



1-D Vertically Aligned Hetero-epitaxial ZnO/CdS Core/Shell Nanorod Array with Enhanced Visible Light Driven Photoelectrochemical Performance

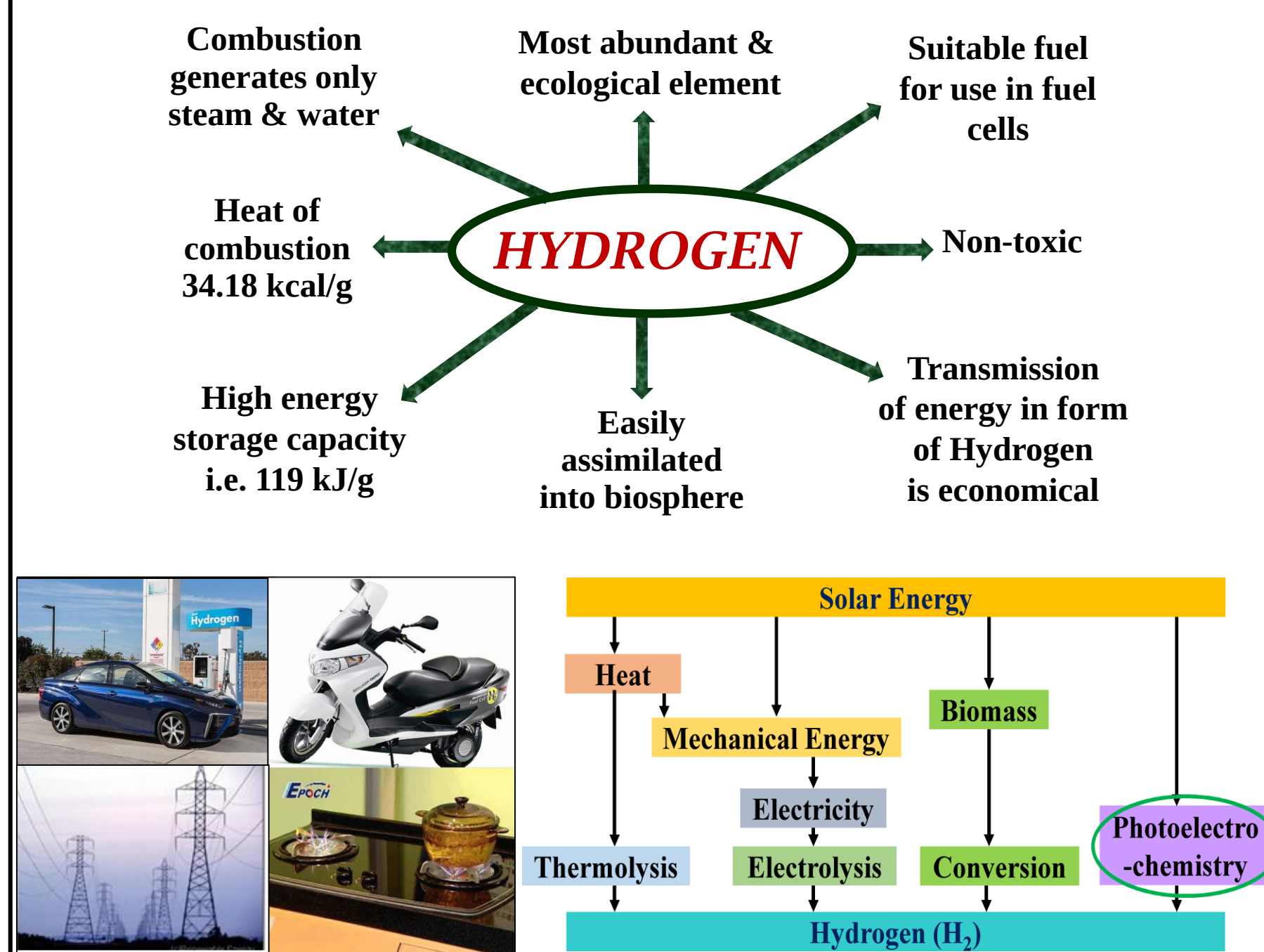
Rekha Bai*, Sujeet Chaudhary and Dinesh K. Pandya

Thin Film Laboratory, Department of Physics, Indian Institute of Technology Delhi, New Delhi-16

