Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information :

Tunable surface plasmon resonance and enhanced electrical conductivity of In doped ZnO colloidal nanocrystals

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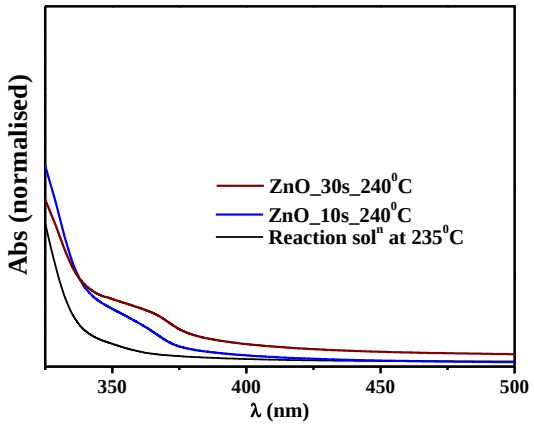


Fig. S1: Appearance of band gap absorbance after 10 secs of reaction

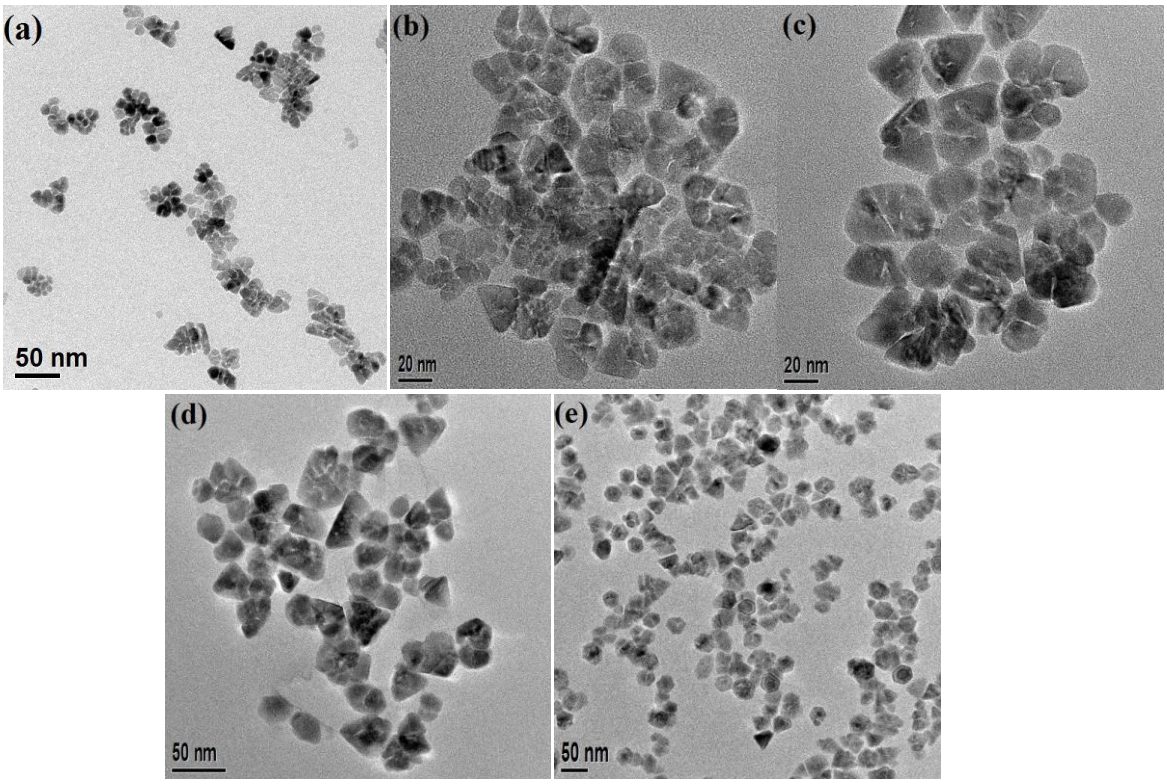


Fig. S2: Temporal growth evolution of ZnO NCs from $Zn(acac)_2$ synthesized at 240 °C; TEM images at different time (a) 10 s, (b) 1 min, (c) 10 min, (d) 15 min, (e) 30 min.

Fig. S3a shows FT-IR spectrum of OLAH, $Zn(acac)_2$ and mixture of OLAH and $Zn(acac)_2$ heated at 90 ^{0}C in vacuum. The FTIR peaks appear at 1578 and 1517 cm^{-1} in $Zn(acac)_2$ due to the symmetric and antisymmetric COCC stretching vibration of acetylacetonate ligand[1] and the stretching frequency for carbonyl group of oleic acid is found at 1711 cm^{-1}. After 15 min of reaction at vacuum the intermediate zinc complex shows a stretching band at 1536 cm^{-1} corresponding to COCC group of $acac^-$ ligand (19 cm^{-1} up field compare to pure one)[1], whereas the carbonyl stretching band for oleate group appears at 1550 cm^{-1} along with the presence of Stretching band for free oleic acid at 1711 cm^{-1}. More than 30 minute of heating at 90 °C under vacuum, results in the formation of $Zn(OLA)_2$ complex with total consumption of oleic acid (diminution of peak at 1711 cm^{-1}). FTIR spectra of $Zn(OLA)_2$ complex dissolved in ODE (Fig. S4) shows a bidentate binding of oleate ($\Delta\nu_{as\text{-}s}$ = 149 cm^{-1}, where ν_{as} = 1555 cm^{-1} and ν_s = 1406 cm^{-1}) but in the intermediate complex (Fig. S3a), probably the free neutral oleic acid increases the bridging contact between $Zn(acac)_{2-x}(OLA)_x$ units, which yields a downfield shift (from 1555 to 1550 cm^{-1}) of oleate ligand.[2]

