nanocrystals) was taken in a 10 mm cuvette into which a concentrated drop of p-NP solution was added and absorbance of the p-NP was adjusted to ~1.0 (at 401 nm). To this solution, 0.004 gm of solid sodium borohydride was added followed by gentle shaking followed by irradiation. The irradiation of the mixture solution was performed by placing the cuvette in between two 6 W UV-lamps (Aldrich, catalog no Z169625) at a distance of ~5 cm each. The whole reaction was monitored spectrophotometrically. The irradiation process was performed under the excitation of the respective nanocrystals; 254 nm for ZnS and 365 nm for ZnSe, CdS, CdSe and ZnTe nanocrystals.

### **Instrumentation:**

#### **Transmission Electron Microscopy (TEM):**

TEM images were taken on a JEOL-JEM 2010 electron microscopy using 200kV electron source. JEM 2100 F model using 200kV electron source. Specimens were

prepared by dropping a drop of nanocrystal solution in chloroform on a carbon coated copper grid, and the grid was dried under air.

**X-ray Diffraction (XRD):**

XRD of the ZnS nanocrystals was taken by Bruker D8 Advance powder diffractometer, using Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) as the incident radiation.

**Optical measurements:**

UV-vis measurements were taken with Agilent 8453 spectrophotometer. Photoluminescence spectra were collected using a Horiba Jobin Yvon Fluoromax -4 spectrofluorometer.

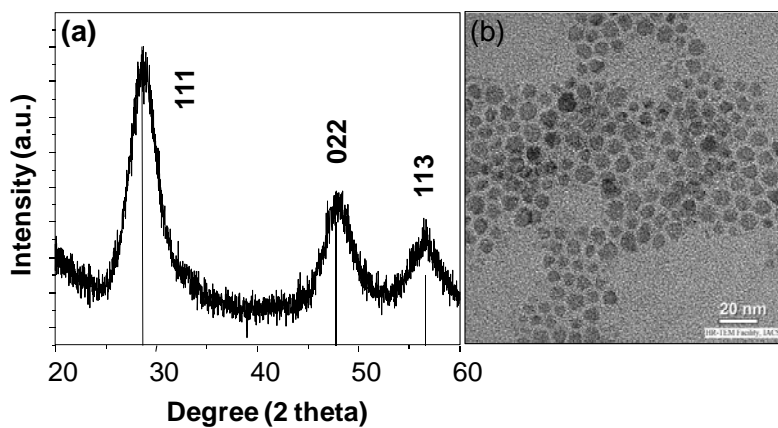
**Lifetime measurements:**

For the time correlated single photon counting (TCSPC) measurements, the samples were excited at 295 nm using a picosecond diode laser (IBH Nanoled107) in an IBH Fluorocube apparatus (JY1IBH15000M). The fluorescence decays were collected on a Hamamatsu MCP photomultiplier. The fluorescence decays were analyzed using DAS6 software.

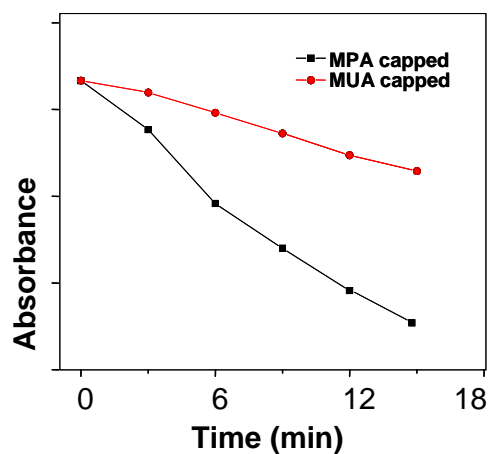
**Cyclic voltammetry:**

Cyclic voltammetry was performed in a conventional electrochemical instrument with a glassy carbon electrode as the working electrode and a platinum wire as counter electrode, using Ag/AgCl, Cl $^-$  as reference electrode with a scan rate of 100 mV/s. We have used sodium bicarbonate buffer (pH=10) as the medium for the measurement of formal reduction potential of p-NP in basic medium.

**Supporting Figures:**

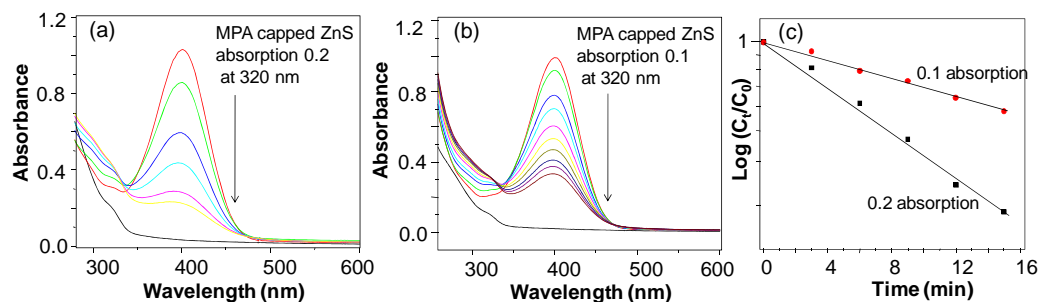


**Fig. S1** (a). Represents the XRD of the as synthesized purified ZnS nanocrystals and (b) represents the corresponding Transmission Electron Microscopic image.