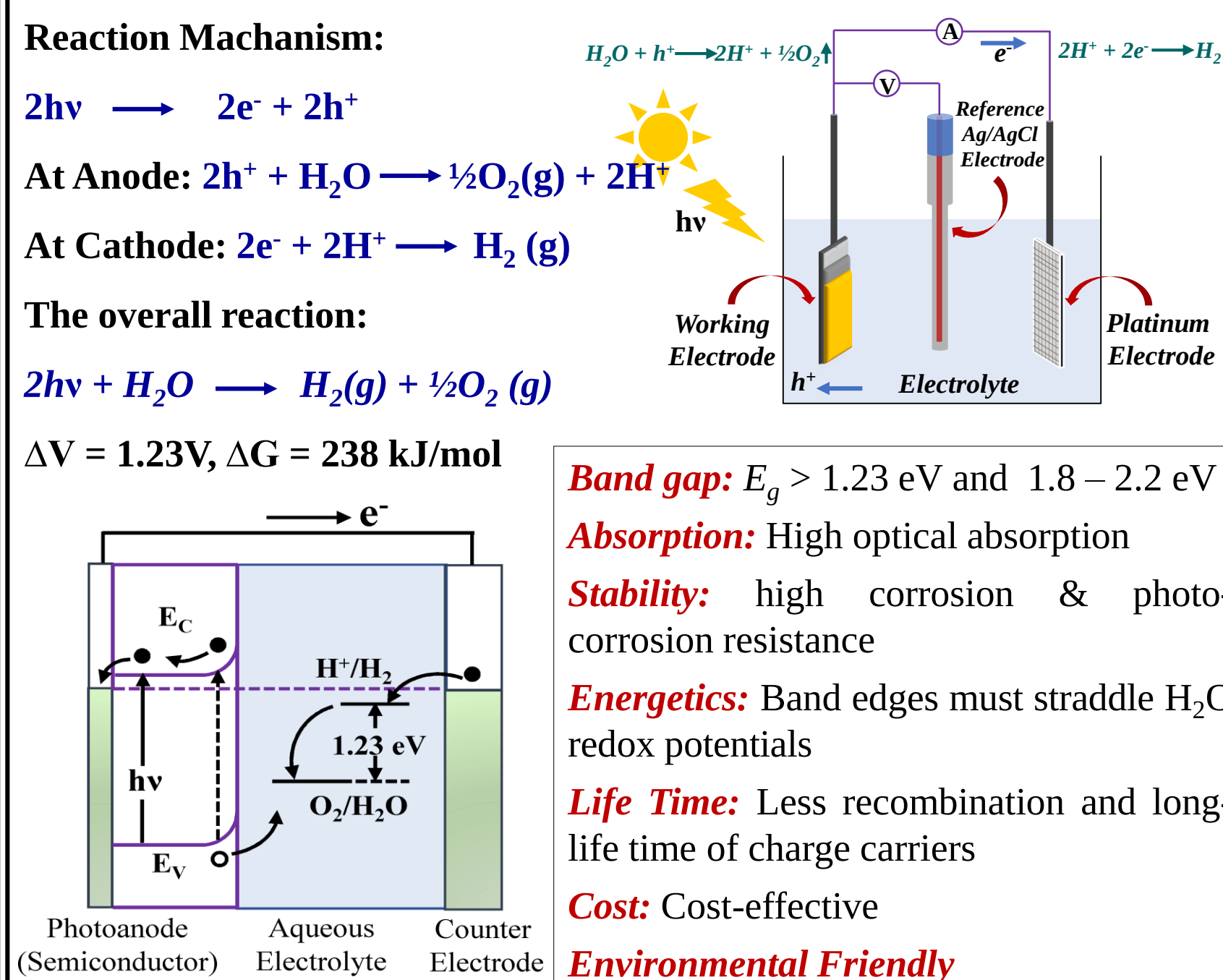
*E-mail: rekha.mittal07@gmail.com



Solar Hydrogen: Fuel for Future

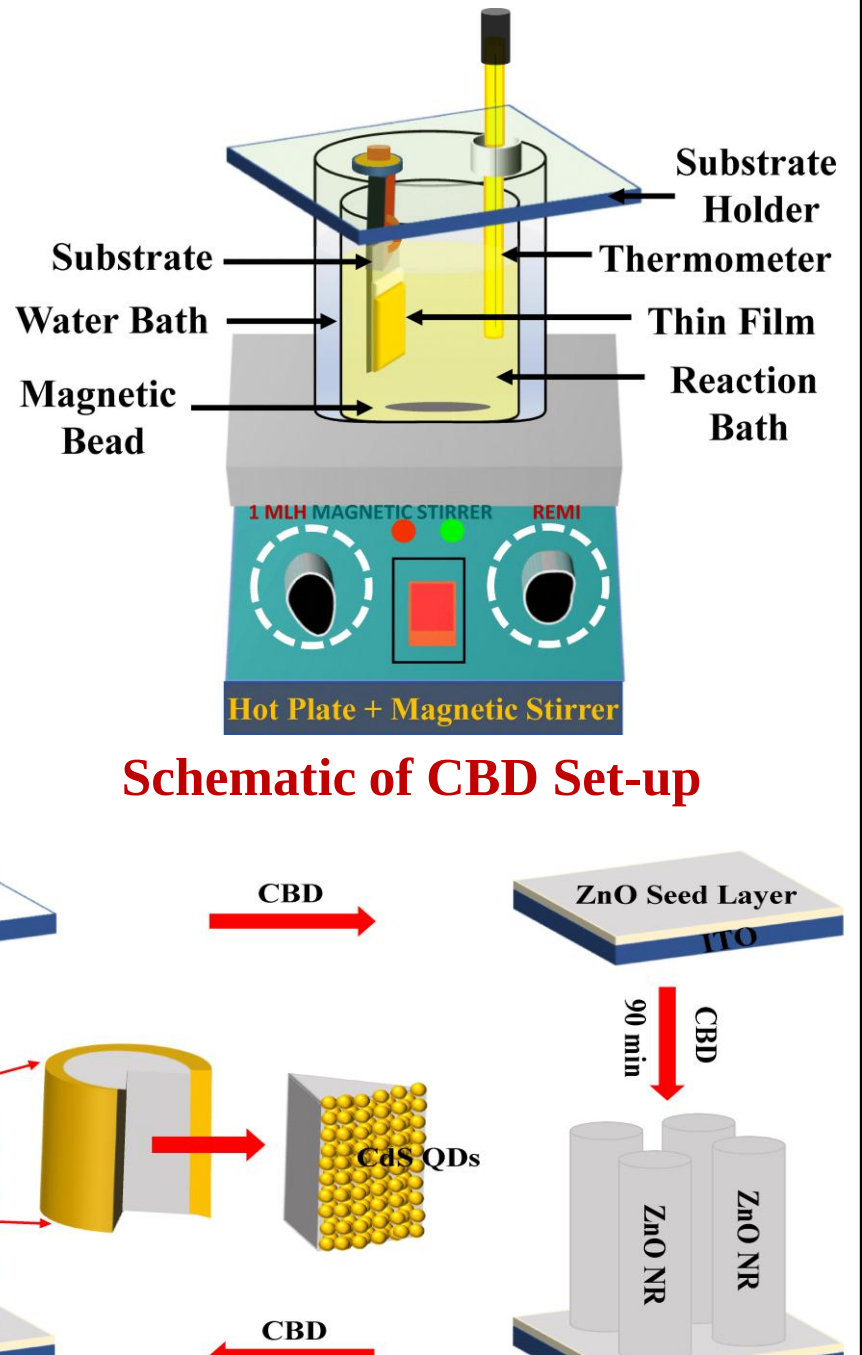


Photoelectrochemical (PEC) cell

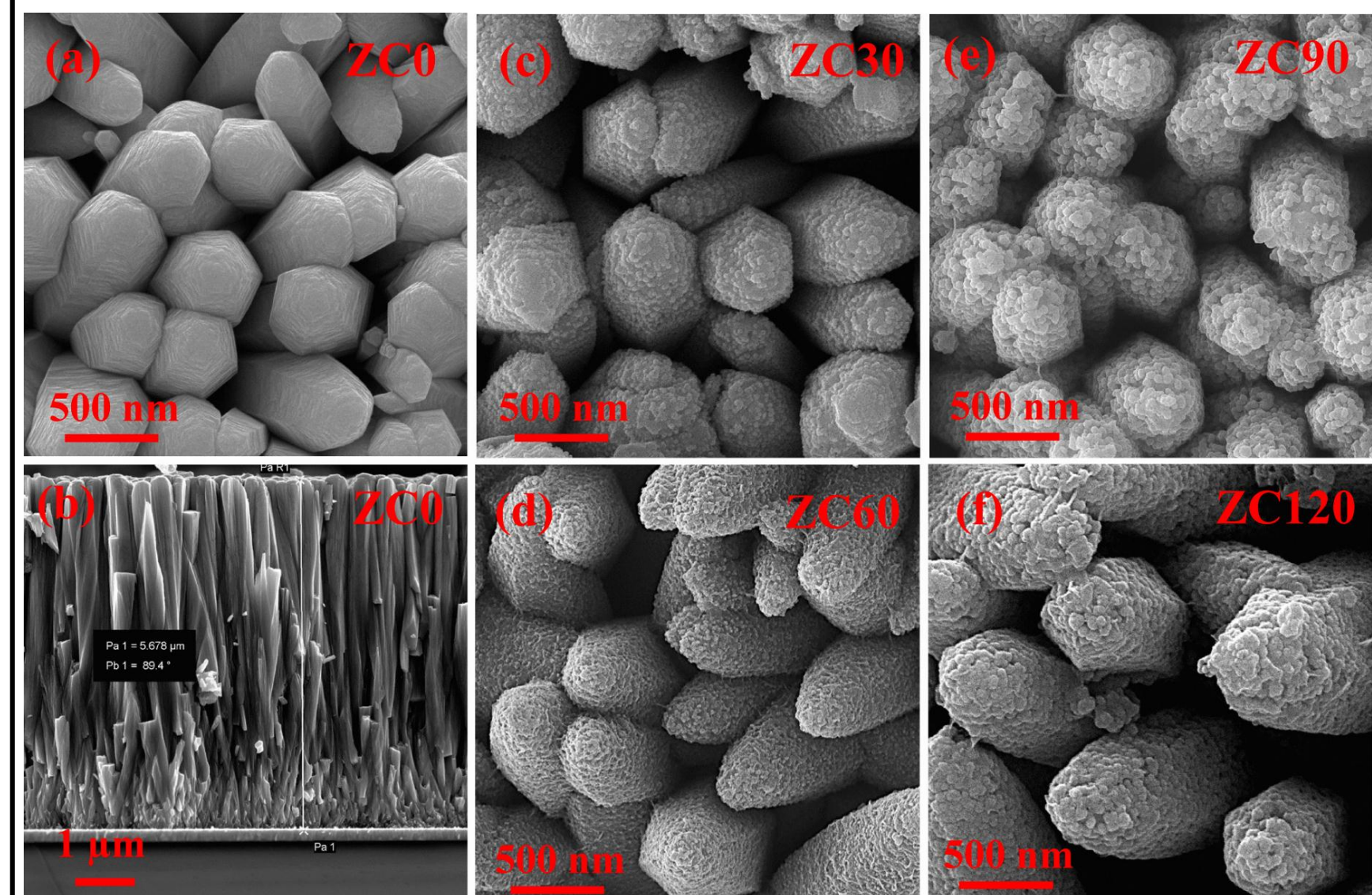


Fabrication of ZnO/CdS Core/Shell

Zinc Chloride	100 mM
Cadmium Acetate	100 mM
ZnO Bath Temperature	75 °C
ZnO Bath pH	~10.0
Annealing Temperature	300 °C
CdS Bath Temperature	75 °C
CdS Bath pH	~12.0
CdS Deposition Time	0-120 sec