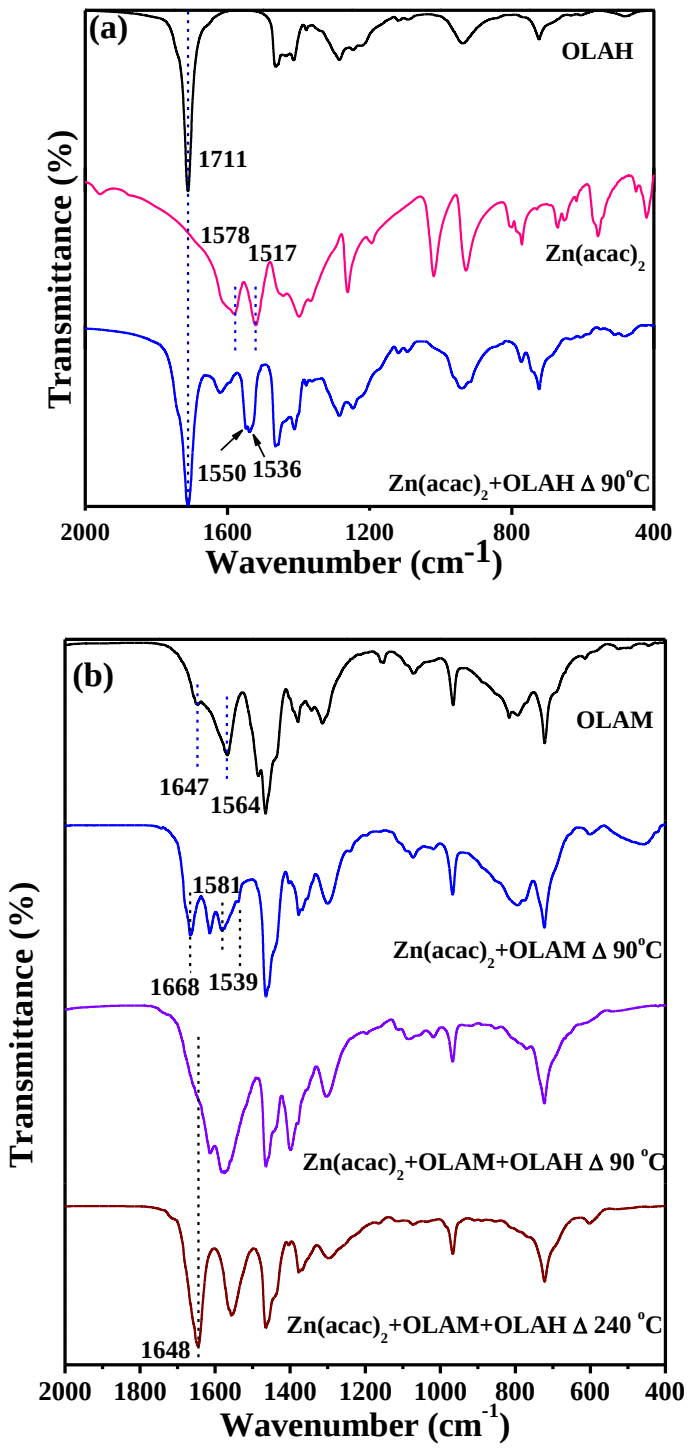


Fig. S3

Fig. S3:. (a) FTIR spectra of OLAH, $Zn(acac)_2$ and mixture of OLAH and $Zn(acac)_2$ heated at 90 ˚C. (b) FTIR spectra of OLAM, mixture of OLAM and $Zn(acac)_2$ heated at 90 ˚C, mixture of OLAH, OLAM and $Zn(acac)_2$ heated at 90 ˚C and 240 ˚C respectively. Formation of amide at nucleation temperature.

By FTIR spectroscopy (Fig. S3b) it was very clear that amide (-CO-NH-, 1649 cm^{-1} for stretching vibration of CO) was a by-product of the NC growth reaction.

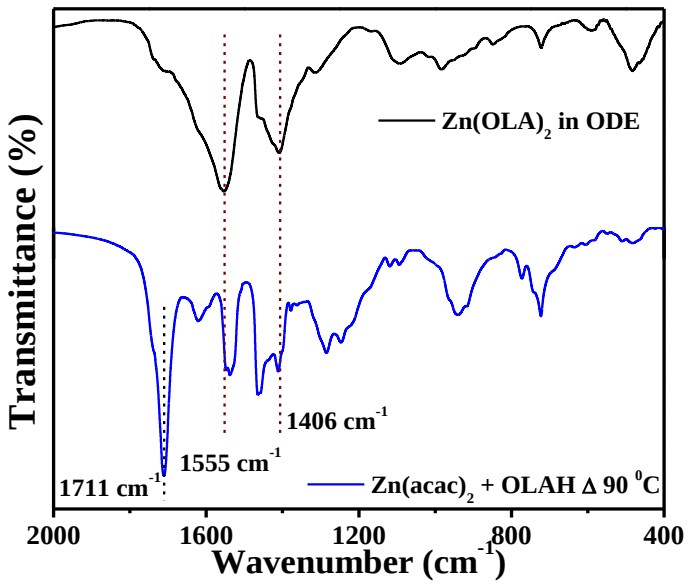


Fig. S4

Fig. S4 shows the FTIR spectra of $Zn(OLA)_2$ and the mixture of $Zn(acac)_2$ and OLAH heated at 90 ˚C in vacuum. It shows the presence of free OLAH in mixture and downfield shifting of antisymetric stretching band from 1555 cm^{-1} to 1550 cm^{-1} also confirms the bridging interaction between $Zn(acac)_{2-x}(OLA)_x$ units.

