



Photo-Gated Intervalence Charge Transfer of Ethynylferrocene Functionalized Titanium Dioxide Nanoparticles



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ABSTRACT

Ethynylferrocene-functionalized titanium dioxide nanoparticles (TiO₂-eFc) were synthesized, for the first time ever, by a modified two-phase hydrothermal method. Transmission electron microscopic measurements showed that the nanoparticles were rather uniform in size, with an average diameter of 4.0 ± 0.5 nm and well-defined lattice fringes that were consistent with those of anatase TiO₂. ¹H NMR, FTIR and XPS measurements confirmed the attachment of the ferrocenyl ligands onto the nanoparticle surface, most likely forming Ti–C≡C–Fc interfacial bonds. The resulting nanoparticles exhibited a bandgap of ca. 3.3 eV, and two emission bands in photoluminescence measurements at 351 and 460 nm, with the former due to the TiO₂ cores whereas the latter from intraparticle charge delocalization between the nanoparticle-bound acetylene moieties under UV photoirradiation. In electrochemical measurements, only one pair of voltammetric peaks were observed in the dark, due to the redox reactions of the nanoparticle-bound ferrocenyl groups. However, when subject to photoirradiation with UV lights (254 and 365 nm), two pairs of voltammetric peaks appeared, with a respective peak spacing of 174 and 198 mV, suggesting intervalence charge transfer (IVCT) between the ferrocenyl moieties bound on the nanoparticle surface. This arose from photo-enhanced electrical conductivity of the TiO₂ cores that served as part of the chemical linkage bridging the ferrocenyl moieties. Significantly, such photo-gated IVCT varied with the photoexcitation energy that dictated the intraparticle charge transfer pathways.

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1. Introduction

Intervalence charge transfer (IVCT) refers to a unique process typically observed with organometallic complexes consisting of two or more chemically identical redox-active metal centers that are bridged by conjugated chemical linkages, such as ferrocene oligomers and the Creutz-Taube ion [1,2]. At mixed valence, rapid metal-metal charge transfer (MMCT) occurs, which leads to the emergence of new optical and electrochemical properties [3–7]. Based on the degree of intramolecular charge delocalization, the mixed valence species are generally categorized as Class I, II or III compounds, as suggested by Robin and Day [8–10]. Recently, it has been found that IVCT may also be achieved with metal nanoparticles whereby functional moieties are bound onto the nanoparticle surface through conjugated metal-ligand interfacial

bonds and the metallic nanoparticle cores act as conducting spacers to facilitate intraparticle charge delocalization [11–13]. Experimentally, a variety of conjugated metal-ligand interfacial bonds have recently been formed for nanoparticle surface functionalization. For instance, metal-carbene bonds (M=CH–), metal-vinylidene bonds (M=C=CH–), metal-acetylide bonds (M–C≡C–), and metal-nitrene (M=N) bonds have been formed for the functionalization of a variety of transition-metal nanoparticles including ruthenium, platinum, gold and palladium [14–20].

One may notice that these prior studies are largely confined to metal nanoparticles by taking advantage of the strong affinity of transition metal surfaces to various organic functional moieties. An immediate question arises. Is it possible to extend the chemistry to semiconductor nanoparticles where the nanoparticle photoactivity may be exploited as a new, effective variable in the manipulation of intraparticle charge delocalization? Specifically, because of the apparent bandgap, the low electrical conductivity of semiconductor nanoparticles in the dark would diminish the

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electronic communication between the particle-bound functional moieties; whereas under photoirradiation with photon energy greater than the nanoparticle bandgap, the enhanced electrical conductivity is anticipated to facilitate intraparticle charge transfer. This photo-gating effects have indeed been observed in recent studies with semiconducting Pt₁₀ nanoclusters [12] and silicon nanoparticles [21]. Yet, in these earlier studies [12,21], the nanoparticle-mediated IVCT remained very weak even under photoirradiation, where the resulting nanoparticles behaved analogously to a Class I/II compound, as manifested in spectroscopic and electrochemical measurements. This is the primary motivation of the present study where we used ethynylferrocene functionalized titanium dioxide (TiO₂-eFc) nanoparticles as the illustrating example to demonstrate that with a proper alignment of the photon energy and the nanoparticle bandgap energy, nanoparticle-mediated IVCT may be enhanced significantly.

Herein, stable TiO₂-eFc nanoparticles were synthesized, for the first time ever, by a simple two-phase hydrothermal method using titanium(IV) *n*-propoxide as the titanium source and ethynylferrocene as the capping ligands. The resulting nanoparticles exhibited well-defined lattice fringes that were consistent with those of anatase TiO₂, and an average diameter of 4.0 ± 0.5 nm, as manifested in transmission electron microscopic measurements. Spectroscopic measurements confirmed the successful attachment of the ligands onto the nanoparticle surface, most likely forming Ti–C≡C–Fc interfacial bonds. Interestingly, electrochemical measurements in the dark exhibited only a single pair of voltammetric peaks, signifying the lack of electronic communication between the particle-bound ferrocenyl moieties. Yet under UV photoirradiation, apparent IVCT was observed, as evidenced by the emergence of two pairs of voltammetric peaks, and the nanoparticle-mediated IVCT was found to vary with the photoirradiation wavelength. This was likely due to a deliberate control of the intraparticle charge transfer pathway.

