

## Charge Separation and Catalytic Activity of Ag@TiO<sub>2</sub> Core–Shell Composite Clusters under UV–Irradiation

Tsutomu Hirakawa<sup>†,§</sup> and Prashant V. Kamat<sup>\*,†,‡</sup>

Contribution from the Radiation Laboratory and Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556-0579

Received November 23, 2004; E-mail: pkamat@nd.edu

**Abstract:** Photocatalytic properties of Ag@TiO<sub>2</sub> composite clusters have been investigated using steady state and laser pulse excitations. Photoexcitation of TiO<sub>2</sub> shell results in accumulation of the electrons in the Ag core as evidenced from the shift in the surface plasmon band from 460 to 420 nm. The stored electrons are discharged when an electron acceptor such as O<sub>2</sub>, thionine, or C<sub>60</sub> is introduced into the system. Charge equilibration with redox couple such as C<sub>60</sub>/C<sub>60</sub><sup>•−</sup> shows the ability of these core shell structures to carry out photocatalytic reduction reactions. The charge separation, charge storage, and interfacial charge-transfer steps that follow excitation of the TiO<sub>2</sub> shell are discussed.

### Introduction

Noble metal nanoparticles such as Ag and Au in the nanosize domain (<10 nm) exhibit unusual catalytic, electric, and optical properties.<sup>1–12</sup> For example, Au nanoparticles of 3–8 nm diameter have been shown to tune the catalytic properties of TiO<sub>2</sub>.<sup>13–15</sup> In an earlier study, we have shown that metal nanoparticles deposited on TiO<sub>2</sub> nanostructures undergo Fermi level equilibration following the UV-excitation and enhance the efficiency of charge-transfer process.<sup>16,17</sup> In most of the catalytic studies metal nanoparticles are dispersed on an oxide surface (See for example, refs 18–26). Such a catalyst structure, though

effective, result in exposing both metal to reactants and the surrounding medium. Corrosion or dissolution of the noble metal particles during the operation of a photocatalytic reaction is likely to limit the use of noble metal such as Ag and Au.<sup>27–29</sup>

A better synthetic design can significantly improve the catalytic performance of oxide-metal composite. Silica has been widely employed as a shell to protect Ag and Au nanoparticles and stabilize them against chemical corrosion. Preparation and characterization of Au@SiO<sub>2</sub> and Ag@SiO<sub>2</sub> core–shell cluster have been reported for metal coreoxide shell clusters.<sup>30–35</sup>

Significant advances have been made in recent years to design metal core-semiconductor shell clusters.<sup>30–32,36–39</sup> Yet, the efforts to utilize these core–shell structures as photocatalysts in the light energy conversion systems (e.g., photoelectrochemical cells, hydrogen production etc.) are limited. In this context, it is important to elucidate the influence of the metal core on the photocatalytic properties of outer TiO<sub>2</sub> shell (Scheme 1). The obvious questions that need to be addressed include, how does the photoinduced charge separation in TiO<sub>2</sub> is influenced

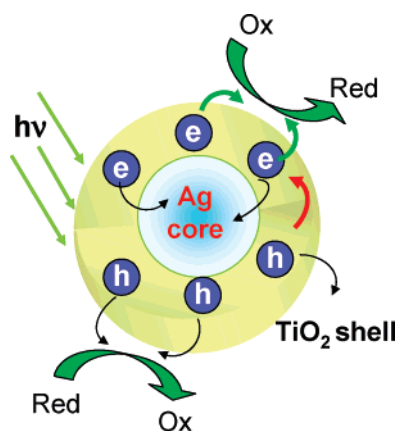
<sup>†</sup> Radiation Laboratory.

<sup>‡</sup> Department of Chemical and Biomolecular Engineering.

<sup>§</sup> Present Address: National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

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Scheme 1



by the metal core? How does the charge equilibration occur between the metal and semiconductor following the band gap excitation? Can these core–shell structures be superior catalysts? To address these questions we have now prepared Ag@TiO<sub>2</sub>, Ag@SiO<sub>2</sub>, and TiO<sub>2</sub> colloids in DMF/ethanol medium and their behavior under UV-excitation are compared. In a preliminary communication we reported the ability of the Ag@TiO<sub>2</sub> clusters to store electrons under UV-irradiation and discharge them on demand in the dark.<sup>40</sup> The factors that control the charge separation and photocatalytic properties of core–shell nanostructures are presented in this paper. A better understanding of the charge transfer properties is likely to pave the way to develop improved photocatalysts for light energy conversion.

