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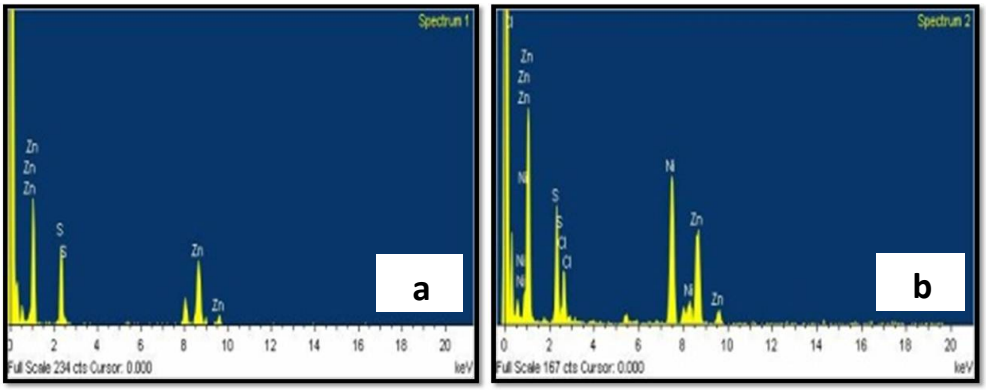
Supplementary Information's

Figure S1. EDAX spectrum of ZnS QDs and ZnS QDs/β-carotene hybrids by chemical method



(The ratio between Zn and S is 46:54 for ZnS QDs and it is 48:52 for ZnS QDs/β-carotene hybrids by chemical method)

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Fig. S2

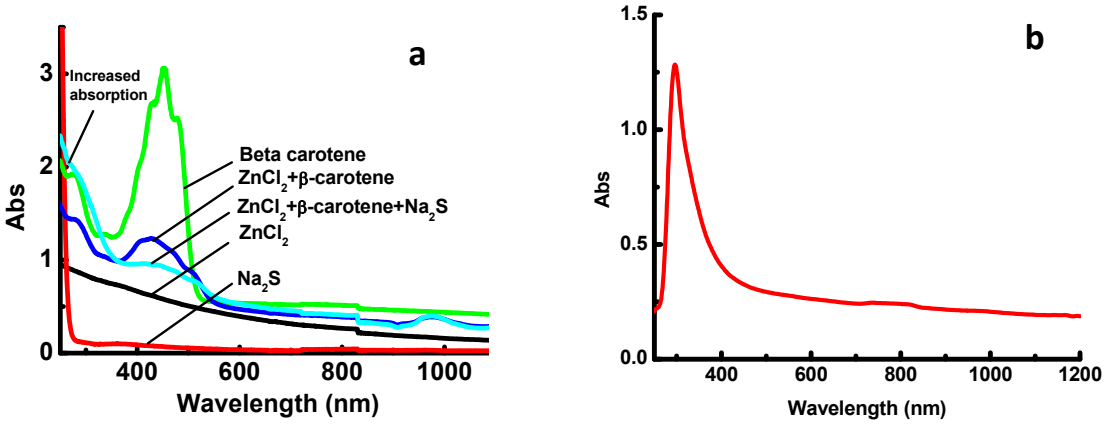

Fig. S2(a) Optical absorption spectrum from precursor solutions
Fig. S2(b) Optical absorption spectrum from hybrid sample (chemical method)

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Figure S3: Excitation energy spectrum