2. Experimental Section

2.1. Chemicals

Titanium(IV) *n*-propoxide (99%, ACROS), *tert*-butylamine (99%, ACROS), ethynylferrocene (eFc, 97%, ACROS), 4-ethynylphenylacetylene (EPA, 97%, ACROS), and ferrocenecarboxylic acid (FCA, 97%, ACROS) were all used as received without any further purification. Tetra-*n*-butylammonium perchlorate (TBAP, 98%, TCI America) was used after recrystallization 4 times in ethanol. Solvents were purchased at the highest purity available from typical commercial sources and also used as received. Water was deionized with a Barnstead Nanopure Water System (18.3 MΩ cm).

2.2. Synthesis of TiO₂-eFc nanoparticles

TiO₂-eFc nanoparticles were synthesized via a two-phase hydrothermal approach. Experimentally, 50 μL of *tert*-butylamine was dissolved in 5 mL of water and the solution was transferred into a 20 mL Teflon-lined stainless-steel autoclave, into which was then added 4 mL of toluene. Separately, 75 mg of titanium(IV) *n*-propoxide (0.25 mmol) and 35 mg (0.17 mmol) of eFc were dissolved in 1 mL of toluene, and then the mixture was added to the toluene layer in the autoclave gently without any stirring. The autoclave was sealed and heated up to 180 °C and kept at this temperature for 12 h. After it was cooled down to room temperature, the toluene layer was collected and dried by rotatory evaporation. The obtained products were rinsed by pentane for five times to remove excess free ligands and other by-products. The purified products were denoted as TiO₂-eFc.

Two control samples were also prepared in the same fashion except that the capping ligand eFc was replaced by EPA or FCA. The resulting nanoparticles were denoted as TiO₂-EPA and TiO₂-FCA, respectively.

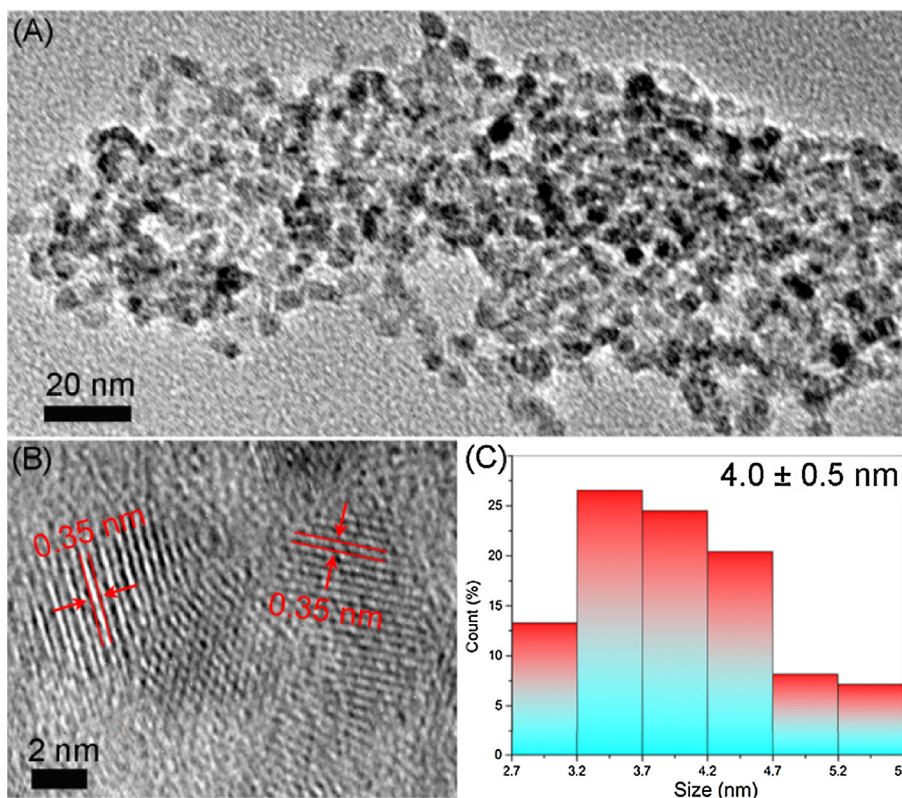


Fig. 1. (A, B) Representative TEM images of TiO₂-eFc nanoparticles. Scale bars are (A) 20 nm and (B) 2 nm. (C) The corresponding nanoparticle core size histogram.

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