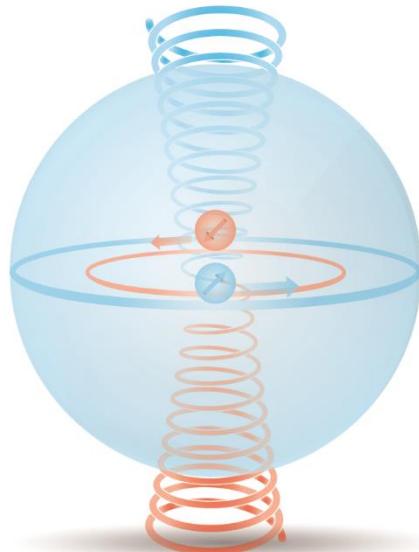


# Plasmontronics: Manipulating Quantum States in Plasmonic Semiconductor Nanocrystals



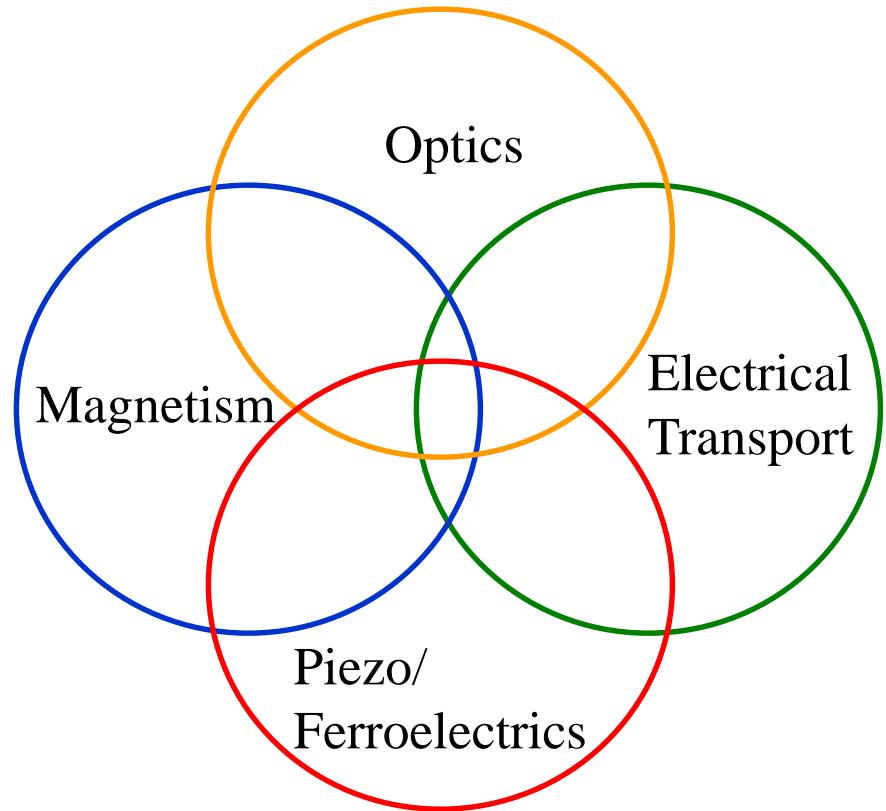
**Radovanovic**  
RESEARCH GROUP

Pavle V. Radovanović  
Department of Chemistry



# Multifunctionality at Nanoscale

- Simultaneous control and manipulation of different functionally relevant properties (which often do not stand together)
- Expanding the inherent degrees of freedom in reduced dimensions
- In strongly correlated electron systems electronic properties arise from complex interplay of multiple (sometimes competing) degrees of freedom

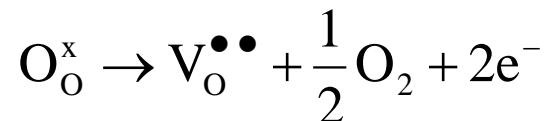


# Plasmonic Nanocrystals

- The localized surface plasmon resonance (LSPR) is the result of the collective oscillation of conduction electrons in the particle upon interaction with light.
- The resonant conditions of the plasmon are sensitive to the surrounding medium – suitable applications as sensors, chemical probes, light concentrators in solar cells, surface-enhanced Raman spectroscopy (SERS)
- Gold and silver nanocrystals are most commonly used nanostructured plasmonic materials – easy to synthesize, relatively inert to oxidation and other reactions, have high carrier concentrations
- Issues with metal nanoparticles: high optical losses (due to electronic transitions), cost, inability to tune charge carriers