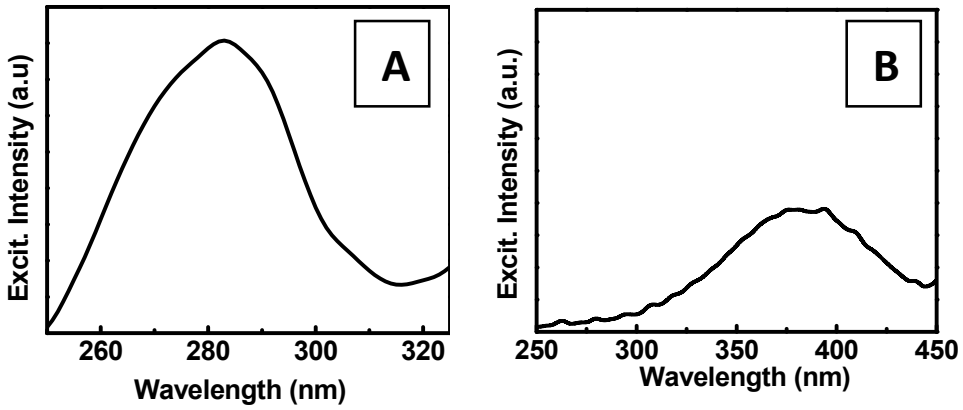

Figure S3 (A) Excitation energy spectrum of pure ZnS QDs by chemical method.
Figure S3(B) Excitation energy spectrum of pure ZnS QDs/*β*-carotene hybrid by chemical method.

(ZnS QD's excitation energy maximum is matching with the absorption maximum at 280 nm. On the other hand, in case of ZnS QDs–*β*-carotene hybrid sample prepared by chemical method, the excitation energy maximum is shifted to a value of 385 nm as shown in figure B and we attribute this to virtual up shift of valence band edge state.)

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Figure S4 XRD, HR-TEM and optical data of cadmium doped ZnS QDs and its hybrids by chemical method

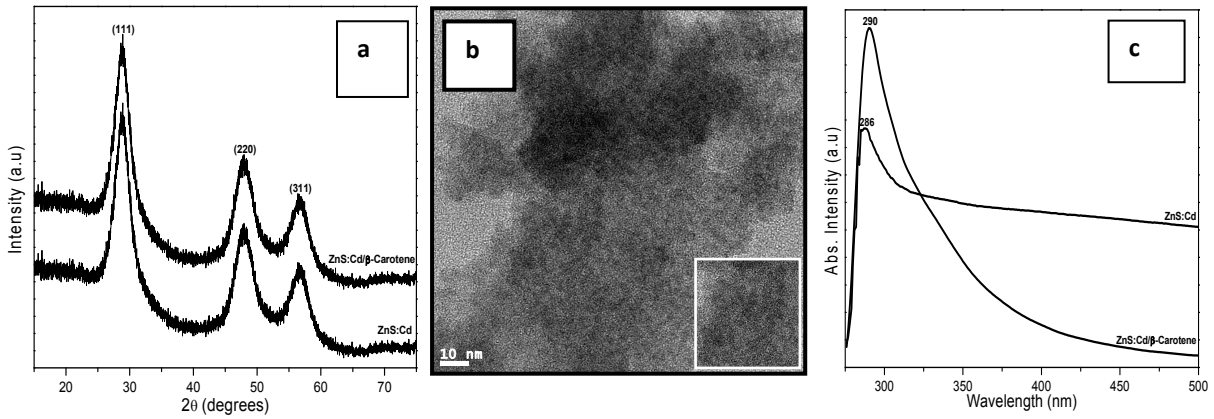

Figure S4(a) XRD pattern of ZnS:Cd QDs and ZnS:Cd/*β*-carotene hybrid by chemical method.
Figure S4(b) HR-TEM image of ZnS:Cd/*β*-carotene hybrid by chemical method.
Figure S4(c) UV absorption spectra of ZnS:Cd QDs and ZnS:Cd/*β*-carotene hybrid system by chemical method.