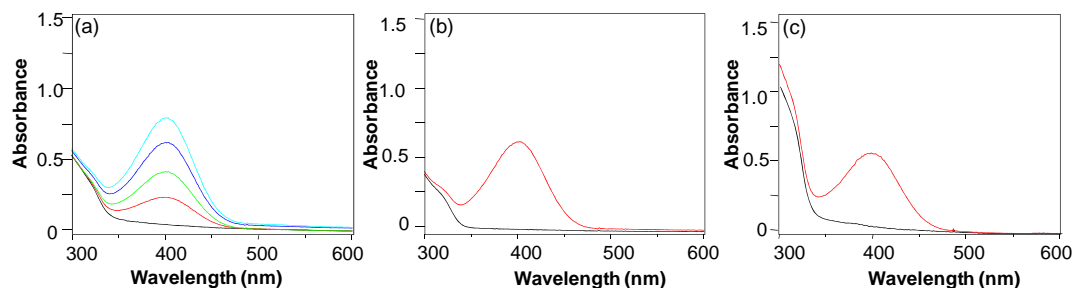


**Fig. S2** The reduction kinetics of p-NP in presence of ZnS nanocrystals capped with MPA and MUA with all identical reaction conditions.

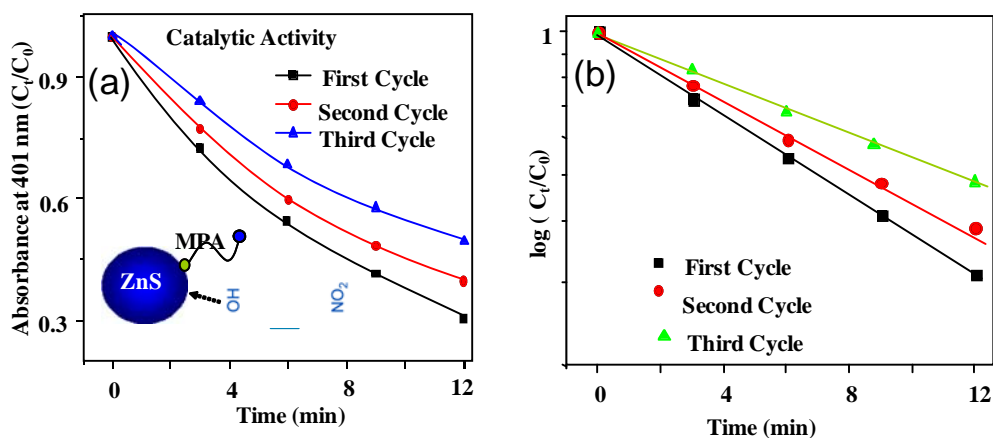




**Fig. S3** (a) and (b) Represent the successive UV-vis spectra of p-NP with identical reaction conditions with different amount of MPA capped ZnS nanocrystals in 2 ml fixed solution in a 10 mm cuvette. Each spectrum has been collected after 3 min of interval under 254 nm UV lamp irradiation. (c) Represents the comparative  $\text{Log}(C_t/C_0)$  Vs  $t(\text{time})$  plot for the two different reactions with different ZnS concentrations. The estimated rate constant ( $k$ ) is found to be  $0.0015 \text{ s}^{-1}$  and  $0.0010 \text{ s}^{-1}$  with 0.2 and 0.1 absorption of MPA capped ZnS at 320 nm respectively.  $C_t$  and  $C_0$  represent the concentration of p-NP at time  $t$  and at 0 min respectively.