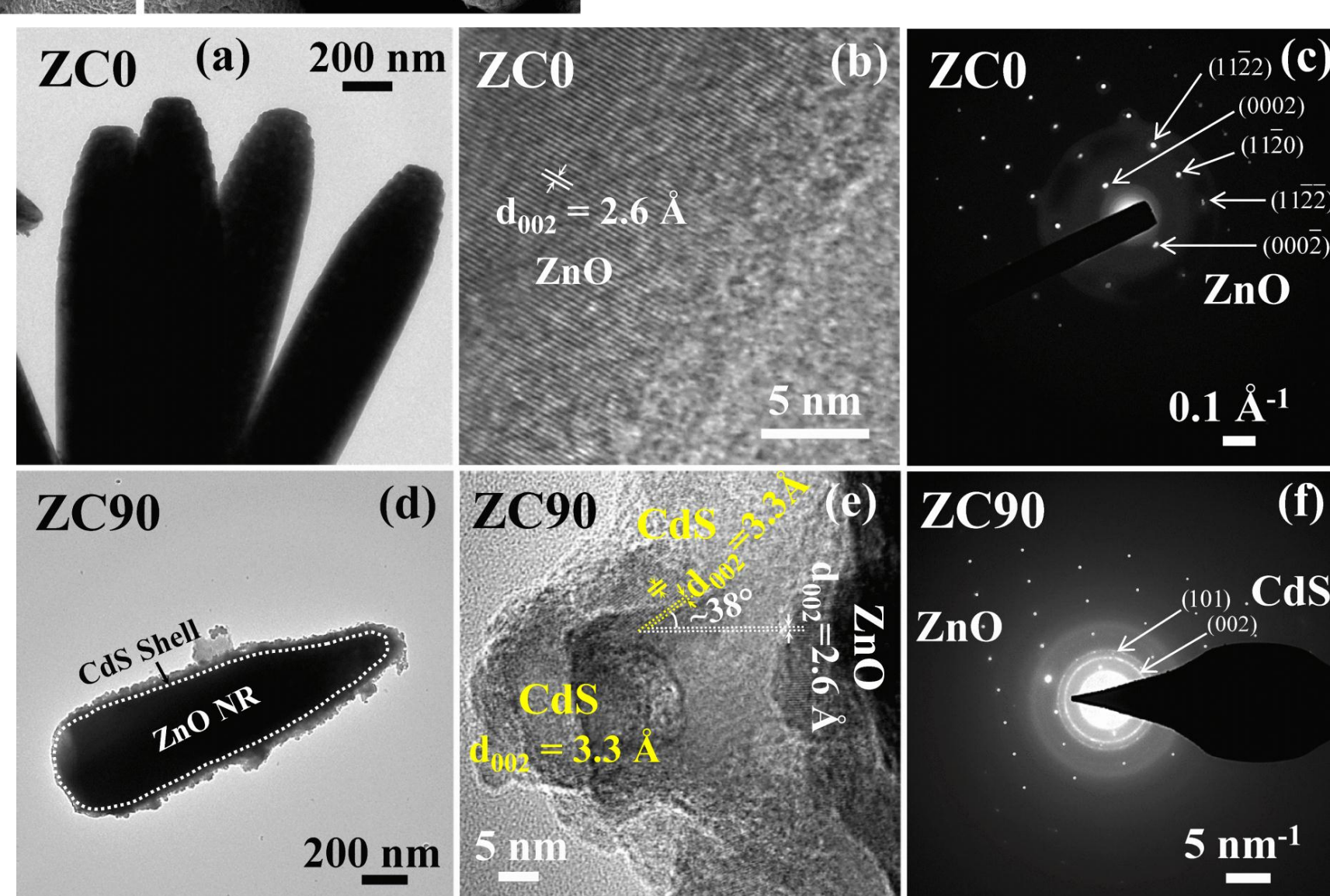


Morphological Properties

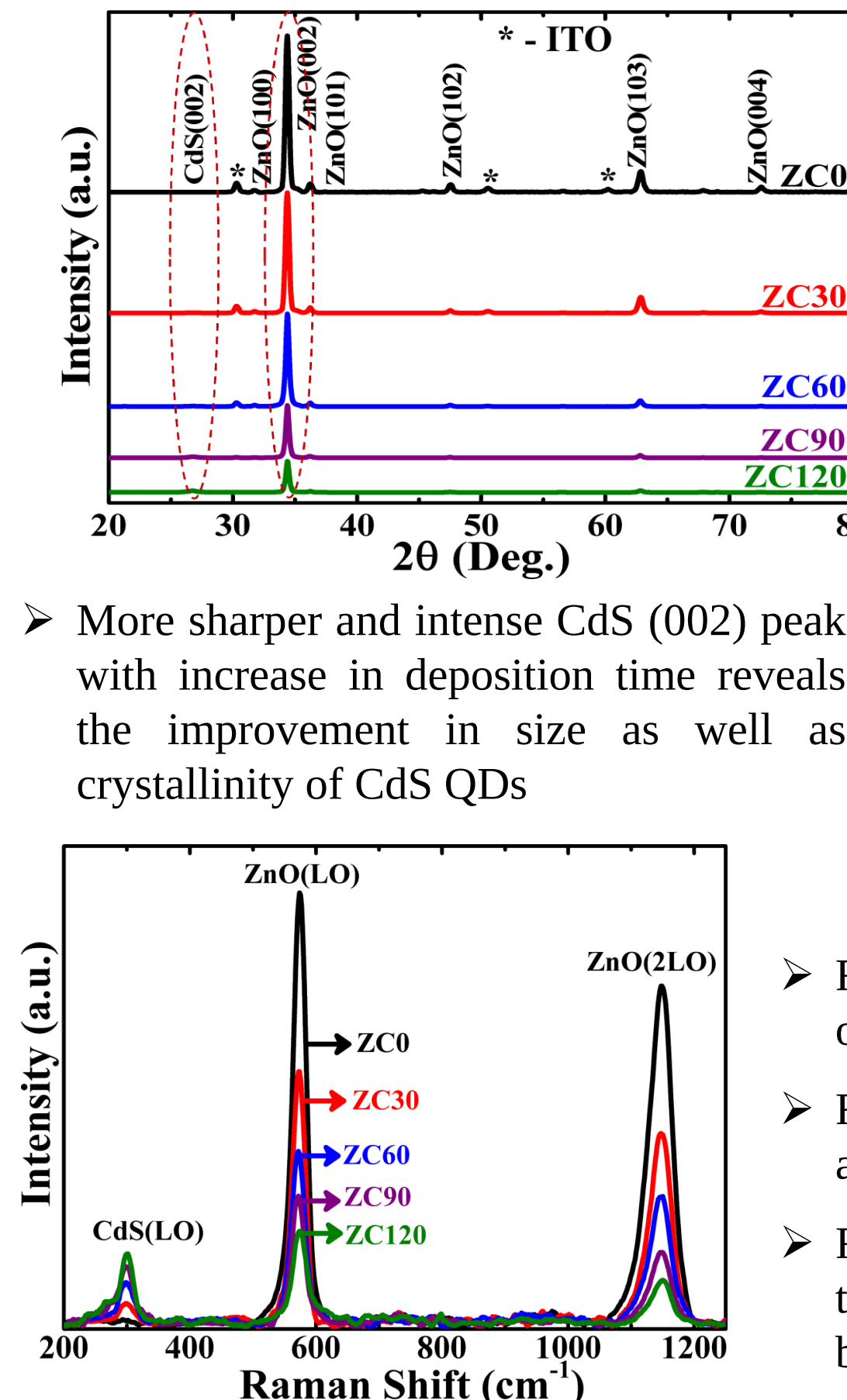


- ✓ Prismatic ~5.7μm long ZnO NRs with typical size of ~300-400nm with preferential growth along c-axis
- ✓ Low ion-flux of Cd²⁺ and S²⁻ ions promotes the topotaxial growth of CdS QDs followed by controlled ion-by-ion growth mechanism
- ✓ For t ≥ 90s, CdS QDs get uniformly decorated on surface of ZnO NRs with QDs being compact and larger in size

- ✓ Stoichiometric deposition of CdS shell on ZnO core
- ✓ ZnO NRs are uniformly decorated with thin layer (~30 nm) of CdS QDs shell
- ✓ (002)_{ZnO}/(002)_{CdS} hetero-epitaxial growth of CdS QDs on ZnO NRs
- ✓ Preferred (002) orientation of both ZnO NRs and CdS QDs may produce an appropriate ZnO/CdS interface with less lattice mismatch

