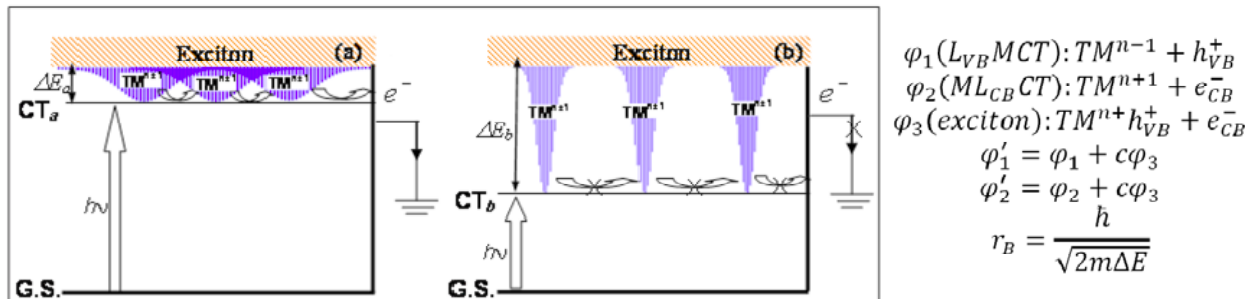


ELUCIDATING THE PROCESS OF PHOTOSENSITIZED CHARGE SEPARATION IN TRANSITION METAL DOPED SEMICONDUCTORS

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Parallel application of electronic absorption, magnetic circular dichroism (MCD), and photocurrent action spectroscopy (PCA) was used to analyze the process of photosensitized charge separation in transition metal doped semiconductors and to rationalize the role of dopants in photon energy conversion. The subjects of study included $\text{Co}^{2+}:\text{ZnO}$, $\text{Ni}^{2+}:\text{ZnO}$, $\text{Cr}^{3+}:\text{TiO}_2$, $\text{Co}^{2+}:\text{TiO}_2$, and $\text{Ni}^{2+}:\text{InTaO}_4$, which are known to exhibit photochemical behavior. Films of these oxides were fabricated by spin coating materials on transparent conducting glass. Photovoltaic cells were constructed from the oxide photoanodes, an I^-/I_3^- electrolyte, and platinum electrode.

Aside from straightforward bandgap excitation, we found a strong correlation between photocurrent activity and charge transfer transitions arising from transition metal dopant to conduction band ($\text{ML}_{\text{CB}}\text{CT}$) or metal to valence band charge transfer ($\text{L}_{\text{VB}}\text{MCT}$). In general, all the charge transfer regions were found to be photoactive and only certain spin allowed ligand field regions were active. The d-d transitions that were inactive were much lower in energy than the charge transfer transitions. In addition, the closer the charge transfer to the bandgap, the more efficient the photoaction. These data agree quite well with the proposed configuration interaction model below, where escape of the photogenerated carrier is facilitated by the degree of mixing between charge transfer and excitonic states. If ΔE is small, the large effective Bohr radius will allow extensive mixing of the two states and carrier migration is possible (a). On the other hand, if ΔE is large, the effective Bohr radius will be small, limiting the amount of mixing of the two states. As a result, carrier migration to the electrical contact will be inefficient (b). As for the ligand field regions, IQEs were generally extremely small and the above method did not apply. This suggests that they are photoactive through mixing with charge transfer and not excitonic states.



Configuration interaction model of carrier migration from mixing of charge transfer and excitonic states.