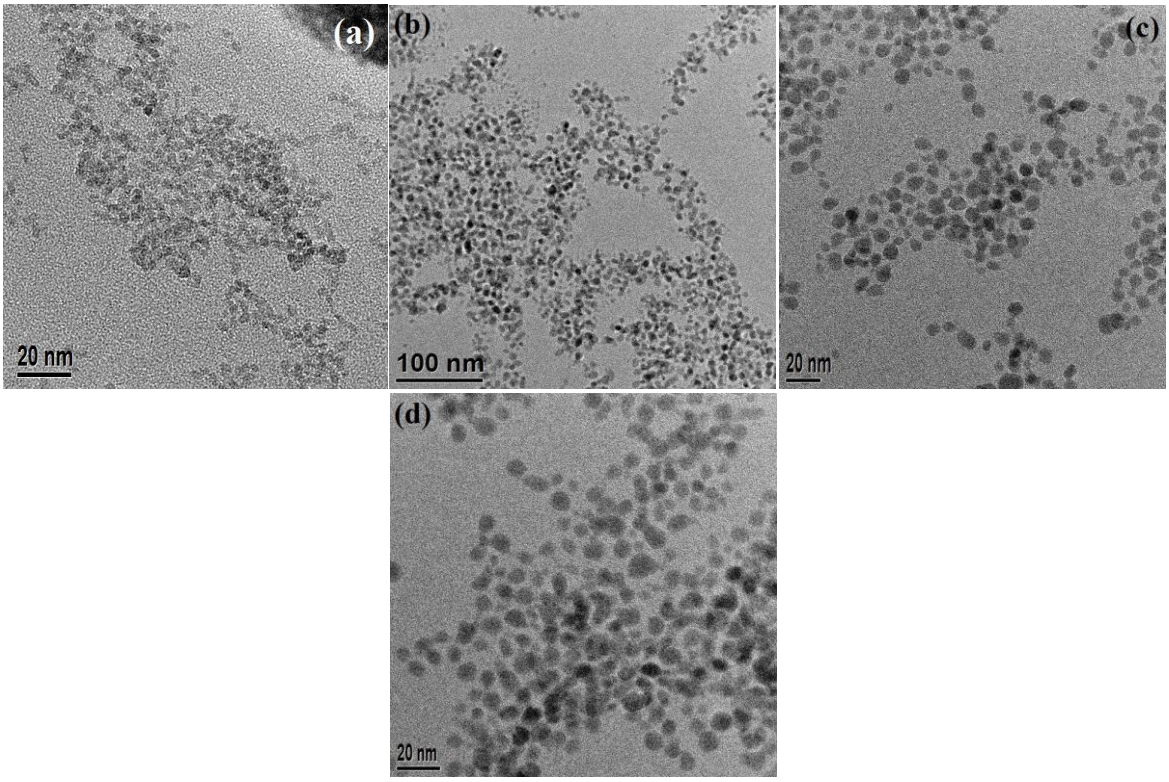


Fig. S5: Temporal growth evolution InO NCs from $In(acac)_3$ derived precursor where the reaction was carried out at 240 °C; TEM images at different time interval (a) 10s, (b) 1 min, (c)10 min, (d) 30 min.

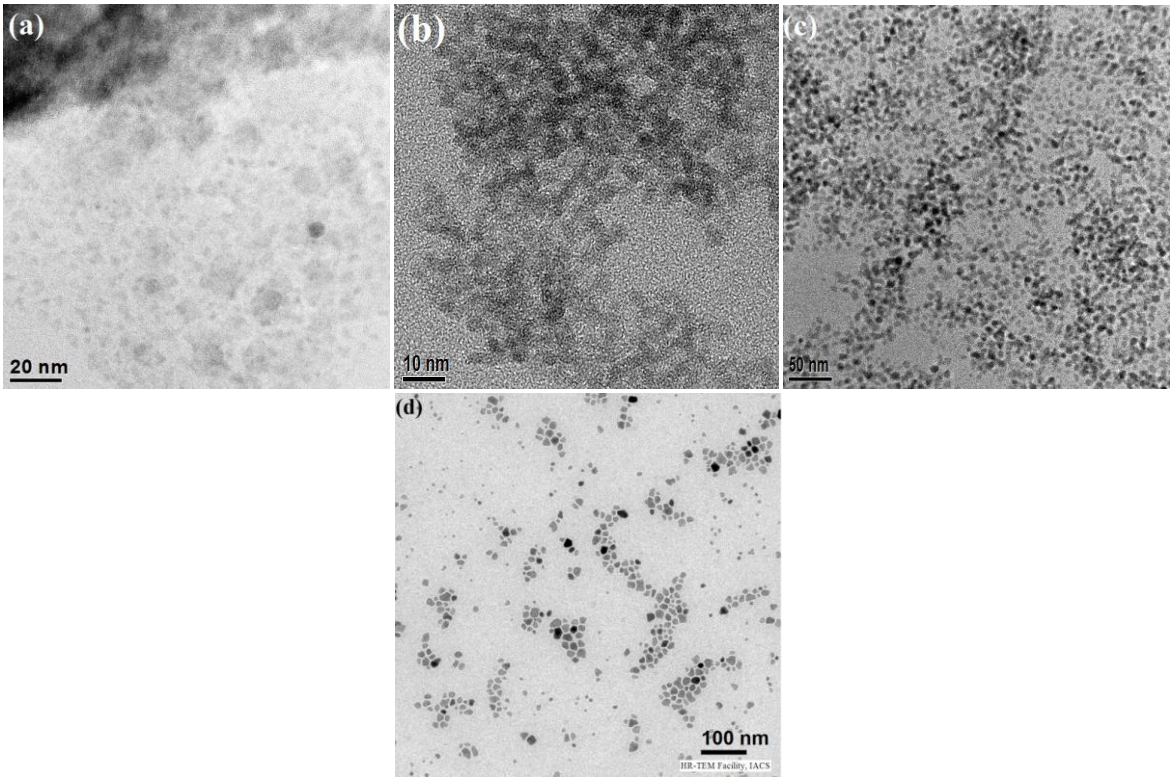


Fig. S6: Temporal growth evolution of In_2O_3 NCs from $In(OAc)_3$ derived precursor where the reaction was carried out at 290 °C; TEM images of product at different time interval (a)10s, (b) 1 min, (c) 5 min and (d) 30min.

