

Design and charge transfer in TiO₂ hybrid architectures using avidin-biotin connectors

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Rational design of protein-TiO₂ hybrid architectures enables coupling of photoinduced charge separation in nanocrystallites with the charge-transfer induced chemistry on proteins. Thus, hybrid architectures and consequent chemistries can either utilize or alter protein functionality. High affinity of a avidin-biotin system (association constant of 10¹⁵ M⁻¹) was exploited for host-guest assembly of protein-TiO₂ hybrid architecture. In titanium dioxide particulate nanocrystallites, the Ti atoms are hexacoordinated (octahedral) in the bulk, whereas they are pentacoordinated (square pyramidal) at the surface. Enediol ligands like dopamine have a large affinity for these undercoordinated surface sites, restoring the Ti atoms to the octahedral coordination and forming charge transfer complexes. Additionally, enediol ligands are shown to act as conduits and bridge the electronic properties of titanium dioxide to attached electroactive biological moieties such as DNA.¹

Taking advantage of the enediol ligands selectivity for surface states, we have conjugated biotin to TiO₂ nanocrystallites of different shapes. The conjugation was performed by the condensation reaction of amino groups on dopamine and N-hydroxy-succinimide on a biotin derivative. In the first step the succinimidyl group on the end of the valeric acid chain of biotin is replaced with dopamine through its terminal amino group. In the second step TiO₂ nanocrystallites were added into a solution. Dopamine end-labelled biotin binds to the surface of TiO₂ through the bidentate complex of dopamine OH groups with undercoordinated Ti atoms. We have examined two types of nanocrystalline TiO₂: 4.5 nm nanoparticles and 400 nm elongated nanorods. The formation of hybrid particulate TiO₂/biotin-avidin composites was demonstrated using 4-hydroxy-azobenzene-2-carboxylic acid (HABA) assay. When axially anisotropic nanorods were used the selective conjugation of biotin to corner sites at the tips was obtained. The undercoordinated Ti sites in 400 nm nanorods are located at the tips and are the result of surface curvature as was demonstrated previously for nanoparticles.² The selectivity of dopamine to bind strongly to undercoordinated Ti atoms enables selective hybridization of nanocrystallites. As a consequence, supramolecular architecture, Figure 1 (end-to-end wire, or tripod nanocomposite configuration depending on the ratio of nanorods and avidin), was obtained upon addition of avidin. The avidin is capable of binding up to four biotin molecules.

The photoinduced charge transfer between TiO₂ nanoparticles and biotin was investigated using low temperature Electron Paramagnetic Resonance (EPR) spectroscopy. It was found that photogenerated holes localize on biotin molecules (resulting in formation of sulfur and/or carbon centered radicals) revealing extended charge separation. When avidin binds to the biotin molecule on the surface of nanoparticles, a new radical that is a result of the oxidation of amino acid group(s) of

avidin is observed. We have studied the effect of spacer distance between TiO₂ and avidin on overall charge transfer. The extension of the valeric acid side chain in biotin from 13.5 to 22.4 Å results in the decrease in the yield of avidin oxidation. The photoexcitation of nanorods results in charge separation from corner sites as identified by EPR spectroscopy. In that respect, corner defects in nanorods behave as corner defects in nanoparticles, and could be exploited in complex electron transport including vectorial transport (end-to-end wire architecture) necessary for creating an efficient photoconversion system.

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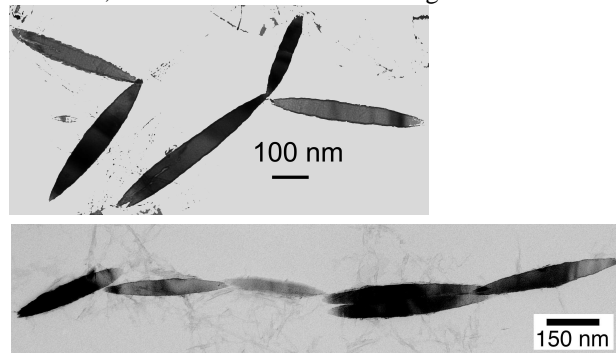


Figure 1. TEM images of organized hybrid TiO₂/biotin-avidin nanorods.

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