

PHOTOINDUCED CHARGE INJECTION INTO TiO₂ THROUGH VARIOUS ANCHORS AND LINKERS AS CHARACTERIZED BY THz SPECTROSCOPY

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Sensitization of metal oxide wide-bandgap semiconductors with light harvesting molecules as employed in Grätzel cells is a strategy that could potentially be used for the light driven synthesis of solar fuels. An example is the production of hydrogen from sunlight by splitting water using nanostructured titania sensitized with biologically inspired manganese containing dyes; a system we are currently working on at Yale. In addition to the development of novel chromophores, a successful water-splitting system also requires anchors and linkers that are stable under oxidative conditions and aqueous environments. These linkers need to provide both a robust linkage between the chromophore and metal oxide surface, and allow efficient charge injection from the sensitizer to the metal-oxide (and preferably not the reverse).

Time-resolved THz spectroscopy (TRTS) is a non-contact electrical probe capable of measuring charge injection rates into, and the carrier lifetime within, semiconductors on a sub-picosecond to nanosecond timescale. In this work we have characterized charge injection through catechol, siloxane and acac derived anchor/linker complexes, and compared their performance with the injection rates of standard carboxylic acid anchors and ruthenium based dyes. TRTS measurements reveal that for all the linkers and dyes studied the ligand to titania interfacial charge transfer is completed in approximately 300 femtoseconds after photoexcitation of the system. However, the quantity of charge injected using the siloxane derived linkers was at least a factor of ten smaller compared to using a carboxyl linkers. On the other hand, TRTS showed that catechol and acac linkers have comparable charge transfer efficiencies to carboxyl linkers. However, the acac linker has superior stability in aqueous environments, and therefore is a promising candidate for use in water splitting systems.