# Transparent Conducting Oxides (TCOs)

- Combine transparency and conductivity (key functionalities that do not naturally stand together)
- Wide band gap (3.7 eV for  $\text{In}_2\text{O}_3$ )
- High charge carrier density and mobility (oxygen vacancy is the major donor which causes the n-type conductivity)

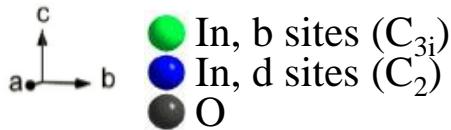
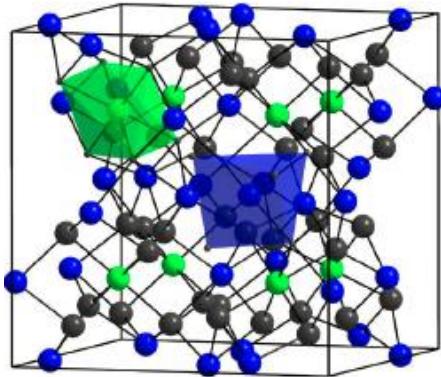


- Possibility of coupling plasmon and exciton in a single phase as active degrees of freedom

# Model System: $\text{In}_2\text{O}_3$

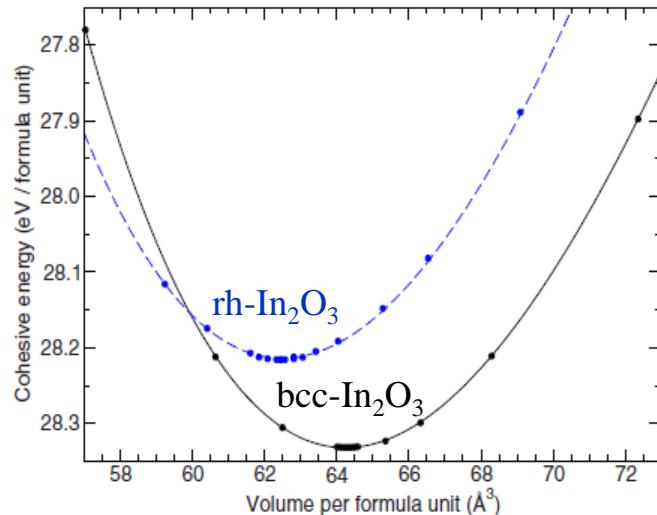
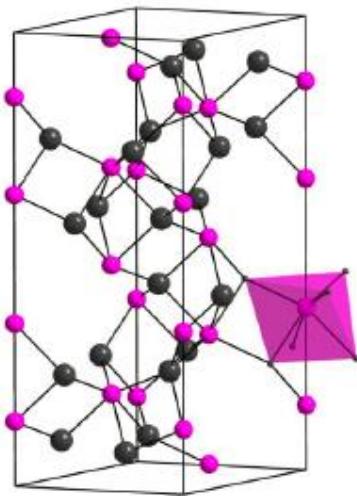
Bixbyite