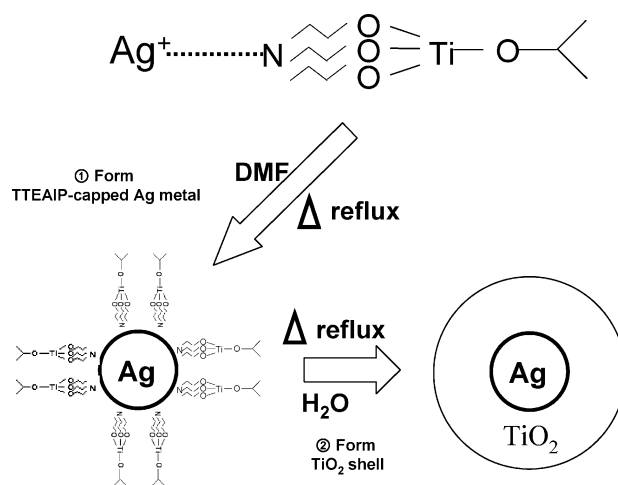
## Experimental Section

**Materials and Measurements.** Titanium-(triethanolamino) isopropoxide (N((CH<sub>2</sub>)<sub>2</sub>O)<sub>3</sub>TiOCH(CH<sub>3</sub>)<sub>2</sub>) TTEAIP and dimethyl formamide, DMF were purchased from Aldrich. AgNO<sub>3</sub> (Fisher ACS grade) was used as received. Active silica (Na<sub>2</sub>O(SiO<sub>2</sub>)<sub>3–5</sub>, 27 wt % SiO<sub>2</sub>) was obtained from Aldrich. Care should be taken to handle toxic solvents such as DMF and hygroscopic materials such as TTEAIP.

The absorption spectra were recorded using UV–vis spectrophotometer (Varian CARY 50 Bio UV–vis Spectrophotometer and SHIMADZU UV-3101 PC UV–vis–NIR Scanning Spectrophotometer). Transmission electron microscopy (TEM) was carried out with JEOL TEM-100SX Electron Microscope and HITACHI H-600 Electron Microscope. Particle size and shape were analyzed with image magnification.

**Ag@TiO<sub>2</sub> and Ag@SiO<sub>2</sub> Colloids.** For synthesizing Ag@TiO<sub>2</sub> shell cluster, we modified the procedure of reduction of metal ions in dimethylformamide.<sup>41</sup> Desired concentration of TTEAIP (8.3 mM, unless otherwise specified) was prepared in 2-propanol. Two mL of 15 mM AgNO<sub>3</sub> solution was mixed with 18 mL of TTEAIP solution. Ten mL of DMF was then added into TTEAIP–Ag solution. The concentration of Ag<sup>+</sup> and TTEAIP in the reaction mixture was 1 mM and 5 mM, respectively. This volume ratio of DMF and *i*-PrOH was optimized by carrying out several batch preparations. When the amount of DMF was too little or when *i*-PrOH was excluded, aggregation of clusters is observed. The volume ratio of DMF and *i*-PrOH hence is an important factor in the preparation of the Ag@TiO<sub>2</sub> clusters. The solution was stirred first for 15 min at room temperature and then refluxed with continued stirring. With continued heating of the solution, the color slowly changed from colorless to light brown. After 90 min, the color of the suspension turned to dark brown. At this point, the

Scheme 2



heating was stopped and the suspension was stirred until it cooled to room temperature.

The procedure described above was also employed for preparing silica capped Ag particles (viz., Ag@SiO<sub>2</sub>). Active silica was added to the reaction mixture instead of TTEAIP. The details of the method can be found elsewhere.<sup>31</sup> The cluster suspension of Ag@TiO<sub>2</sub> and Ag@SiO<sub>2</sub> was centrifuged and resuspended in ethanol solution. The procedure was repeated at least 3-times to minimize the content of water and DMF in the suspension.

**TiO<sub>2</sub> Colloids.** TiO<sub>2</sub> colloidal suspension was prepared by the procedure similar to the one used for Ag@TiO<sub>2</sub> colloids except the step of AgNO<sub>3</sub> addition. The slow hydrolysis of TTEAIP produced transparent sol of TiO<sub>2</sub>.

**Laser Flash Photolysis.** Experiment of nano-second laser flash photolysis was performed with 308-nm laser pulses from Lambda Physik excimer laser system (Laser pulse width is 10 ns, intensity was ~10 mJ/pulse). Unless otherwise specified, all the experiments were performed under N<sub>2</sub> purging condition.

Steady-state photolysis experiments were conducted by photolyzing N<sub>2</sub>-purged solution with UV–visible light (250 W xenon lamp). A CuSO<sub>4</sub> filter was introduced in the path of the light beam to cutoff light below the wavelengths of 300 nm.

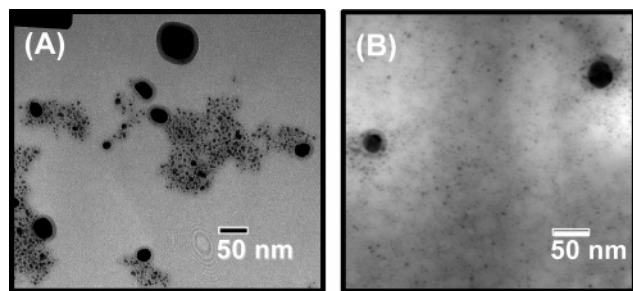
## Results and Discussion

**Synthesis of Ag@TiO<sub>2</sub> Cluster Suspension.** Metal core-oxide shell structures were prepared by one pot synthesis that involved reduction of metal ions and hydrolysis of Titanium-(triethanolamino)isopropoxide in dimethylformamide (DMF).<sup>41</sup> The solvent, DMF plays an important role of reducing the Ag<sup>+</sup> ions first, followed by the slow hydrolysis of TTEAIP to form a shell around the metal core. Increasing the amount of DMF increases the primary step of reduction rate of Ag<sup>+</sup> ion to Ag<sup>0</sup>. It is important that the reduction rate of Ag<sup>+</sup> ion is greater than the rate of formation of TiO<sub>2</sub> shell. After several initial attempts we have found that the experimental conditions that employ 33% DMF in *i*-PrOH yields stable suspension of core–shell particles. As Ag<sup>+</sup> ions are reduced by DMF to form small metal particles, they quickly interact with the amine groups of TTEAIP. The condensation polymerization of TTEAIP slowly progresses on the surface of Ag particles to yield TiO<sub>2</sub> shell. Formation of core–shell cluster is illustrated in Scheme 2.