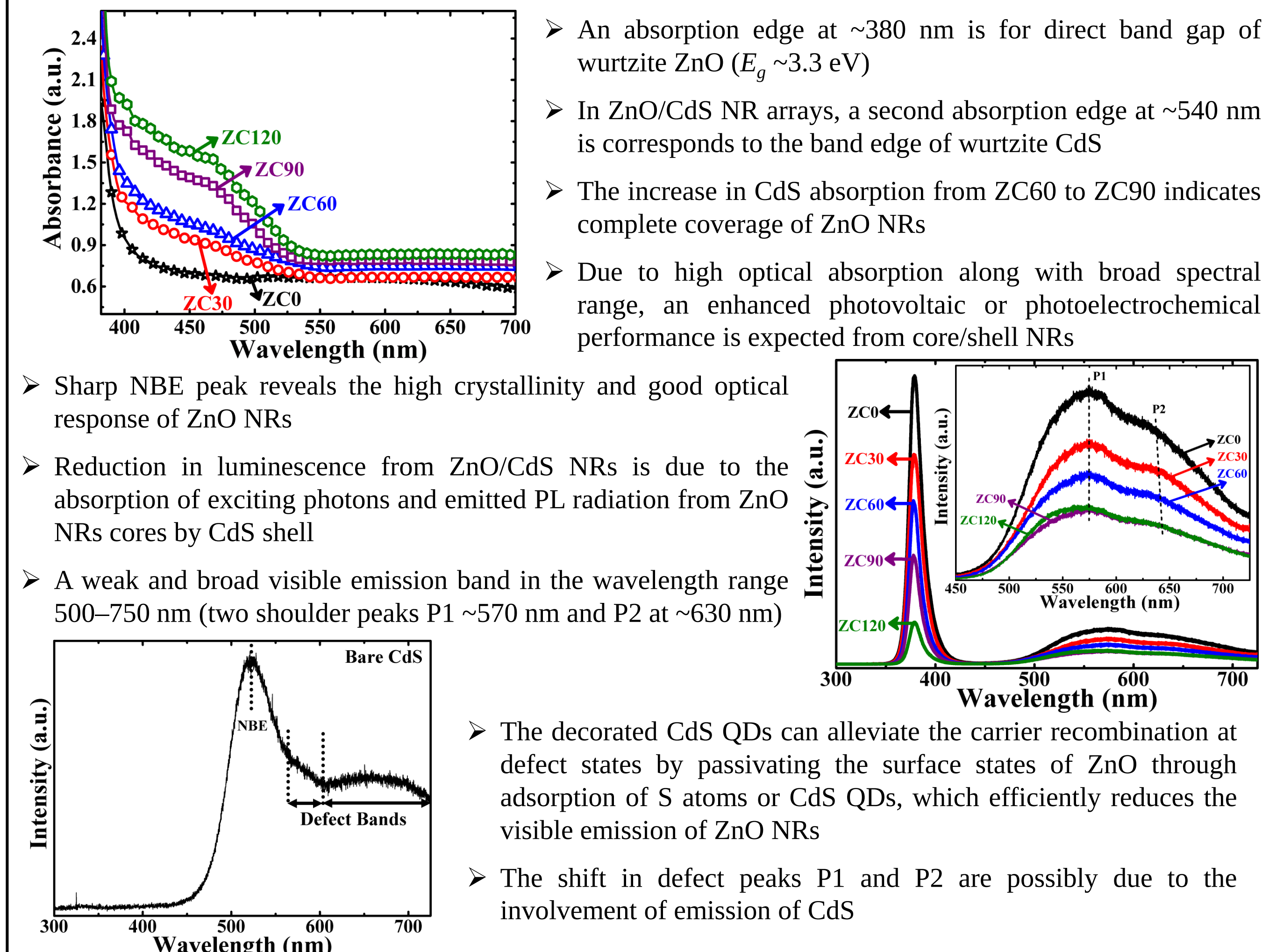


Structural Properties



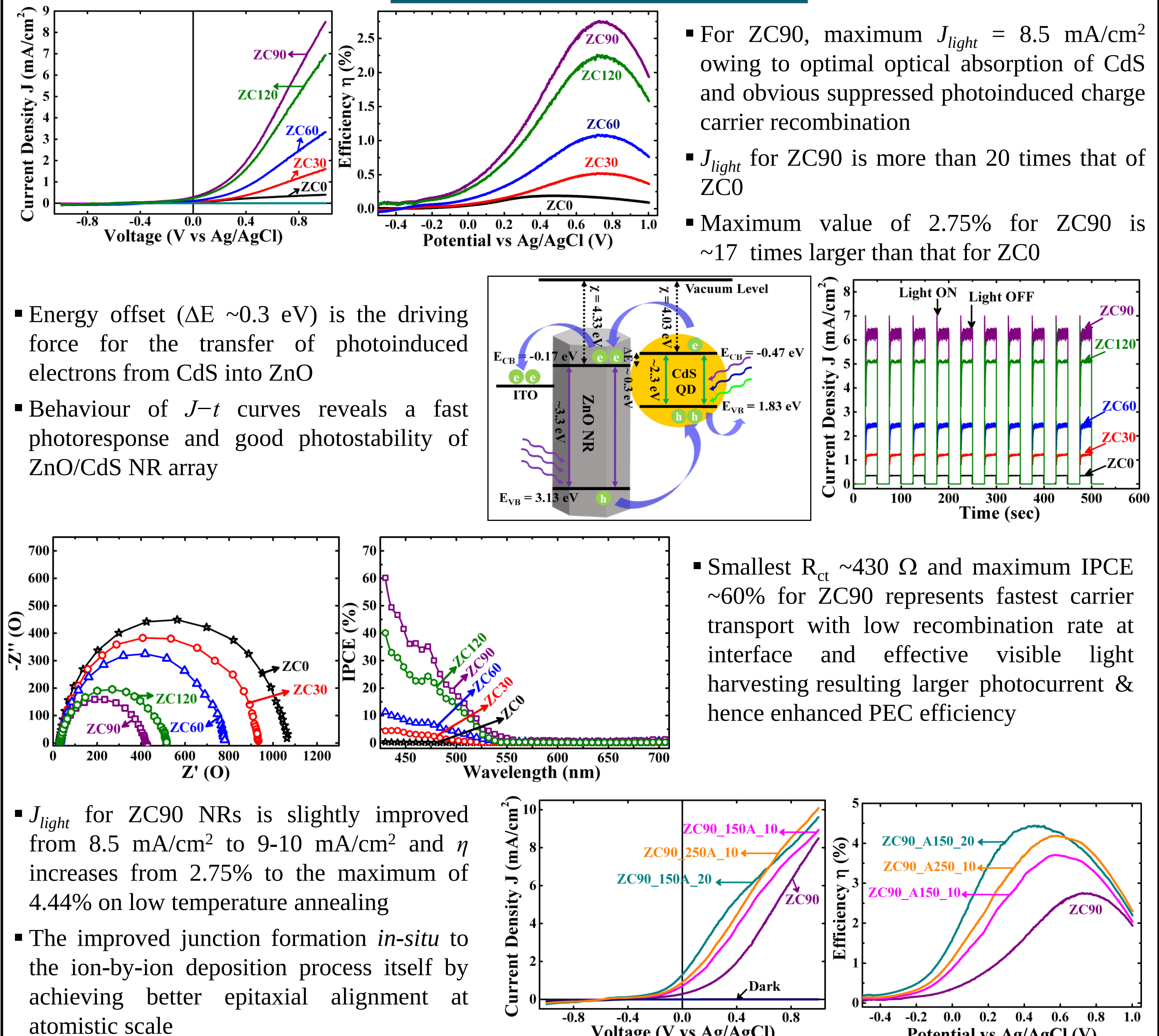
- Sharp and intense (002) peak confirms the almost single crystalline ZnO NRs oriented along c-axis normal to the substrate
- Broad (002) diffraction at 26.7° of CdS QDs reveals the wurtzite structure of CdS shell grown topotaxially with c-axis preferential orientation
- More sharper and intense CdS (002) peak with increase in deposition time reveals the improvement in size as well as crystallinity of CdS QDs
- For ZC0 sample, (1LO) and (2LO) modes of wurtzite ZnO are observed at 575 and 1150 cm⁻¹ respectively
- For ZnO/CdS core/shell NRs, one additional peak at ~300 cm⁻¹ is attributed to the (1LO) phonons of wurtzite CdS
- Reduction in intensity of Raman peaks of ZnO may be possibly due to the enhancement in absorption of exciting and scattered photons by the CdS shell