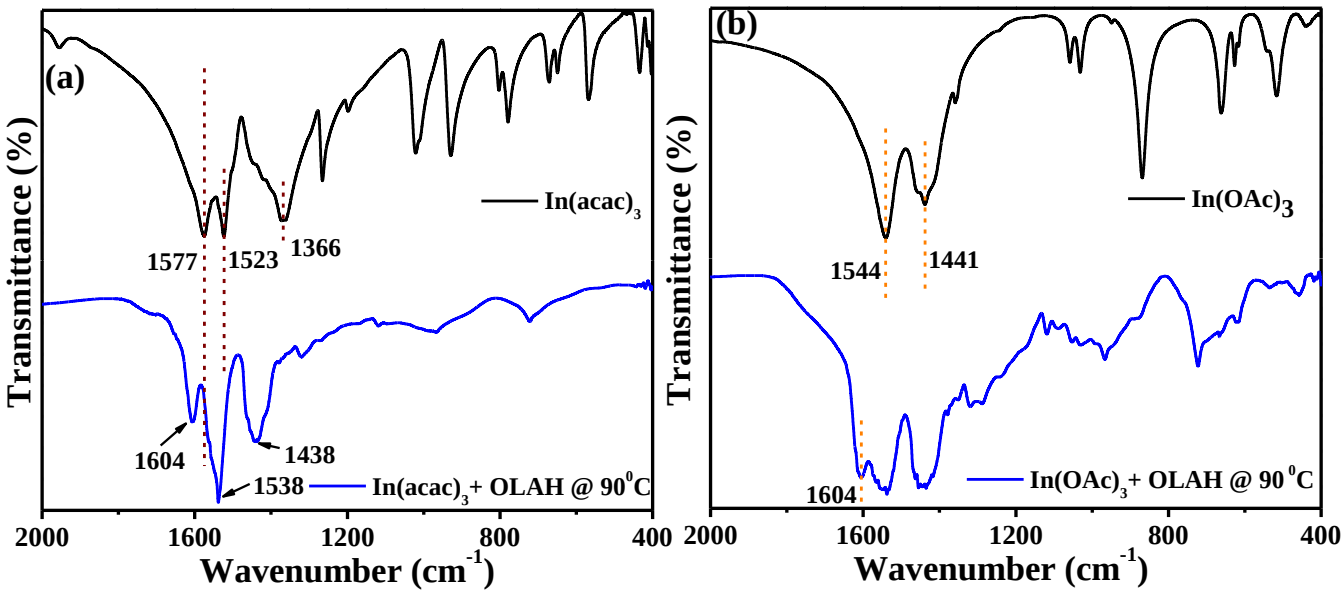
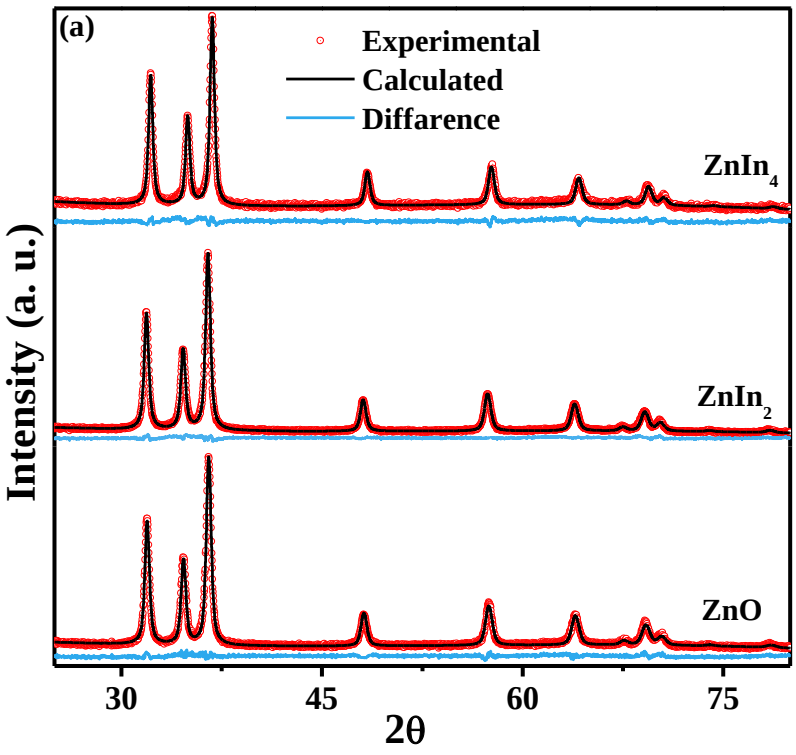


Fig. S7: Formation of In intermediate complex, Total consumption of 2 mmol of OLAH by both $In(acac)_3$ and $In(OAc)_3$ results formation of $In(acac)(OLA)_2$ and $In(OAc)(OLA)_2$.

Fig. S8(a) shows the Rietveld fitting of sample ZnO, $ZnIn_2$ and $ZnIn_4$. Whereas Fig. S8(b) shows unit cell volume expansion with increase in In^{3+} concentration.



