Optical Quantum Confinement and Photocatalytic Properties in Low Dimensional ZnO and Fe_2O_3

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Optical quantum confinement and how one can describe this in the framework of the Fermi Golden rule and the effective mass approximation are reviewed. The optical response in a direct semiconductor (ZnO) and indirect semiconductor (Fe_2O_3) in the quantum confined region are then shown as well as new methods to extract the absolute band edge energies and fluorescing trap states in nanoparticles and quantum dots. The discussion is also extended to phonon confinement and Stark effects where photocatalytic properties ZnO quantum dots as a function of particle size are quantified. Hematite has been suggested in application in everything from cancer treatment and water cleaning, but also as a non-toxic, cheap and abundant material for photocatalytic water splitting. Here, the optical absorption is analyzed in detail as a function of film thickness for 35 thin films of hematite ranging between 2 and 70 nm. The hematite was deposited by atomic layer deposition on FTO-substrates using $Fe(CO)_5$ and O_2 as precursors. For film thicknesses below 20 nm the optical properties are severely affected as a consequence of quantum confinement. One of the more marked effects is a blue shift of up to 0.3 eV for thinner films of both the indirect and direct transitions, as well as a 0.2 eV shift of the absorption maximum. Raman measurements revealed no peak shift or change in relative intensity for vibrations for the thinnest films indicating that the decrease in indirect transition could not directly be assigned to depression of any specific phonon but instead seems to be a consequence of isotropic phonon confinement or diminished photon-phonon coupling due to only electronic effects. Elemental diffusion of Si, Sn and F from the Fluorine doped SnO_2 substrate upon thermal treatment of the hematite electrodes and the implications for the catalytic activity in water splitting and the resulting photocurrents are also discussed.