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Size-Controlled Interparticle Charge Transfer between TiO_2 and Quantized Capacitors

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Metal-coated semiconductor nanoparticles have been the focus of numerous investigations in recent years in photocatalysis and solar energy conversion.[1] A noble metal such as Pt or Au acts as a sinker for photoinduced charge carriers, promoting charge separation and catalytic activity. A significant challenge in developing these catalysts is controlling the charge separation and transfer to carry out a selective catalytic reaction. There has been notable progress made recently in molecular catalysts capable of controlled charge transfer.[2] However, significantly less progress has been made in nanoparticle catalysts which often exhibit unusual catalytic activities owing to quantum size effects.[3] This report provides the first quantitative results demonstrating the charge transfer between semiconductor and metal nanoparticles can be controlled by the size-dependent capacitance of metal nanoparticles.

Monolayer-protected metal clusters (MPCs) are stable, structurally well-defined nanoparticles and display size-dependent optical and electrochemical properties.[4,5] An interesting electrochemical property of these MPCs is the ability to control the transfer of electrons into and out of the metallic core. The controllability of the electronic charging is a fundamental result of the small, attofarad (aF) capacitance (C_{MPC}) of a MPC, which has been successfully modeled[6] as a capacitance of metallic spheres with insulating dielectric monolayers:

$$C_{MPC} = 4\pi\epsilon_0\epsilon(r/d)(r + d) \tag{1}$$

where ϵ_0 is the permittivity of free space, ϵ is the static dielectric constant of the monolayer around the metal core, r is the radius of metal core, and d is the monolayer thickness. Capacitor-like quantized double layer (QDL) charging voltammetry has been observed for MPCs with core diameters of 1.6−3.7 nm.[4,7] In the interest of extending this controllability to photocatalysts, we have explored the possibility of controlling the transfer of photogenerated electrons by size-controlled MPC capacitors.

Hexanethiolate-coated Au MPCs with core diameters of 1.1−4.9 nm were synthesized by using a modified Brust method[8] in which the core size was controlled by employing a varied thiol/gold molar ratio (1:1, 3:1, or 5:1) and solvent fractionated to reduce size dispersity. The isolated MPC core diameters determined by transmission electron microscopy (TEM) images (Figure S1, Supporting Information) were 1.1, 1.7, 2.2, 2.9, and 4.9 nm, corresponding to, respectively, Au_{38}, Au_{140}, Au_{309}, Au_{807}, and Au_{4033}.[8] Absorbance spectra of these MPCs (Figure S2, Supporting Information) show size-dependent optical properties; namely, the damping effect of the surface plasmon band at ~520 nm becomes evident with decreasing core size. When core size is further decreased to Au_{38}, distinct steplike structures emerge, indicative of molecule-like properties and transitions to discrete energy levels.

A colloidal suspension of 3 nm diameter TiO_2 nanoparticles (Figure S3, Supporting Information) was prepared according to a literature procedure.[9] Briefly, 6.25% Ti(IV) isopropoxide in 2-propanol was hydrolyzed in ethanol under constant stirring and then diluted with an equal amount of toluene to obtain a particle concentration of 13.3 μM. Band-gap illumination of TiO_2 colloids in deaerated ethanol−toluene using a 400-W xenon lamp with wavelength >340 nm using a cutoff filter (UV-34, HOYA) excites electrons to the conduction band while the holes are scavenged by ethanol, resulting in electron accumulation in the conduction band (Figure 1a). Such accumulation can be monitored by the blue coloration of the TiO_2 suspension since the absorbance is related to the excited-electron concentration trapped at Ti^{4+} sites.[9b] The blue coloration remains unchanged at least for a day upon stopping the illumination as long as an inert atmosphere is maintained.

To probe the charge transfer between TiO_2 and MPC nanoparticles, we first photolyzed the TiO_2 solution for 1 h until the absorbance at 620 nm reached ~0.5 under an anaerobic atmosphere. A known amount of a deaerated toluene solution of a MPC was then added to the TiO_2 solution. After each addition, the mixture was stirred to equilibrate for 10 min and an absorbance spectrum was recorded. All measurements were performed at room temperature. Figure 1b shows the resulting spectra recorded following each addition of a MPC (Au_{140}) solution, displaying a gradual decrease in the visible region. The change in absorbance at 620 nm with successive additions of 1.1−4.9 nm diameter Au MPCs are shown in Figure 1c. Since the blue coloration is related to the concentration of the excited electrons, the decrease in absorbance indicates a loss of excited electrons in TiO_2 by the addition of Au MPCs. It is apparent from Figure 1c that the excited-states quenching occurs with all MPCs and the quenching efficiency increases with MPC core size. In recent studies,[1c,9] it has been demonstrated that when metals such as Ag or Au nanoparticles come in contact with a charged semiconductor, the Fermi levels of the two components equilibrate and the metals accept charges. Since the Fermi level of Au MPCs is more positive (E_F = 0.0 V vs NHE)[4] than the conduction-band edge of TiO_2 (E_F* = −0.5 V vs NHE),[9b] the charge transfer from the excited TiO_2 to Au MPCs would be thermodynamically favorable. In other words, the Au MPC would serve as an effective quencher of the excited TiO_2 electrons. To compare the MPC quenching efficiency in Figure 1c, we have extended the Stern−Volmer equation derived for describing the relationship between collisional quenching of excited states and quencher concentration:[10]

$$A_0/A - 1 = K_Q[\mathrm{MPC}] \tag{2}$$

where A_0 and A are the excited TiO_2 absorbance in the absence and presence of MPC, respectively, and K_Q is the Stern−Volmer quenching constant for collisional quenching. The quenching constants (K_Q) taken from slopes in Figure 1d are reported in Table S1 (Supporting Information), which exhibit a remarkable increase with increasing MPC core size; K_Q increases from 5.6×10^5 to 4.09×10^7 by more than 70-fold as core size increases from Au_{38} to Au_{4033} with a largest increase from Au_{38} to Au_{140}.