bcc- $\text{In}_2\text{O}_3$

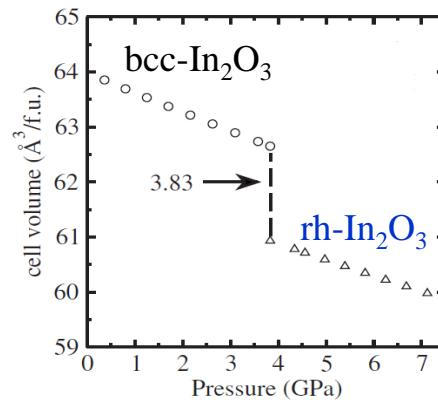


Corundum

rh-In<sub>2</sub>O<sub>3</sub>

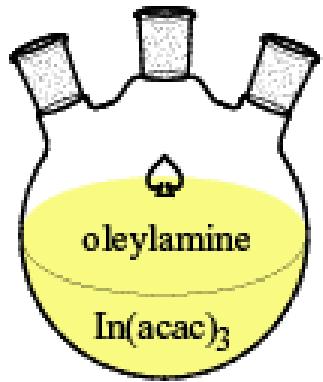


Phys. Rev. B 2008, 77, 155107



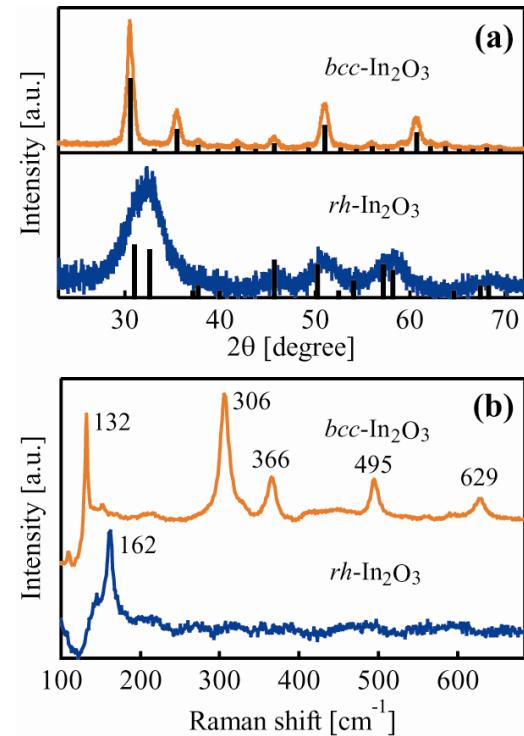
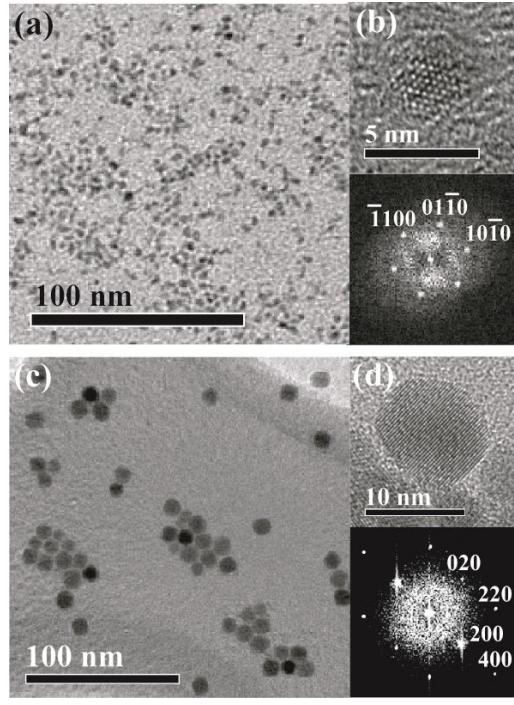
Phys. Rev. B 2007, 76, 075129