Preparation details of of ZnS:Cd QDs and ZnS:Cd/*β*-carotene hybrid system:

Cadmium doped ZnS QDs and ZnS:Cd/*β*-carotene hybrid system was prepared and their structure and photophysical properties were analyzed. For the preparation of ZnS:Cd QDs, zinc chloride ($ZnCl_2$) solution was freshly prepared by dissolving the same in double distilled water (DD water). Keeping the solution under ultrasonic agitation, freshly prepared cadmium chloride ($CdCl_2$) solution was added in the $ZnCl_2$ solution. Later, an equimolar amount of freshly prepared sodium sulfide (Na_2S) solution was added drop wise into the mixture solution of $ZnCl_2$ and $CdCl_2$ to obtain a white colloidal suspension. For the preparation of ZnS:Cd/*β*-carotene hybrid system, a similar procedure as it was used to prepare ZnS:Cd QDs was followed but *β*-carotene solution was added drop wise before the addition of Na_2S solution. In both the experiments, the reaction was carried out at room temperature. The final solution was colloidal suspension, and which was washed several times in DD water to remove any un-reacted or excess precursor molecules. After washing several times, the dispersed particles were centrifuged at 10,000 rpm for about 10 minutes and then dried under a rotary vacuum condition for few days. Samples were also prepared by physical method, and which is nothing but, the direct mixing of as prepared ZnS:Cd QDs with *β*-carotene.

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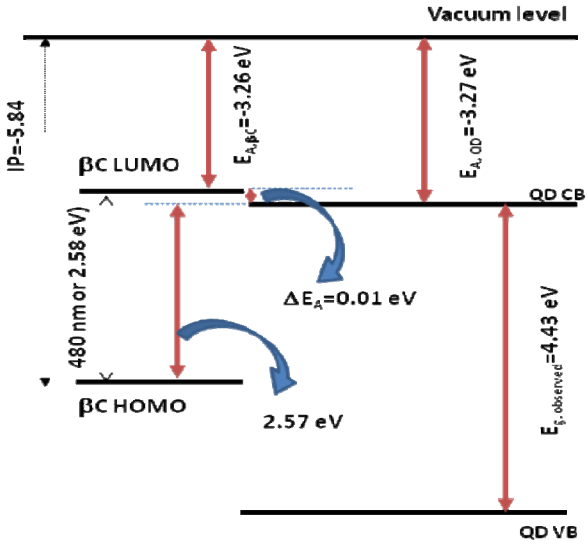
Calculation of interfacial energy level separation



Interfacial energy diagram between ZnS QD and *β*-carotene molecule

To calculate the difference between the conduction band edge state of ZnS QD and the HOMO level of *β*-carotene, at first we have calculated the difference in energy between the electron affinity values of the respective systems and which is negligibly small about 0.01 eV. Later this value was subtracted from the experimental energy band value of *β*-carotene molecule (obtained the first optical absorption maximum of beta carotene at 480 nm), to get a difference of 2.57 eV. This difference in energy value is closely matching with the experimental emission band position at 480 nm.

The electron affinity value of the molecule is about 3.26 eV and which was obtained by subtracting the experimental band gap ($E_{g,molecule}$) value of the molecule from its ionization potential energy (I_P =5.84 eV)[1]. The electron affinity of QD ($E_{A,\ QD}$) is size sensitive and therefore we have calculated this value by using the given below relation.[2]

$$E_{A,QD}=E_{A,bulk}+(E_{g,observed}-E_{g,bulk})(m_h/m_h+m_e)$$

The bulk band gap value of ZnS ($E_{g,bulk}$ = 3.67 eV), the observed band gap value of ZnS QD ($E_{g,observed}$ = 4.43 eV, from optical absorption maximum), the bulk electron affinity of ZnS ($E_{A,bulk}$ = 3.8 eV)*, the electron (m_e=0.25m_e) and hole (m_h=0.59m_e) effective masses of ZnS were used to calculate the $E_{A,QD}$. The as calculated $E_{A,QD}$ value is 3.27 eV.

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(* Bulk electron affinity value of ZnS has range of values between 3.8 to 3.9 eV[3, 4] and here have used a value of 3.8 eV for our calculation purpose).

References

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