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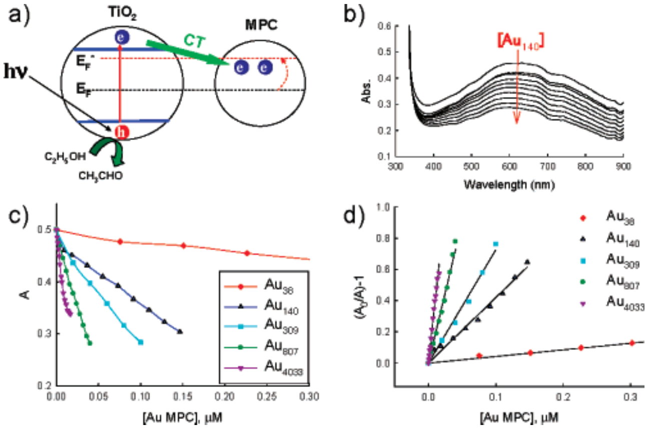

Figure 1. (a) Charge transfer (CT) and Fermi level equilibration between photoexcited TiO$_2$ (E_F*) and MPC (E_F) nanoparticles. The curved arrow denotes lifting of E_F upon charge transfer to MPC core. (b) Absorbance spectra change of 13.3 μM photoexcited TiO$_2$ nanoparticle suspension in 1:1 (v/v) ethanol−toluene upon addition of Au$_{140}$ MPC solution. (c) Decrease in absorbance at 620 nm upon addition of Au$_{38}$, Au$_{140}$, Au$_{309}$, Au$_{807}$, and Au$_{4033}$ MPC solutions. (d) Corresponding Stern−Volmer plots and best fit lines (black lines).

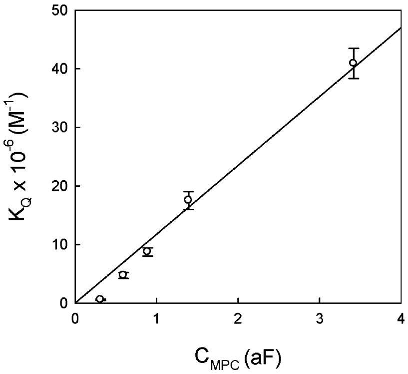

Figure 2. Relationship between the quenching constant (K_Q) and MPC capacitance (C_{MPC}) calculated from eq 1 for 1.1−4.9 nm diameter Au MPCs.

It is well-known that metal surfaces are potent quenchers of molecular excited states.[11] Au nanoparticles are also quenchers of excited states and have shown some size-dependence in fluorescence quenching of dye molecules.[12] Our analysis builds on the work by Wood et al.[1c] who showed that metal particles equilibrate with illuminated ZnO quantum dot. The effect of metal particle size on the Fermi level equilibration has also been investigated with TiO$_2$−Au nanoparticles.[9a] If indeed the Fermi level equilibration occurs between TiO$_2$ and Au MPCs, the charge transfer and distribution between them should be related to the capacitance of the charge acceptors (Au MPCs). Table S1 shows that the calculated capacitance (C_{MPC}) from eq 1 increases from 0.31 to 3.42 aF as the core size increases from Au$_{38}$ to Au$_{4033}$. It also shows the predicted number of electrons to be added to MPC to equilibrate with the excited TiO$_2$. Apparently, the larger MPC has higher capacitance (C_{MPC}) and thus needs more electrons to raise its Fermi level.

Figure 2 shows that there is a good linear correlation between K_Q and MPC capacitance (C_{MPC}), suggesting that the quenching process is closely associated with the capacitance of the electron acceptor (Au MPC). The core size-dependence of K_Q in Figure 1d can therefore be explained by the size-dependent MPC capacitance. Interestingly, the largest change (>8-fold) in K_Q in Figure 1d is found between Au$_{38}$ and Au$_{140}$ although their core size difference (0.6 nm) is similar or smaller than other size gaps. In addition, Figure 2 reveals a significant negative deviation for Au$_{38}$; K_Q is about 9-fold smaller than that predicted by the K_Q−C_{MPC} correlation (Table S1). This may reflect the size-dependent opening of an energy gap at the Fermi level for molecule-like MPCs. As revealed previously,[8b,13] Au$_{38}$ MPCs display a wide opening of an electrochemical HOMO−LUMO (the highest occupied and lowest unoccupied molecular orbitals) gap of 1.62 V. The charge transfer to the elevated LUMO of Au$_{38}$ would thus be energetically less facile, resulting in a significant decrease in quenching efficiency. Understanding of the relative energetics of TiO$_2$ and MPC is crucial in this interpretation and will be the focus of future studies.

In summary, these are the first quantitative results that show the charge transfer between photoexcited TiO$_2$ and Au MPC can be controlled by the size-controlled quantized MPC capacitance. The coupling of the unique charge-transfer property of Au MPCs to the photogenerated electrons may lead to a novel photocatalyst whose reactivity can be tuned and controlled by its quantized charging characteristics.

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Supporting Information Available: Absorbance and TEM data for Au MPCs and TiO$_2$, Δ*A*-[Au MPC] plots, and C_{MPC} and K_Q data (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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