# Phase-Controlled Synthesis of $\text{In}_2\text{O}_3$ NCs



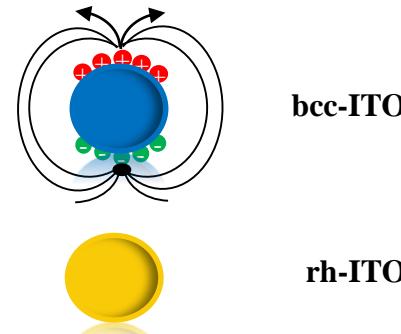
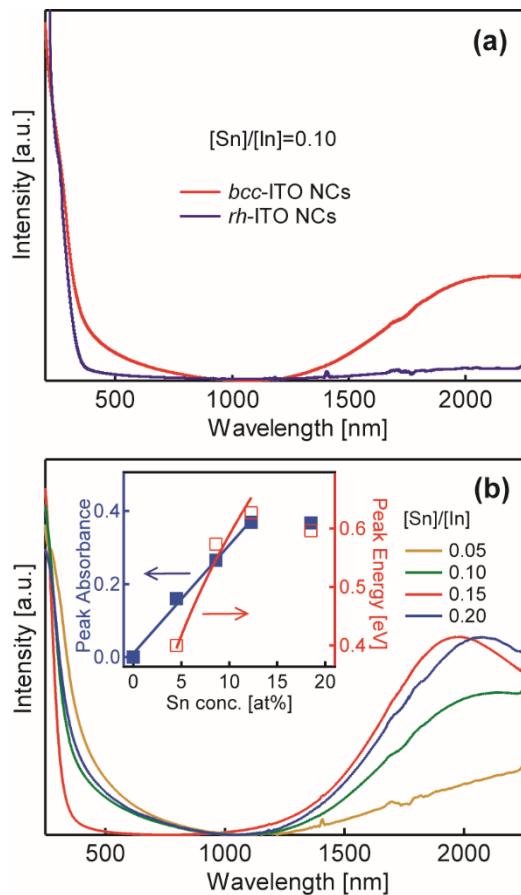
$200^\circ\text{C}$   
30 h

$250^\circ\text{C}$   
7 h



Farvid, S. S.; Dave, N.; Radovanovic, P. V. *Chem. Mater.* **2010**, 22, 9-11.