The TEM images of two different sets of cluster preparations are presented in Figure 1. The concentrations of TTEAIP in these two sets of synthesis were 0.03 and 5 mM respectively while maintaining the concentration of AgNO<sub>3</sub> at 1 mM. In both

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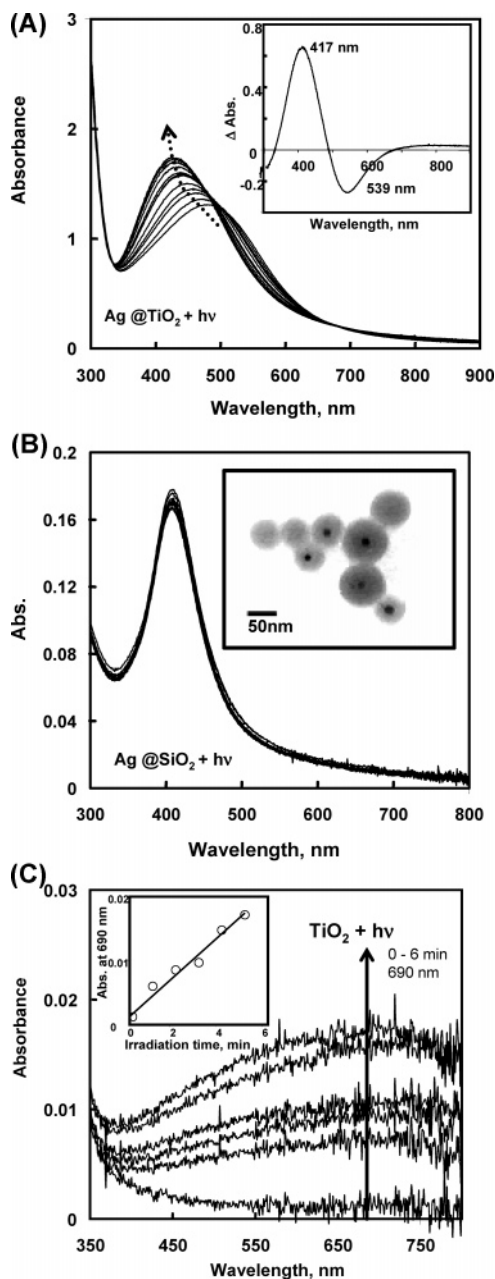
**Figure 1.** Transmission electron micrographs of Ag@TiO<sub>2</sub> colloids which were prepared using the composition of (A) 5 mM TiO<sub>2</sub> and 1 mM Ag and (B) 5 mM TiO<sub>2</sub> and 1 mM Ag. (C) Absorption spectra of colloidal (a) Ag@TiO<sub>2</sub> (b) Ag@SiO<sub>2</sub> and (c) TiO<sub>2</sub> suspension in ethanol.

cases the Ag core was similar with particle diameter of 3–4 nm. The TEM image shows a majority of dark images of Ag core in this size regime. All these particles have a thin capping of TiO<sub>2</sub> shell of thickness in the range of 1.5–3 nm. The core–shell structure is clearly evident in the few larger fully grown particles (30–65 nm) that coexist with smaller size particles (Figure 1A).

Capping of TiO<sub>2</sub> shell on the Ag core was confirmed by checking the stability in an acidic solution (HNO<sub>3</sub>). The Ag cluster, stabilized by citric acid, is readily dissolved in acidic solution (pH = 2). Ag@TiO<sub>2</sub> on the other hand is quite stable in HNO<sub>3</sub> solution even when the TiO<sub>2</sub> shell was thin. If the formation of TiO<sub>2</sub> clusters in DMF was independent such that both clusters are formed separately or in the form of a TiO<sub>2</sub>/Ag sandwich structure, we would have observed dissolution of silver clusters. The stability test in acidic solution asserts the argument that the TiO<sub>2</sub> shell on the Ag core is uniform and provides the protection against acid induced corrosion.

One approach to increase the shell thickness is to increase the concentration of the precursor of TiO<sub>2</sub> (TTAEIP in the present case). Similar approach has been widely used for preparing silica capped metal nanoparticles.<sup>31</sup> Thus, for Ag@TiO<sub>2</sub> colloids prepared using higher TTAEIP concentrations we would have expected to see a thicker TiO<sub>2</sub> shell. However, we observe the formation of independent TiO<sub>2</sub> clusters with smaller size Ag@TiO<sub>2</sub> clusters of core diameter of <2 nm (Figure 1B). Unlike silica capped Ag clusters, we cannot grow thicker TiO<sub>2</sub> shell by increasing the concentration of TTAEIP.<sup>42</sup> The hydrolysis of TTAEIP thus, competes with Ag<sup>+</sup> reduction and yields TiO<sub>2</sub> clusters with and without Ag core at high TTAEIP concentration. These results show the necessity for optimizing the concentration of TTAEIP for achieving uniform capping of Ag nanocore.