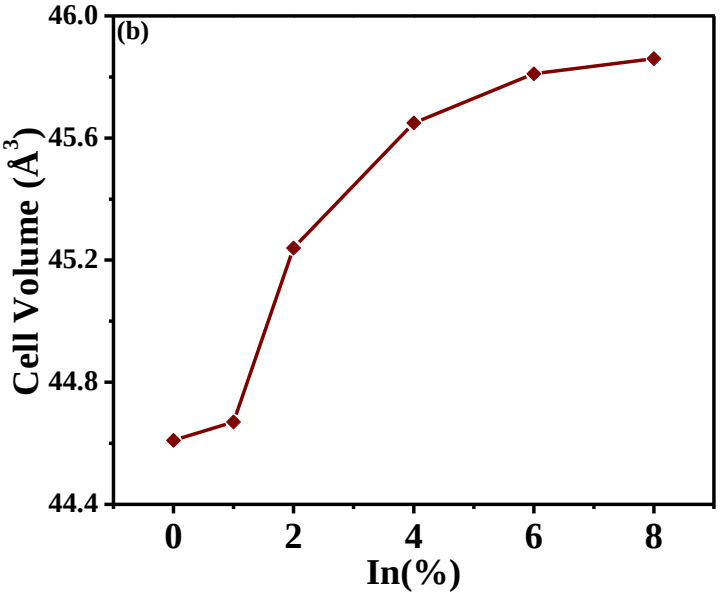


Fig. S8

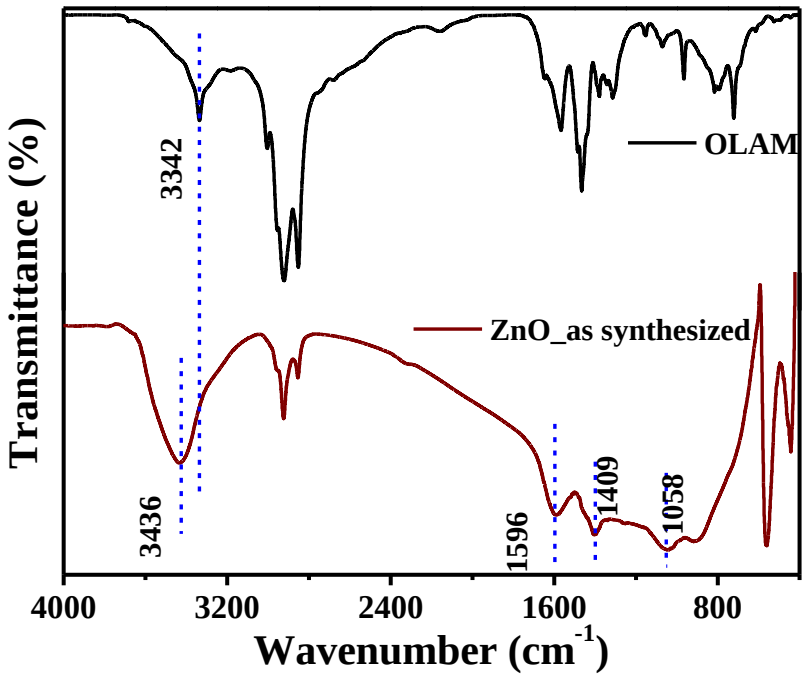


Fig. S9: shows FTIR spectra of as-synthesized ZnO nanocrystals which confirms the nanocrystals surface was well protected by OLAM.

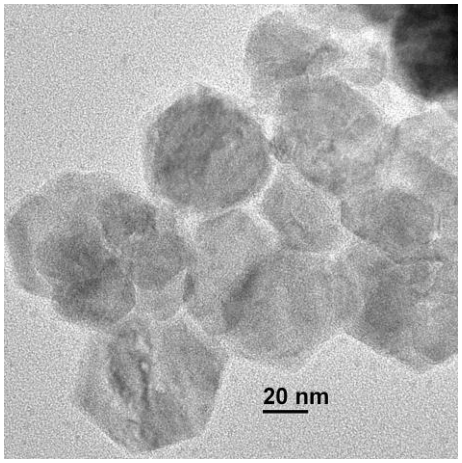


Fig. S10: Formation of irregular shaped ZnO nanocrystals upon addition of OLAM at ~ 240℃. Inhomogeneous crystal growth was observed as OLAM acts as only the capping agent and not participated in complex formation.

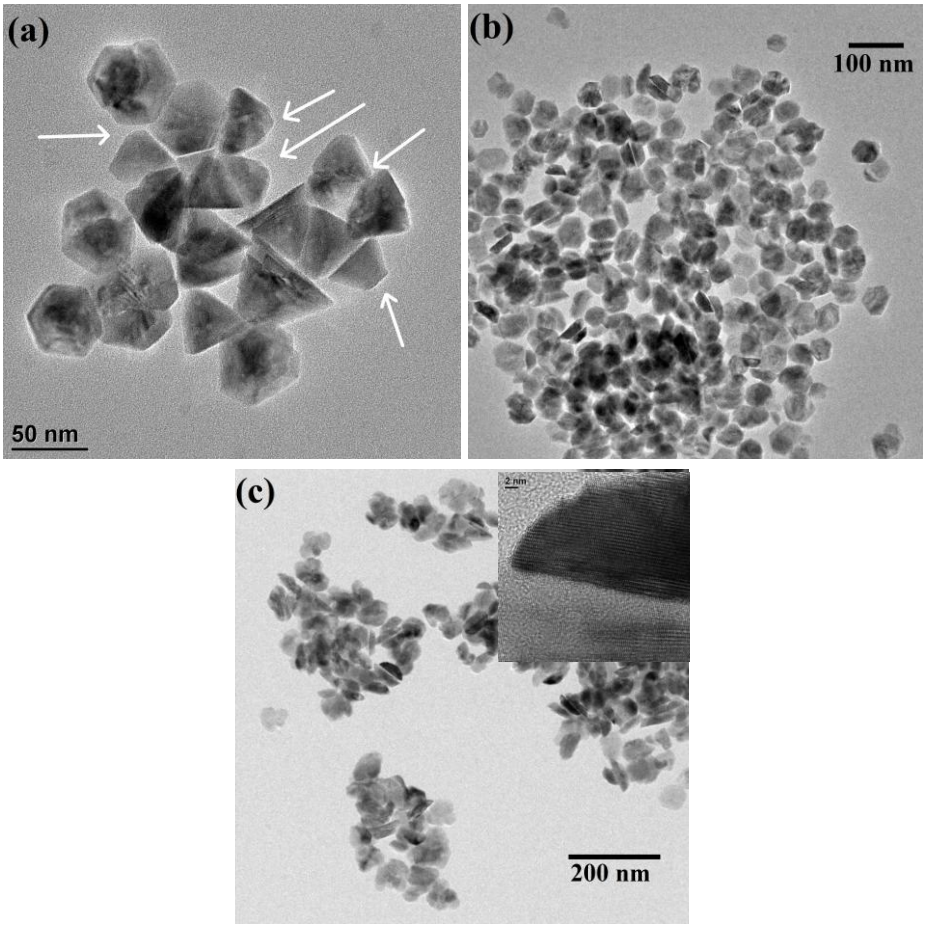


Fig. S11: (a), (b) and (c) represents the TEM images of $ZnIn_2$, $ZnIn_4$ and $ZnIn_6$ nanocrystals respectively. The TEM images clearly indicates the decrease of pyramid height and lesser exposure of $\{10\bar{1}1\}$ surface. Inset of Fig. S11(c) is HRTEM image of $ZnIn_6$ samples.