# Plasmonic Properties of Colloidal ITO NCs



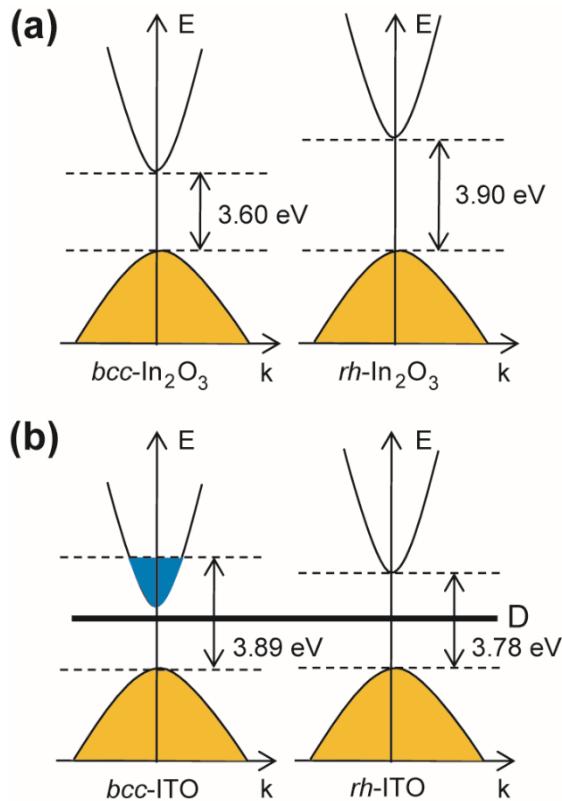
## Drude-Lorentz Model

$$\alpha_{free-electrons} = \frac{Ne^2}{m^* \epsilon_0 n c \tau \omega^2}$$

$$\omega_p = \sqrt{\frac{Ne^2}{m^* \epsilon_{opt} \epsilon_0}}$$

Wang, T; Radovanovic, P. V. *J. Phys. Chem. C* 2011, 115, 406–413

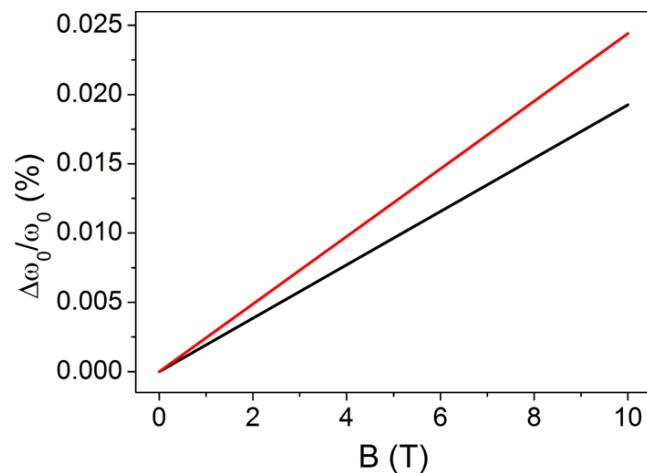
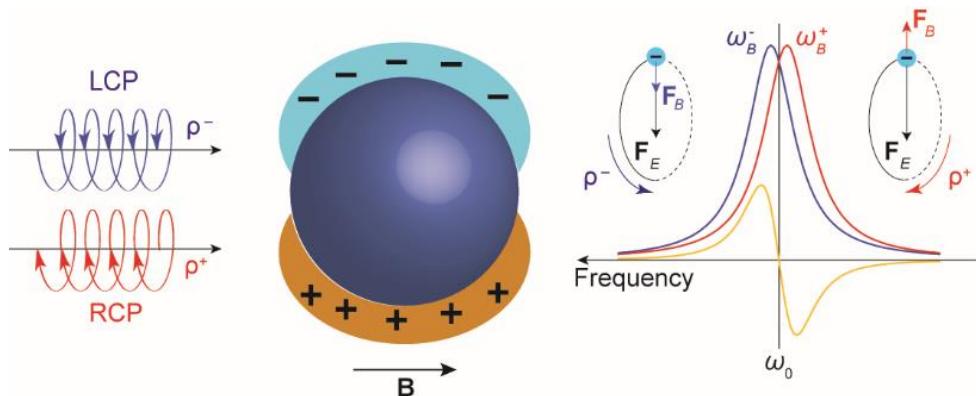
# Origin of Difference in Plasmonic Properties



- **$rh\text{-In}_2\text{O}_3$  has larger band gap relative to  $bcc\text{-In}_2\text{O}_3$**
- This difference in electronic structure leads to larger donor activation energy in  **$rh\text{-ITO}$**
- **$rh\text{-In}_2\text{O}_3$  has low free carrier concentration in the conduction band**

Wang, T; Radovanovic, P. V. *J. Phys. Chem. C* 2011, 115, 406–413

# Magnetic Circular Dichroism of LSPR

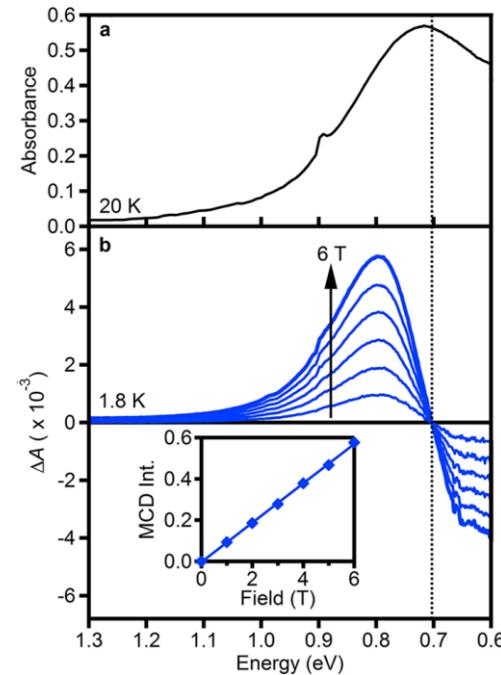


*Nano Lett.* **2013**, *13*, 4785–4789

$$m(d\mathbf{v}/dt) + \gamma m\mathbf{v} = -e\mathbf{E} - e(\mathbf{v} \times \mathbf{B})$$