The particle concentration was estimated by assuming uniform distribution of Ag core particle and an average particle size of 5.12 and 3.65 nm as obtained from Figure 1A and B. The average number of particles in these two preparations were estimated to be  $2.4 \times 10^{14}$  and  $6.3 \times 10^{14}$  per liter, respectively. Figure 2 shows the absorption spectra of Ag@TiO<sub>2</sub>, Ag@SiO<sub>2</sub> and TiO<sub>2</sub> colloids before and after UV-irradiation. Ag@SiO<sub>2</sub> and Ag@TiO<sub>2</sub> exhibit strong absorption in the visible. This visible absorption arises from the surface plasmon band of Ag core and it is strongly influenced by the oxide shell. (Where as SiO<sub>2</sub> itself has no absorption in the UV and visible, TiO<sub>2</sub> exhibits



**Figure 2.** Absorption spectra recorded following UV-irradiation of various colloidal suspensions in ethanol. The direction of the arrow indicates the spectral shift observed during the UV-irradiation. (A) Ag@TiO<sub>2</sub> colloidal suspension. The difference absorption spectrum corresponding to the absorption changes is shown in the inset. (B) Ag@SiO<sub>2</sub> colloidal suspension. The inset shows TEM image of Ag@SiO<sub>2</sub>. (C) TiO<sub>2</sub> colloidal suspension. The inset shows the change in absorbance at 690 nm with UV-irradiation.

strong absorption in the UV). The plasmon absorption band of the small Ag particles prepared using borohydride reduction is around 380 nm. The surface plasmon absorption band of Ag@SiO<sub>2</sub> and Ag@TiO<sub>2</sub> particles is significantly red-shifted and the maximum is seen at 410 and 480 nm respectively. It is evident that the red shift in the plasmon absorption seen in the core shell particle is dependent on the type of the oxide shell. As shown earlier,<sup>2,30,41,43</sup> the high dielectric constant of the TiO<sub>2</sub> shell causes a red shift in the plasmon absorption of the silver core.

(42) Faster capping of Ag nuclei by the amine moieties is likely to suppress the growth of Ag nanoparticles at higher TTAEIP concentration

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The peak shift is brought about by the refractive index of the surrounding medium. In core–shell structure, the plasmon peak position of the metal core can be related using the expression 1<sup>44</sup>

$$\lambda = \{\lambda_p[\epsilon^\infty + 2n_{\text{EtOH}}^2 + 2g(n_{\text{TiO}_2}^2 - n_{\text{EtOH}}^2)/3]\}^{1/2} \quad (1)$$

where  $n$  is refractive index of the surrounding medium,  $\epsilon^\infty$  is high frequency of the core metal,  $g$  is the volume fraction of shell layer,  $\lambda$  is the estimated peak position of metal core, and  $\lambda_p$  is bulk plasma wavelength as represented in eq 2

$$\lambda_p = [4\pi^2 c^2 m_{\text{eff}} \epsilon_0 / N e^2]^{1/2} \quad (2)$$

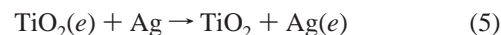
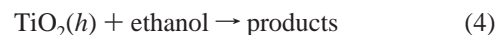
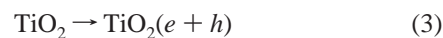
where the  $m_{\text{eff}}$  is effective mass of the free electron of the metal, and  $N$  is electron density of metal core.

For Ag cluster with no medium effect we expect  $\lambda_p$  to be around 136.3 nm. When the Ag cluster was dispersed in water or ethanol the  $\lambda_p$  is observed around 390 nm. Since  $n_{\text{TiO}_2}$  (2.5) for shell is much higher than  $n_{\text{EtOH}}$  (1.359), the plasmon absorption shows a large red shift. With increasing thickness of TiO<sub>2</sub> shell the  $g$  factor in expression (1) becomes close to unity and the red shift of plasmon absorption attains a maximum value for the Ag@TiO<sub>2</sub> cluster. On the basis of the expression 1, we expect the value of  $\lambda$  to be around 463 nm. In the present experiment, we observe rather broad plasmon absorption with a maximum around 480 nm and this red-shifted maximum is close to the value expected from the theoretical prediction. Factors such as scattering effects and adsorbed chemical species are likely to contribute to the small discrepancy between estimated and experimentally observed plasmon absorption peak.