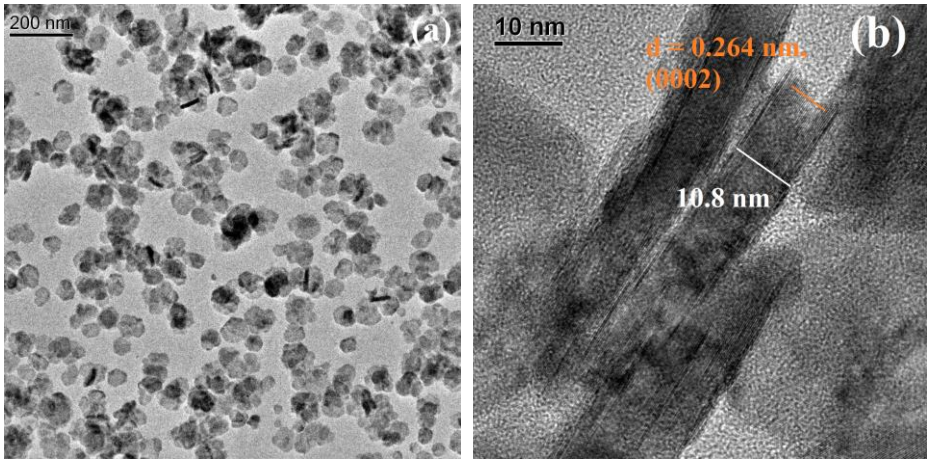


Fig. S12

Fig. S12(a) depicts the TEM image of $ZnIn_8$ nanocrystals. Fig. S12(b) shows the lateral stacking of few hexagonal platelets. The measured thickness for each platelet is found to be ~ 11 nm and the growth plane is (0002).

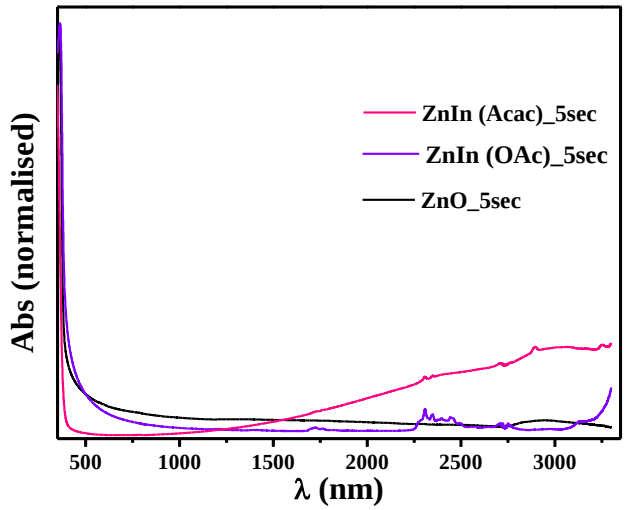


Fig. S13: Appearance of SPR just at 5 sec of reaction when the In-source was $In(acac)_3$

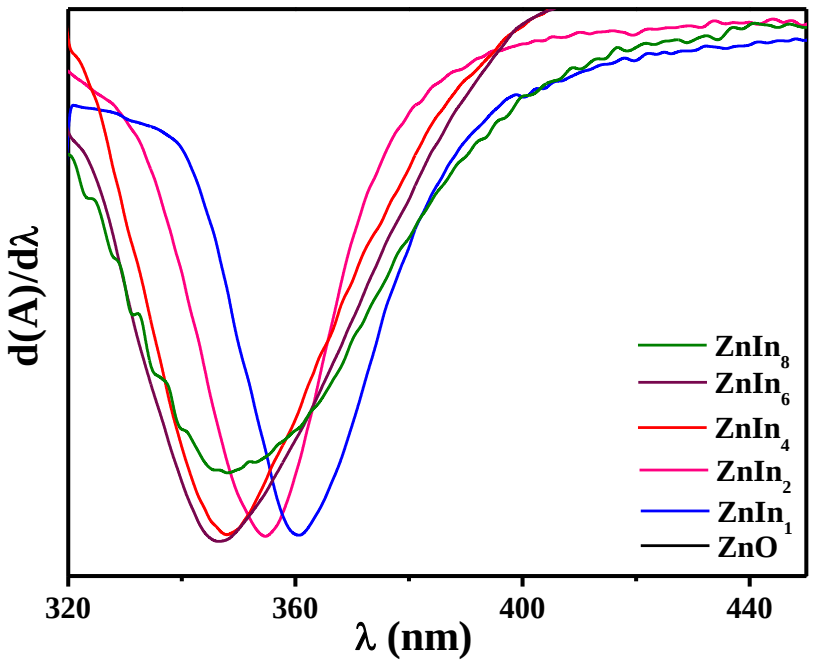


Fig. S14

Fig. S15: Digital photographs of $ZnIn_6$ colloids solution in hexane.

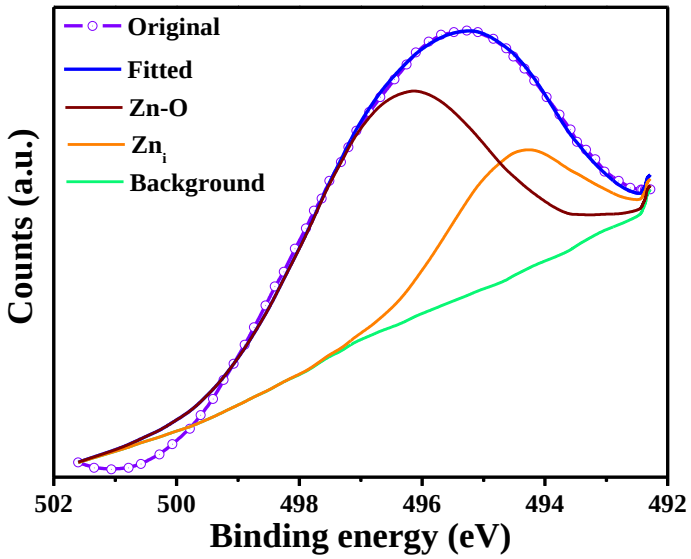


Fig. S16: Fitted Auger peak of Zn $L_3M_{4,5}M_{4,5}$ spectrum of $ZnIn_4$ NC.