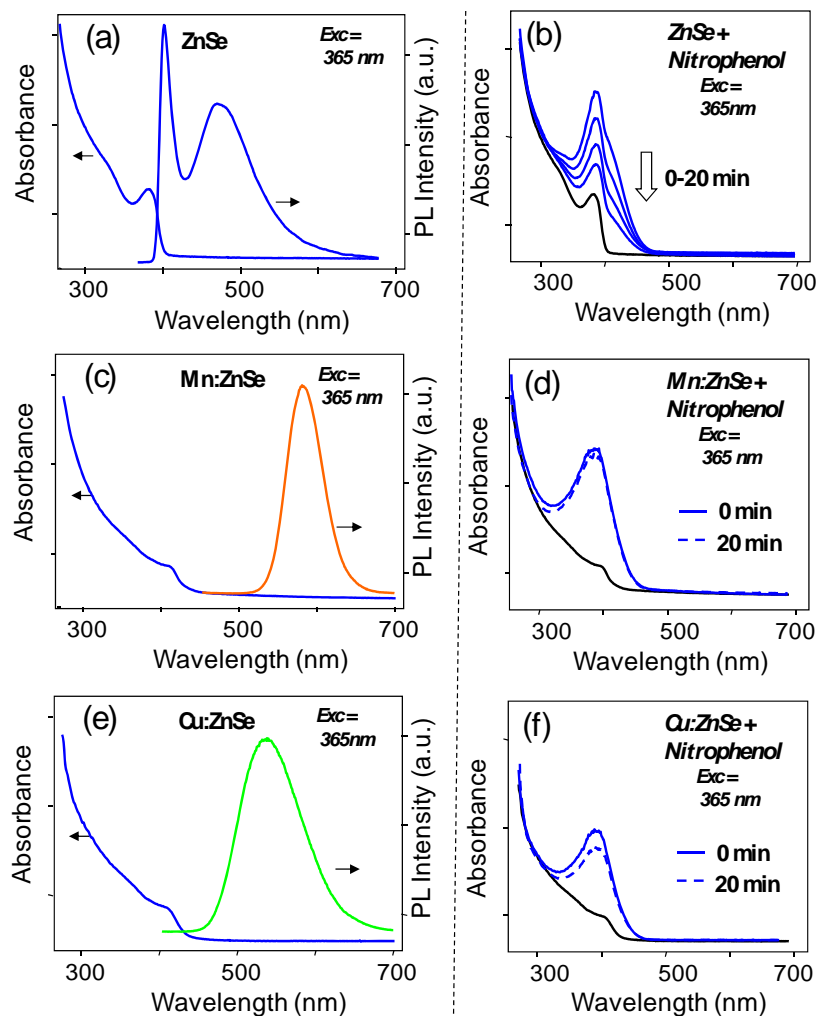


**Fig. S4** (a) Presents the UV-vis spectra for lifetime measurement of ZnS (Fig. 2b in main text) with successive addition of concentrated drop of p-NP solution in presence of sodium borohydride. (b) and (c) Present the same for Mn doped and Cu doped ZnS with sufficient amount of p-NP respectively (Fig. 2c and 2d in the main text).

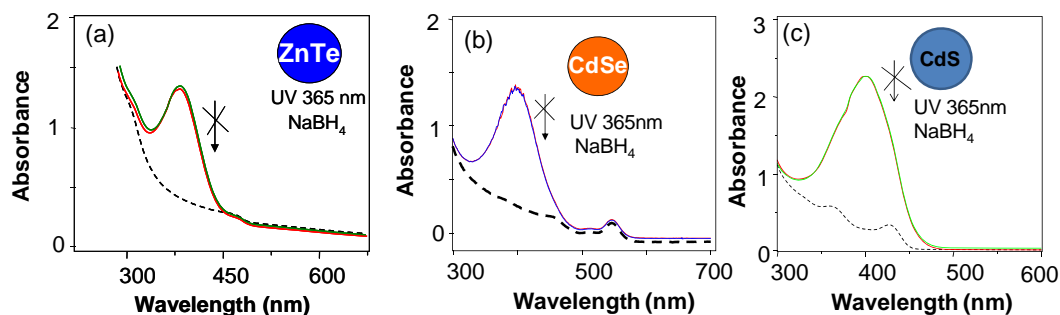


**Fig. S5** (a) and (b) represent the Comparison of reaction kinetics of reduction with successive cycle for a particular set of reaction with 0.2 optical density of MPA capped ZnS nanocrystals at 320 nm in 2 ml solution with successive addition of p-NP after each cycle.  $C_t$  and  $C_0$  represent the concentration of p-NP at time  $t$  and at 0 min respectively.

We have also carried out the same process with ZnSe. ZnSe has relatively low band gap and the p-NP also gets excited under the band edge excitation of ZnSe. With this anomaly compared to ZnS, to our surprise, we have found that the p-NP peak at 401 nm decreases with the time of irradiation but the aminophenol peak does not appear in identical reaction conditions with ZnSe (Fig. S6, ESI). Hence, we believe that the ZnSe scenario is completely different to that of the ZnS and probably it degrades the p-NP rather reduction. Similarly, we have carried out the same process with Mn or Cu doped ZnSe and observed that the Mn:ZnSe remain completely silent whereas the Cu:ZnSe can help to decrease the p-NP absorption peak to a little extent with no aminophenol peak.



**Fig. S6** Left panel: (a), (c) and (e) present the absorption and emission spectra of ZnSe, Mn doped and Cu doped ZnSe nanocrystals respectively. Right Panel: (b), (d) and (f) present the respective absorption spectra obtained insitu from the reaction system having p-NP, nanocrystals and sodium borohydride under band edge irradiation of ZnSe.



**Fig. S7** (a), (b) and (c) Present the absorption spectra obtained from the reaction of p-NP and sodium borohydride with ZnTe, CdSe and CdS in presence of sodium borohydride respectively. The dashed line in each case corresponds to the absorption spectra of the nanocrystals only. In each case two spectra of p-NP and the nanocrystals mixture are shown. One is at zero minutes and another one is after 20 minutes of irradiation.

#### References:

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