**Steady-State Photolysis.** Figure 2A shows the changes in the absorption spectrum following the UV-irradiation of Ag@TiO<sub>2</sub> colloids suspended in deaerated ethanol. Before subjecting the Ag@TiO<sub>2</sub> colloids in ethanol to UV irradiation, the plasmon absorption peak is seen at 480 nm. As these colloids are subjected to UV irradiation we observe a blue shift in the plasmon absorption band. After irradiating with UV-light for ~30 min, the absorption shift attains a plateau with a surface plasmon absorption peak at 420 nm. The shift of 60 nm in the plasmon absorption reflects increased electron density in the Ag core during photoirradiation. Since TiO<sub>2</sub> undergoes charge separation under UV-irradiation, the photogenerated electrons are transferred to Ag nano-core as the two systems undergo charge equilibration. The transfer of electrons from the excited semiconductor to the metal is an important aspect that dictates the overall energetics of the composite and hence the efficiency of photocatalytic reduction process.<sup>17,45–47</sup>

To confirm the participation of TiO<sub>2</sub> shell in transferring electrons to Ag core, we compared the photoresponse with that of Ag@SiO<sub>2</sub> particles. When the UV-irradiation experiments were repeated with the Ag@SiO<sub>2</sub> colloids in deaerated ethanol, we fail to see any changes in the plasmon absorption (Figure 2B). The plasmon absorption band with a maximum at 410 nm remained unperturbed during the UV-irradiation. By comparing the experimental results in Figure 2, parts A and B, we can

conclude that the changes in the absorption seen in Ag@TiO<sub>2</sub> arise from the UV excitation of the shell and not the silver core. The photoactive TiO<sub>2</sub> shell thus, plays an important role of absorbing incident photons and injecting electrons into the silver core. The processes that lead to storing of electrons in the Ag core are summarized below (reactions 3–5).



The photoactivity of TiO<sub>2</sub> colloids was separately checked by carrying out UV-irradiation of TiO<sub>2</sub> colloids in deaerated ethanol. Under UV excitation, TiO<sub>2</sub> undergoes charge separation (reaction 1) followed by charge recombination and interfacial charge-transfer processes. As the photogenerated holes are scavenged by ethanol, the electrons accumulate within the TiO<sub>2</sub> particles. The electron storage in TiO<sub>2</sub> particles is marked by the blue coloration with characteristic broad absorption in the red region (Figure 2C). As shown earlier,<sup>17,48</sup> this absorption arises from electron trapping at Ti<sup>4+</sup> sites. The trapped electrons are long-lived in N<sub>2</sub> purged suspensions and are readily extracted when needed, e.g., by transfer of electrons to acceptor molecules such as thionine or C<sub>60</sub>. Since metal particles such as silver and gold with a favorable Fermi level ( $E_F = 0.4$  V) are good electron acceptors, we expect a facile electron transfer from excited TiO<sub>2</sub>. This property of charge equilibration between semiconductor and metal nanoparticles has been independently confirmed by the addition of metal colloids to preirradiated TiO<sub>2</sub> colloids in ethanol.<sup>16,17</sup> The disappearance of the blue coloration (or absorbance at 600 nm) in this study has been used to determine the quantitative transfer of electrons to metal particles. The spectra recorded in Figure 2A do not indicate absorption in the red-IR region similar to the increase observed in Figure 2C. The lack of blue coloration in UV-irradiated Ag@TiO<sub>2</sub> colloids indicates that the electrons fail to accumulate in the TiO<sub>2</sub> shell, instead they are transferred to the silver core. The only spectral change we observe in this system is the shift in the plasmon absorption arising from the electron accumulation in the metal core.

When the UV-excitation of Ag@TiO<sub>2</sub> is carried out in the presence of an electron acceptor such as thionine dye or oxygen, we do not observe any shift in the plasmon absorption of silver core. As the photogenerated electrons are scavenged by the acceptor molecules, electrons fail to accumulate in the Ag core. These observations parallel the results reported for Ag/ZnO<sup>47</sup> and Au@SnO<sub>2</sub><sup>39</sup> nanoclusters and ascertain the argument that the shift in the plasmon absorption arises from electron storage in the Ag core.

We checked the reproducibility of charging and discharging of Ag@TiO<sub>2</sub> system by repeated cycles of UV-irradiation of deaerated suspension followed by exposure to air. Figure 3 show the reproducibility of plasmon absorption peak response to the UV-irradiation and air exposure in dark. The plasmon absorption band shifts from 470 to 420 nm during 1 min UV irradiation of deaerated Ag@TiO<sub>2</sub> suspension. The plasmon absorption regains the original spectral features when the stored electrons are

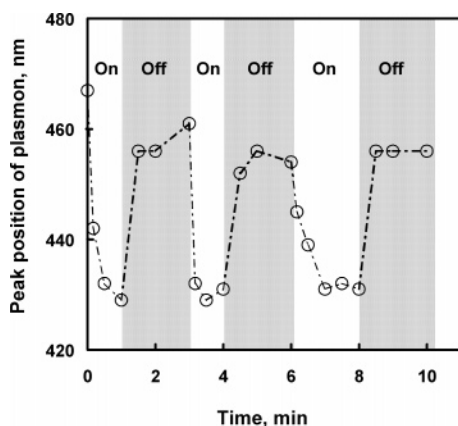
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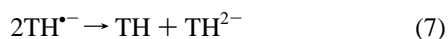
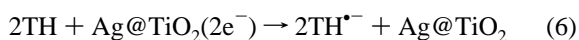


**Figure 3.** Response of plasmon absorbance peak to electron storage following the UV-irradiation of deaerated Ag@TiO<sub>2</sub> colloidal suspension in ethanol and dark discharge in air.