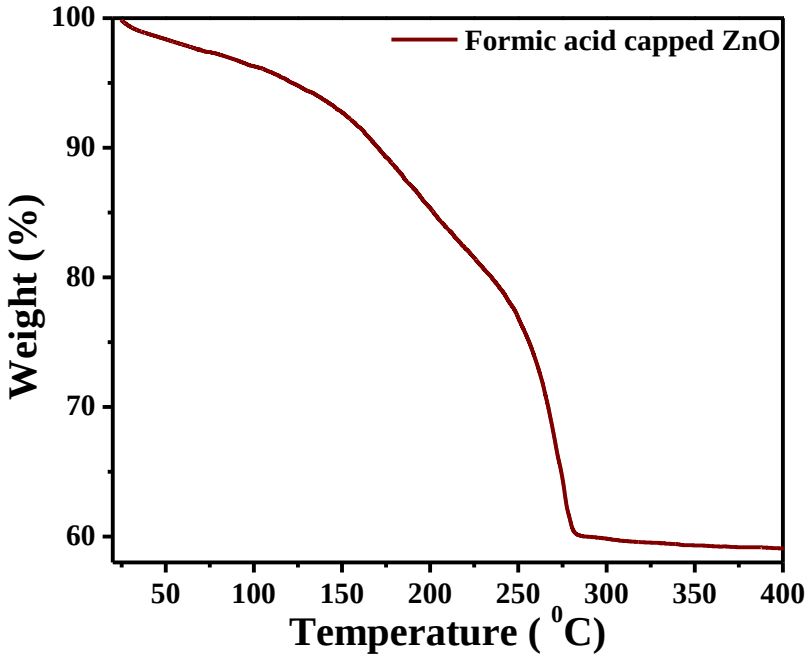


Fig. S17: TGA plot of formic acid capped ZnO nanocrystals shows a sharp decrease in weight % at 250 ˚C to 280 ˚C.

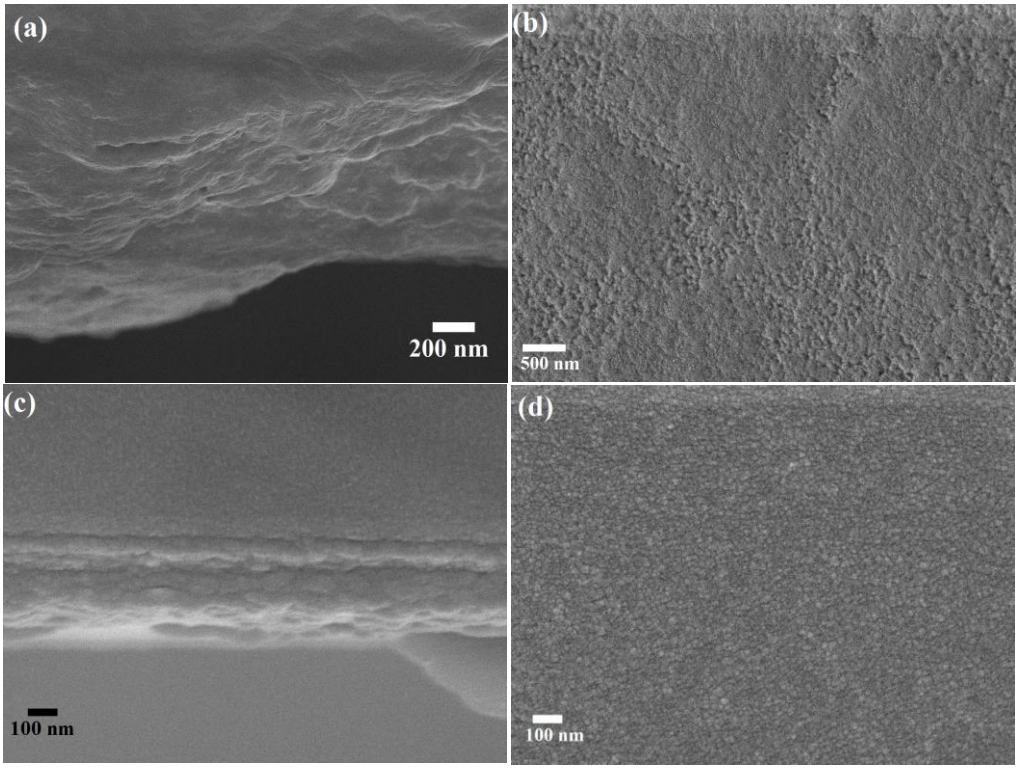


Fig. S18: The cross-section view and top view of as-deposited film of $ZnIn_4$ NC and ligand exchanged film are presented by (a), (b) and (c),(d) respectively.

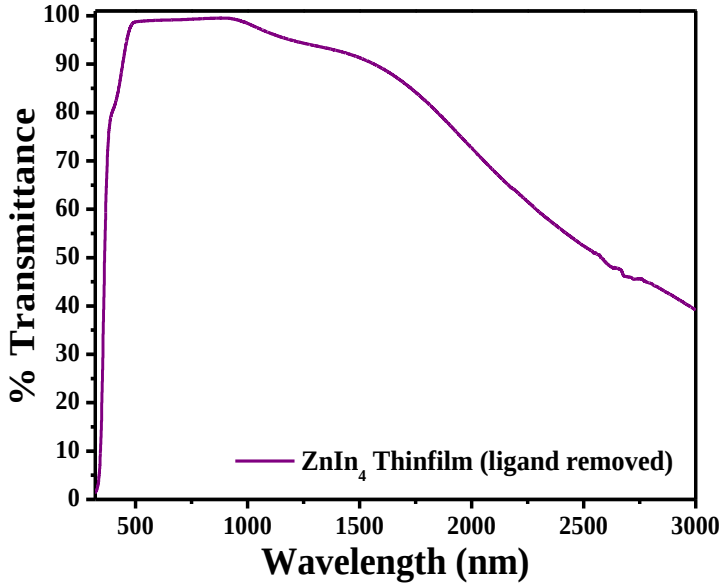


Fig. S19: The ligand stripped film of $ZnIn_4$ NC shows ~ 90 to 95% transmittance in visible range keeping the plasmonic absorption at NIR intact.