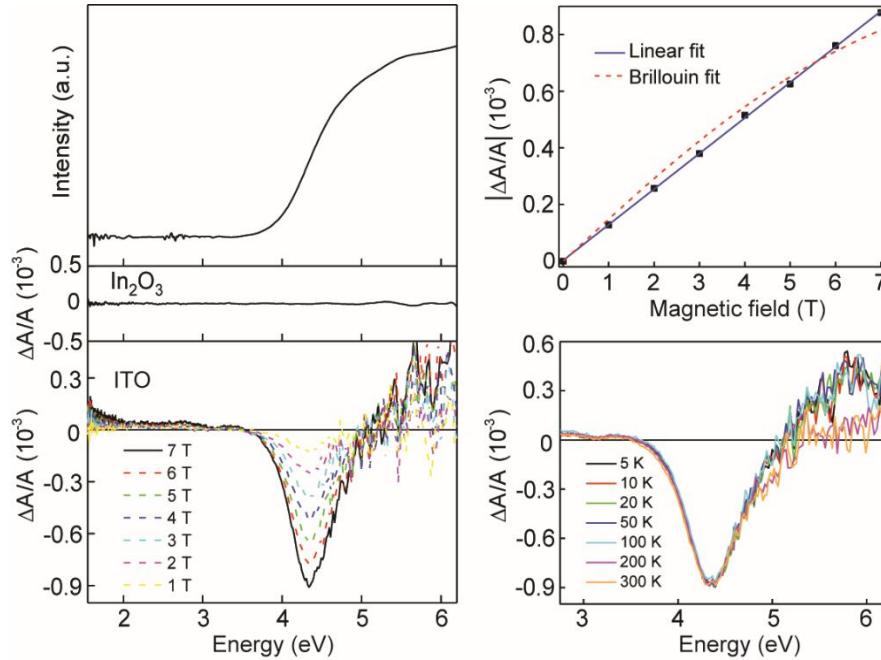
$$\Delta\omega = |\omega_B - \omega_0| = g(\omega_0)B$$

- linear field dependence
- temperature independence



*J. Am. Chem. Soc.* **2015**, *137*, 518–524

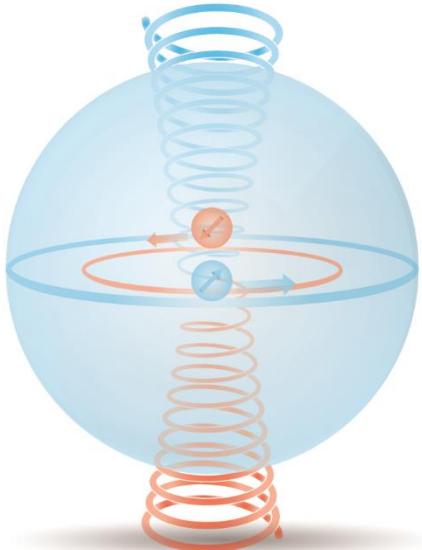
# Plasmon-Induced Exciton Splitting in ITO NCs



- MCD of exciton transition follows the behavior of LSPR:
  - Linear dependence on H
  - temperature independence
- Unlike MCD of LSPR, excitonic MCD signal involves splitting of the discrete quantum states