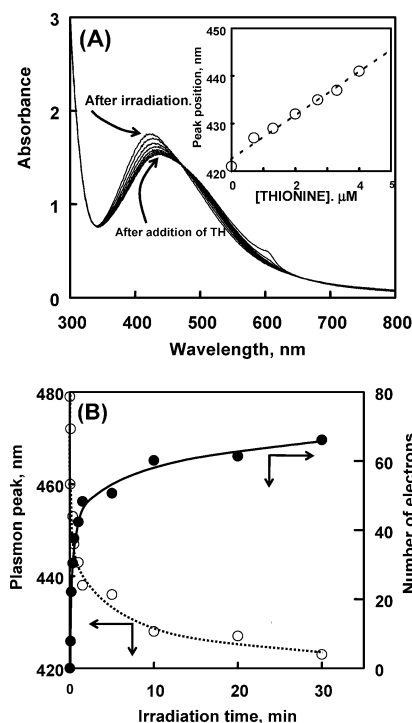
discharged in dark by exposing to air. We can repeat the photoinduced charging and dark discharge cycles repeatedly and reproduce the plasmon absorption response to stored electrons (Figure 3). The suspension was deaerated for 20 min before UV irradiation of each charging cycle. No such absorption changes in the plasmon absorption are seen for Ag@SiO<sub>2</sub> system under similar experimental conditions.

A similar but less pronounced effect was noted for Au capped with SnO<sub>2</sub> particles.<sup>39</sup> The electrons were injected chemically using a reductant, NaBH<sub>4</sub>. The electrons injected into SnO<sub>2</sub> are transferred to Au core until the two systems attain equilibration. However, the dark discharge of electrons takes several hours to take into effect. This is attributed to the fact that the conduction band of SnO<sub>2</sub> is around 0 V versus NHE and is slightly more positive than oxygen reduction potential. On the other hand TiO<sub>2</sub> conduction band is around -0.5 V vs NHE at pH 7 and is energetically capable of transferring electrons to O<sub>2</sub>. It should be noted that both the semiconductor shell and the metal core undergo Fermi level equilibration to attain an energy level close to the conduction band of the semiconductor. In the presence of a redox couple the composite system further attains equilibration by transferring excess charges into the acceptor molecules. By comparing the discharge response of Ag@TiO<sub>2</sub> and Au@SnO<sub>2</sub> to oxygen, we can conclude that Ag@TiO<sub>2</sub> clusters are energetically superior catalyst for promoting reduction process.

**Estimation of Electrons Stored in Ag Core.** Since the electrons stored in the Ag@TiO<sub>2</sub> colloids can equilibrate with the redox couple in solution, it is possible to carry out a redox titration and obtain quantitative information on the stored electrons. The dye thionine with absorption at 600 nm ( $\epsilon = 60\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) is a good electron acceptor that initially produces a one electron reduction product, semithionine (Reaction 6). The semithionine (TH<sup>•-</sup>) immediately disproportionates to produce a two electron reduction product, leuco dye (TH<sup>2-</sup>), with no absorption in the visible (reaction 7).



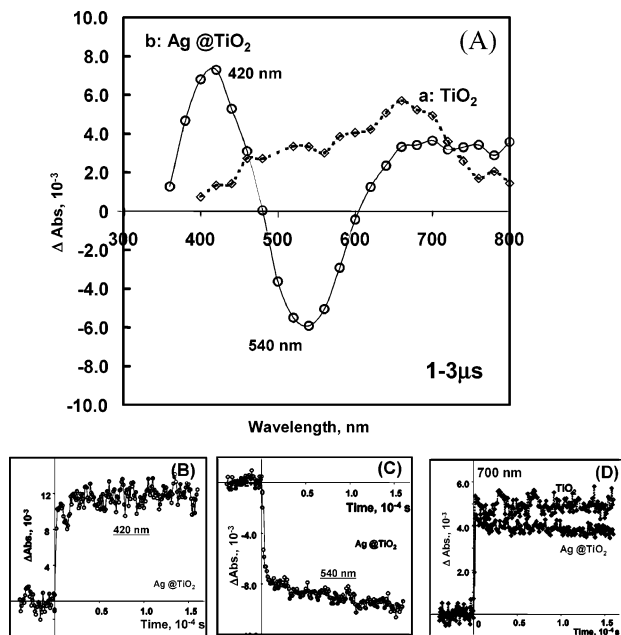
The disappearance of one thionine molecule thus, represents transfer of two electrons. The reduction of thionine thus serves as the basis for titrating electrons stored in the Ag@TiO<sub>2</sub> clusters.



**Figure 4.** (A) Controlled discharge of stored electrons from Ag@TiO<sub>2</sub> suspension (pre-UV-irradiated under deaerated conditions) using known amounts of thionine dye. Inset shows the plasmon absorption peak position with increasing concentration of thionine. (B) Dependence of plasmon absorption peak and number of stored electrons on the time of UV-irradiation. (The number of stored electrons was calculated by titrating with thionine dye)

Known amounts of concentrated thionine solution (degassed) was injected in small increments into the UV-irradiated Ag@TiO<sub>2</sub> suspension. The absorption spectrum was recorded after each addition of thionine. Since the reduced dye does not have any absorption in the visible, we only observe a shift in the plasmon absorption band as the electrons are titrated using thionine. The process of electron transfer to the dye molecules continues until most of the stored electrons are discharged. The presence of any unreduced thionine is marked by the appearance of 600 nm absorption band. The endpoint of titration is thus attained when we observe the appearance of the 600 nm band. Figure 4A shows the changes in the absorption spectrum following the addition of thionine. The plasmon absorption shift and stored electrons were estimated at different irradiation times by titration of the stored electrons with thionine. The dependence of the plasmon shift and the number of stored electrons versus the UV-irradiation time is shown in Figure 4B. Saturation in electron storage is seen as we extend the UV-irradiation for a longer time.