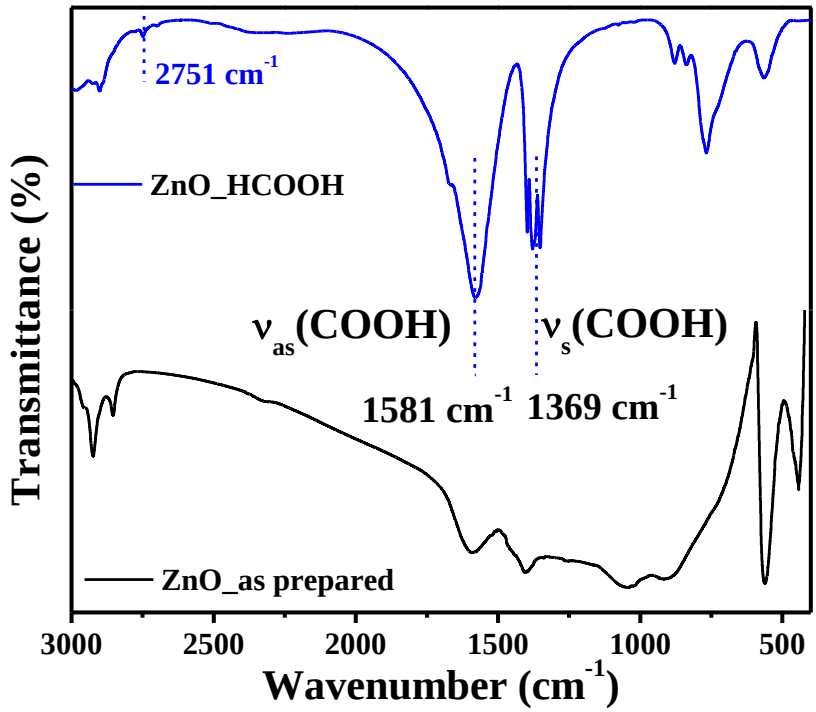


Fig. S20: FTIR spectra of as-synthesized ZnO NC and foumic acid capped ZnO NCs.

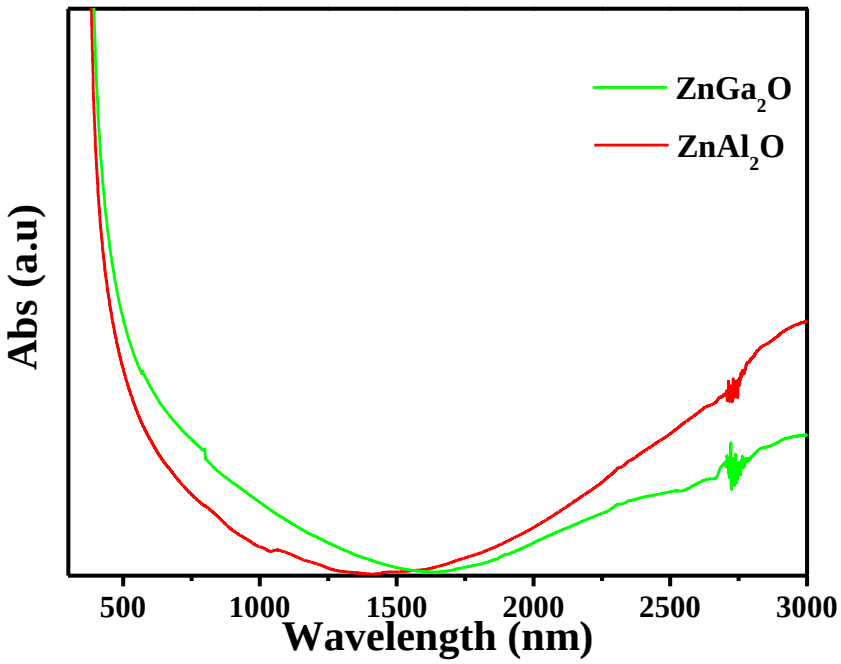


Fig. S21: NIR absorbance of 2 mole% Al and Ga doped ZnO NCs.

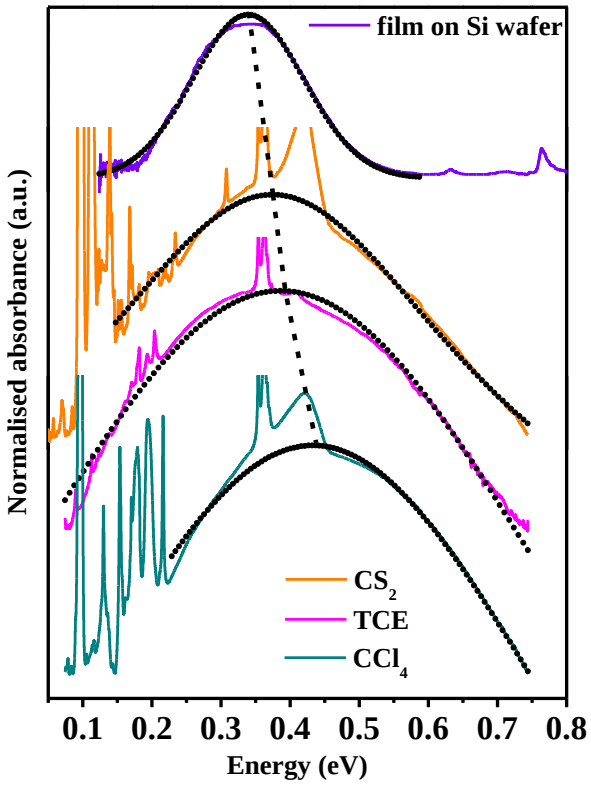


Fig.S22: NIR absorbance spectra for colloidal dispersions of $ZnIn_6$ NCs in different solvent and thin film on Si-wafer. Refractive index for CCl_4, TCE and CS_2 are 1.46, 1.51 and 1.62 respectively. The black dashed lines are the respective best fits of the plasmon peaks.

References:

(1) Bahers, T. L.; Pauporté, T.; Labat, F.; Lefevre, G.; Ciofini, I. *Langmuir* **2011**, *27*, 3442–3450.

(2) Zhang, H.; Ha, D-H.; Hovden, R.; Kourkoutis, L. F.; Robinson, R. D. *Nano Lett* **2011**, *11*, 188–197.