Optical Properties



- An absorption edge at ~380 nm is for direct band gap of wurtzite ZnO (E_g ~3.3 eV)
- In ZnO/CdS NR arrays, a second absorption edge at ~540 nm corresponds to the band edge of wurtzite CdS
- The increase in CdS absorption from ZC60 to ZC90 indicates complete coverage of ZnO NRs
- Due to high optical absorption along with broad spectral range, an enhanced photovoltaic or photoelectrochemical performance is expected from core/shell NRs
- The decorated CdS QDs can alleviate the carrier recombination at defect states by passivating the surface states of ZnO through adsorption of S atoms or CdS QDs, which efficiently reduces the visible emission of ZnO NRs
- The shift in defect peaks P1 and P2 are possibly due to the involvement of emission of CdS

Photoelectrochemical Properties



- For ZC90, maximum J_{light} = 8.5 mA/cm² owing to optimal optical absorption of CdS and obvious suppressed photoinduced charge carrier recombination
- J_{light} for ZC90 is more than 20 times that of ZC0
- Maximum value of 2.75% for ZC90 is ~17 times larger than that for ZC0
- Energy offset (ΔE ~0.3 eV) is the driving force for the transfer of photoinduced electrons from CdS into ZnO
- Behaviour of J-t curves reveals a fast photoresponse and good photostability of ZnO/CdS NR array
- J_{light} for ZC90 NRs is slightly improved from 8.5 mA/cm² to 9-10 mA/cm² and η increases from 2.75% to the maximum of 4.44% on low temperature annealing
- The improved junction formation in-situ to the ion-by-ion deposition process itself by achieving better epitaxial alignment at atomistic scale

Conclusions

- ❖ 1-D vertically aligned hetero-epitaxial ZnO NRs/CdS QDs core/shell arrays having very high visible photoelectrochemical activity are fabricated by low ion-flux nucleation controlled two-step chemical bath deposition
- ❖ Formation of sharp interface between the c-axis oriented ZnO NRs and CdS QDs (thickness ~30 nm) and the epitaxial correlation of (002)_{ZnO}/(002)_{CdS}
- ❖ The highest visible J_{light} = 8.5 mA/cm² and η = 2.75% with IPCE ~60% is observed for hetero-epitaxial ZC90 core/shell NR arrays, which are ~20 times higher than that of the values for pure ZnO NR arrays
- ❖ This significantly high current density is attributed to the defect-free sharp hetero-epitaxial (002)_{ZnO}/(002)_{CdS} interface, large surface to volume ratio, high visible light absorption, efficient charge carrier transport with minimum recombination involving type-II staggered band alignment and good photostability of ZnO/CdS NRs photoanode
- ❖ Such high photocurrent as well as good photostability are immensely important for efficient photoelectrochemical water splitting performance

References

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Publications

1. **Rekha Bai**, Dinesh Kumar, Sujeet Chaudhary, and Dinesh K. Pandya, *Acta Mater.* 131 (2017) 11–21.
2. Dinesh Kumar, **Rekha Bai**, Sujeet Chaudhary, and Dinesh K. Pandya, *Mater. Today Energy* 6 (2017) 105–114.
3. **Rekha Bai**, Sujeet Chaudhary, and Dinesh K. Pandya, *Mater. Sci. Semicond. Process.* 75 (2018) 301–310.
4. **Rekha Bai**, Dinesh Kumar, Sujeet Chaudhary, and Dinesh K. Pandya, *J. Mater. Chem. A (Under Review)*.

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