As discussed in the earlier section, we observe a red-shift in the plasmon absorption band with increased addition of thionine to UV-irradiated Ag@SiO<sub>2</sub> suspension. After attaining the endpoint a small peak corresponding to thionine at 600 nm is seen. The plasmon shift corresponding to the discharge of the stored electrons in the Ag@TiO<sub>2</sub> cluster can thus be related to the concentration of thionine added to discharge the electrons (inset, Figure 4A). From the slope of this linear plot, we estimate that 0.42  $\mu\text{M}$  electrons cause 1 nm shift in the plasmon absorption in a  $2.1 \times 10^{17}$  particles/liter Ag@TiO<sub>2</sub> suspension.

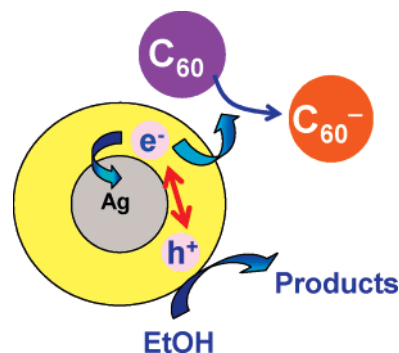


**Figure 5.** (A) Difference absorption spectra of deaerated colloidal Ag@TiO<sub>2</sub> (O) and TiO<sub>2</sub> (◇) suspension recorded following 308 nm laser pulse excitation. (B) Representative absorption–time profiles at 420 nm. (C) 540 nm and (D) 700 nm (experimental conditions are the same as in Figure 5A).

On the basis of the net shift observed in the plasmon band, we expect a maximum storage of about 66 electrons per Ag@TiO<sub>2</sub> core@shell particle. The ability of Ag@TiO<sub>2</sub> to store large number of electrons during UV-irradiation shows the importance of such composite structures in light energy conversion by storing electrons during photoirradiation and delivering these electrons on demand. The capacity of electron storage is determined by the size of the metal core and its ability to undergo charge equilibration with the TiO<sub>2</sub> shell. Once this maximum storage limit is attained, electron–hole recombination in the TiO<sub>2</sub> shell dominates.

**Transient Absorption Studies using Laser Flash Photolysis.** The photoinduced charge-transfer events were probed using nanosecond laser flash photolysis. The transient absorption spectra recorded following 308 nm laser pulse excitation of deaerated colloidal TiO<sub>2</sub> and Ag@TiO<sub>2</sub> suspension are shown in Figure 5 (A). The spectra were recorded 1 μs after laser pulse excitation. The TiO<sub>2</sub> colloids exhibit broad absorption in the 400–800 nm region corresponding to the trapping of electrons at Ti<sup>4+</sup> sites. The Ti<sup>3+</sup> centers formed as a result of electron trapping have been characterized in earlier studies.<sup>49–52</sup> The Ag@TiO<sub>2</sub> clusters exhibit strong bleaching in the plasmon absorption region in addition to the absorption in the red. The absorption band at 420 nm and bleaching at 540 nm is the result of shift in the plasmon band following the electron storage. It is interesting to note that the spectral feature of the transient spectrum (spectrum b in Figure 5A) closely match the difference

**Scheme 3**



spectrum recorded in steady-state photolysis as shown in the inset of Figure 2A. This observation indicates that the absorption change observed in steady-state photolysis is a spontaneous process that follows the excitation of the TiO<sub>2</sub> shell. The transient absorption–time profile (Figure 5B) shows that most of the charge transfer from excited TiO<sub>2</sub> to Ag is completed within the laser pulse duration of few nanoseconds. A slow growth that contributes about 10% of the signal arises from the charge equilibration process which extends up to 150 μs (Figure 5C). The absorption in the red region shows the residual electrons trapped within the TiO<sub>2</sub> nanoparticles. These are excess trapped electrons that survive within the TiO<sub>2</sub> shell following charge equilibration. Figure 5D compares the transient absorption profiles at 700 nm. The maximum absorbance at 700 nm is lower for Ag@TiO<sub>2</sub> than the TiO<sub>2</sub> colloids as a fraction of the electrons are transferred to Ag core immediately following the laser pulse excitation.