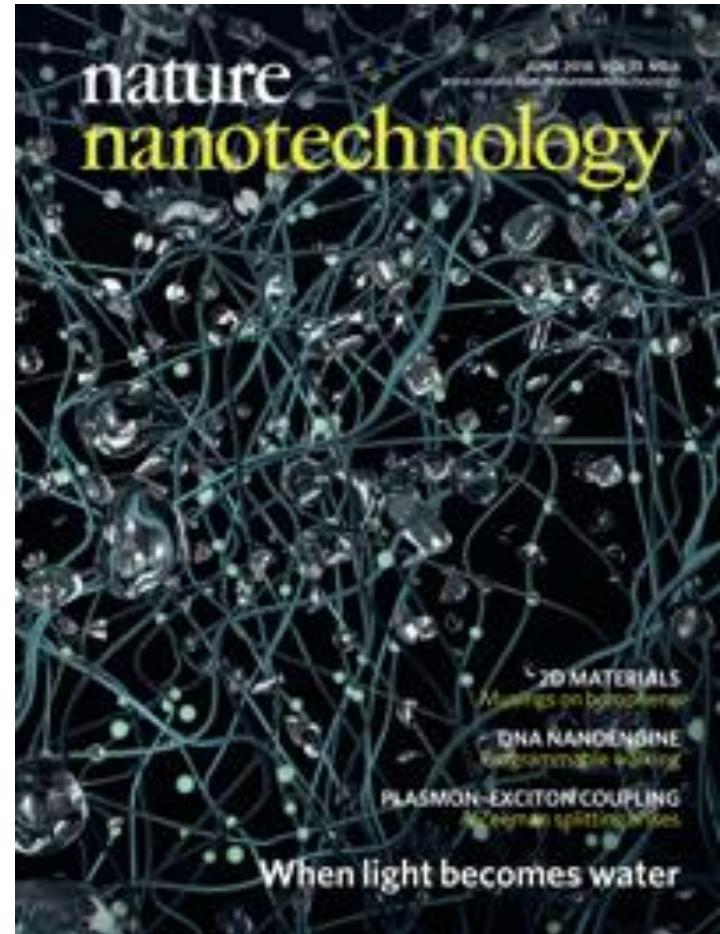
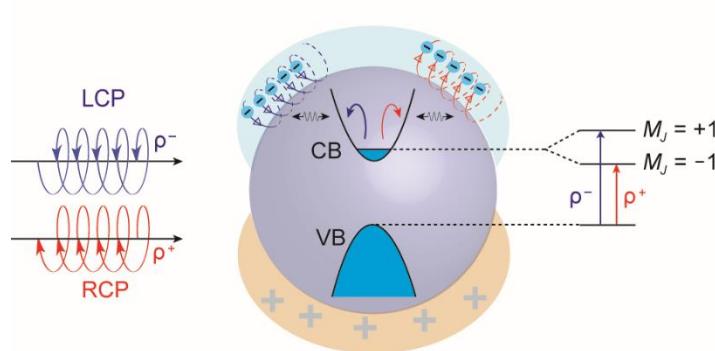
Yin, P.; Tan, Y.; Fang, H.; Hegde, M.; Radovanovic, P. V. *Nat. Nanotech.*, **2018**, 13, 463-467  
Radovanovic, P. V. *Patent Application*, **2018**, PCT/CA2018/050882

# Plasmon-Exciton Coupling



Transfer of the angular momentum from magnetoplasmonic modes to exciton

Plasmon-exciton coupling is non-resonant, and likely involves a mediated process



Yin, P.; Tan, Y.; Fang, H.; Hegde, M.; Radovanovic, P. V. *Nat. Nanotech.*, 2018, 13, 463-467

# Conclusions

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- Demonstrated *in situ* phase transformation of  $\text{In}_2\text{O}_3$  NCs during colloidal synthesis.
- Critical size for stabilization of metastable rhombohedral  $\text{In}_2\text{O}_3$  is ca. 5 nm. Phase transformation from rhombohedral to cubic  $\text{In}_2\text{O}_3$  occurs by surface or interface nucleation, and the mechanism can be controlled by various synthesis parameters.
- Plasmonic properties of  $\text{In}_2\text{O}_3$  NCs are strongly phase and dopant and electronic structure dependent, allowing for broad tunability of LSPR
- Non-resonant plasmon-exciton coupling leads to plasmon-induced carrier polarization
- Correlation between plasmon, charge, and spin degrees of freedom
- Possibility of expanding functionalities and rationally tailoring the properties of complex metal oxide nanostructures through quasiparticle interactions by materials design.

# Acknowledgements:

## Group members:

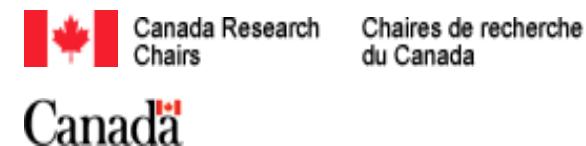
### Current:

- Terry Yin
- Yi Tan
- Shuoyuan Chan
- Wenhuan Lu
- Natalie Garnet
- Paul Stanish
- Nathaniel Smith
- Chenwei Zhang

### Past:

**Postdocs:** Manu Hegde, Josh Byers, Ian Hosein

**Graduate students:** Hanbing Fang, Yunyan Wang, Shokouh Farvid, Ting Wang, Lisa Hutfluss



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