**Photocatalytic Activity of Ag@TiO<sub>2</sub> Particles.** We compared the photocatalytic activity of the Ag@TiO<sub>2</sub> with that of TiO<sub>2</sub> colloids by carrying out reduction of C<sub>60</sub> following 308 nm laser pulse excitation (Scheme 3). In our earlier studies, we have shown that C<sub>60</sub> is an excellent probe to study the interfacial electron transfer in colloidal semiconductor systems.<sup>53</sup> The formation of C<sub>60</sub><sup>•−</sup> with characteristic absorption in the IR region (1075 nm) can be conveniently used to obtain quantitative information on the electron-transfer yield. Figure 6(A) shows the difference absorbance spectrum obtained after 308 nm laser pulse excitation of Ag@TiO<sub>2</sub> colloids in the presence of C<sub>60</sub>. The absorption maximum at 1075 nm indicates formation of C<sub>60</sub> anion, C<sub>60</sub><sup>•−</sup>, as the excited Ag@TiO<sub>2</sub> transfer electrons to C<sub>60</sub>. As can be seen from the inset of Figure 6A the C<sub>60</sub><sup>•−</sup> formation is completed in 100 μs. The slow formation of C<sub>60</sub><sup>•−</sup> is the indication of the time required to attain charge equilibration between C<sub>60</sub> and Ag@TiO<sub>2</sub> system (Since C<sub>60</sub> also absorbs at the excitation wavelength, we observe triplet C<sub>60</sub> formation (absorption maximum at 740 nm) along with the C<sub>60</sub><sup>•−</sup> formation. The excited C<sub>60</sub> is practically inert under present experimental conditions as it does not interact with the TiO<sub>2</sub> surface.)

The maximum absorbance recorded 100 μs after laser pulse excitation was used to determine the relative yield of electron-transfer process in TiO<sub>2</sub> and Ag@TiO<sub>2</sub> colloids. Figure 6B shows the photocatalytic reduction yield as a function of the concentration of added C<sub>60</sub> for the two systems. The electron transfer yield increased initially with increasing concentration of C<sub>60</sub> and reaching a plateau at C<sub>60</sub> concentration > 30 μM.

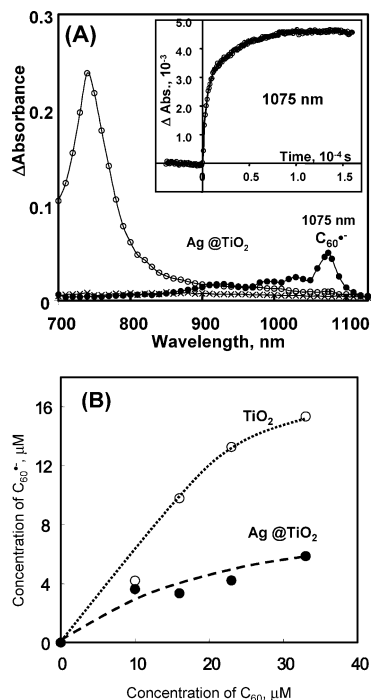
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**Figure 6.** (A) Difference absorption spectra recorded 0.1  $\mu\text{s}$  (○) and 15  $\mu\text{s}$  (●) after 308 nm laser pulse excitation of deaerated Ag@TiO<sub>2</sub> colloidal suspension in ethanol containing 32  $\mu\text{M}$  C<sub>60</sub>. Inset shows the growth of C<sub>60</sub><sup>•-</sup> as monitored from the absorbance at 1075 nm. (B) Yield of C<sub>60</sub><sup>•-</sup> (as monitored from the absorbance at 1075 nm,  $\epsilon=16000\text{M}^{-1}\text{cm}^{-1}$ ) with increasing concentration of C<sub>60</sub> present in colloidal Ag@TiO<sub>2</sub> suspension (deaerated with N<sub>2</sub>, Ex., 308 nm).

The electron transfer from excited TiO<sub>2</sub> and Ag@TiO<sub>2</sub> to C<sub>60</sub> proceeds until the two systems attain redox equilibration. Although we expected to see a higher catalytic activity for the Ag@TiO<sub>2</sub> clusters, the experimental results show an opposite trend. The photocatalytic reduction efficiency of Ag@TiO<sub>2</sub> is lower than that of TiO<sub>2</sub>. These results suggest that part of the photogenerated electrons reside within the Ag@TiO<sub>2</sub> composite as it attains equilibration with C<sub>60</sub><sup>•-</sup>.

In our earlier study of Au–TiO<sub>2</sub> sandwich structure (i.e., two particles in contact with each other in a coupled geometry), we observed a higher catalytic activity compared to TiO<sub>2</sub>. The increased photocatalytic reduction was attributed to the shift of Fermi level to more negative potentials. Since C<sub>60</sub>/C<sub>60</sub><sup>•-</sup> couple equilibrates with the stored charges within the composite, the yield of C<sub>60</sub><sup>•-</sup> serves as a measure of the apparent Fermi-level. The lower yield of C<sub>60</sub><sup>•-</sup> observed in the present experiments suggests that the apparent Fermi-level of the Ag@TiO<sub>2</sub> composite is lower than TiO<sub>2</sub> alone. The charge equilibration between the metal core and semiconductor shell, thus causes the apparent Fermi-level less negative than neat TiO<sub>2</sub> cluster. Although metal core-semiconductor shell structures are quite efficient for storing photogenerated electrons, their ability to catalyze a reduction process is limited. The results presented here highlight the importance of designing semiconductor-metal composite nanostructures for light energy harvesting applications.

## Conclusions

We have demonstrated the photoinduced charging and dark discharging of electrons in a silver core-semiconductor shell structure. The shift in surface plasmon band serves as a measure to determine the number of electrons stored in the metal core. The charge equilibration between the metal and semiconductor plays an important role in dictating the overall energetics of the composite. These metal core-semiconductor shell composite clusters are photocatalytically active and are useful to promote light induced electron-transfer reactions. Exploring the catalytic activity of such composite structures could pave the way for designing novel light harvesting systems.

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