Photochemistry on Semiconductor Surfaces. Visible Light Induced Oxidation of C_{60} on TiO$_2$ Nanoparticles

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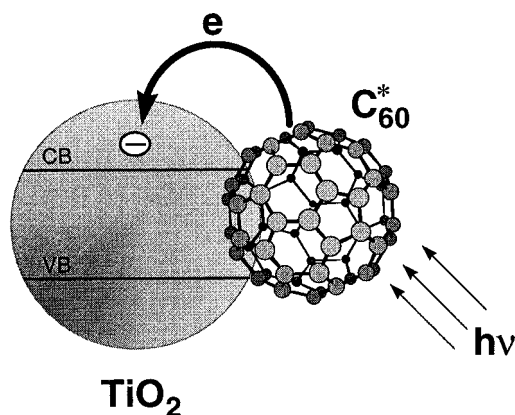
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The photochemical behavior of C_{60} adsorbed on TiO$_2$ particles has been investigated using diffuse reflectance laser flash photolysis. At submonolayer coverages, irreversible oxidation of C_{60} is observed on titanium dioxide particles. A photochemical transient with a difference absorption maxima at ∼390 nm and at wavelengths greater than 700 is observed following the 532 nm laser pulse excitation of the C_{60}-coated TiO$_2$ particles. This transient is not sensitive to the presence of oxygen. The bleaching in the 600 nm region confirms the depletion of C_{60} during the surface photochemical oxidation of C_{60}. Formation of both triplet excited state and the oxidation product are observed at higher coverages. This suggests that direct interaction with the oxide surface is crucial for observing the photochemical oxidation of C_{60}. A biphotonic electron ejection from excited C_{60} is followed by the formation of fullerene epoxide on the TiO$_2$ surface. The diffuse reflectance laser flash photolysis experiments which highlight the surface photochemistry process of C_{60} are presented.

Introduction

Fullerenes have gained a lot of attention in recent years as they exhibit a variety of interesting excited state properties.[1,2] Several researchers have investigated photophysical, photochemical, and charge transfer properties of fullerenes in homogeneous and heterogeneous media, e.g., in organic solvents, cyclodextrins, polymers, Langmuir−Blodgett films, artificial membranes, solid surfaces, thin films, and colloidal semiconductor suspensions (see, for example, refs 3−26). The interest in understanding singlet and triplet excited state properties stems from its potential application in developing photoconductive, photovoltaic, and nonlinear optical devices.[27−31] Basic understanding of the photophysical and photochemical properties is also important in improving the photostability of fullerene-based devices.

Of all the fullerenes that have been investigated to date, only excited C_{60} is known to exhibit prominent bands at 920 and 740 nm corresponding to $^{1}C_{60}^{*}$ and $^{3}C_{60}^{*}$, respectively. Most of the photophysical studies of fullerenes that have been carried out to date have been in solutions or in thin polymer films. Some effort has also been made to investigate its photoactivity in thin films.[32−35] Aggregates formed in Langmuir−Blodgett films at the air−water interface possessed photophysical properties that are significantly different from monomers.[36] Charge transfer complexation with the host is another interesting feature that one might encounter with fullerenes. For example, distinctively different spectral features are observed when C_{60} is dispersed in polymeric films such as poly(vinylcarbazole).[22] The obvious question then would be, "how does the fullerene molecules behave when dispersed on a solid surface such as metal oxide?"

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SCHEME 1: Photoinduced Charge Transfer between TiO$_2$ Semiconductor Colloid and C_{60}

Semiconductor supports such as TiO$_2$ have been shown to participate in the surface photochemical processes resulting in the oxidation of the adsorbed substrate (Scheme 1).[37] Anatase TiO$_2$ is a large bandgap semiconductor (E_g = 3.2 eV) that requires UV light to initiate bandgap excitation. By exciting the adsorbed substrate with visible light, we can therefore avoid direct excitation of the semiconductor support and selectively probe the excited behavior of molecules of interest. By use of a similar approach, it has been possible to study the surface photochemical processes of several sensitizing dyes on oxide surfaces such as TiO$_2$, Al$_2$O$_3$, and SiO$_2$.[38−42]

Although the ground state quenching and triplet−triplet annihilation processes dominate deactivation of the triplet excited states of fullerenes, their solutions in benzene and toluene are considered to be stable to visible light irradiation. However, recent reports suggest the oxidation of fullerenes to their epoxides with UV irradiation.[43−45] For example, photooxidation of C_{60} in benzene solution has been carried out by irradiating oxygenated solutions to UV light, and the photoproduct, fullerene epoxide ($C_{60}O$), has been isolated. Recently,

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Anpo and co-workers[46] have shown that oxide surfaces such as TiO_2 can facilitate production of EPR-active species of C_{60} in air and under ambient conditions or UV irradiation. EPR signals corresponding to $C_{60}-O_n$ system have also been observed by Pace and his co-workers.[47]

We recently reported that C_{70} undergoes photochemical oxidation under visible light irradiation.[48] We have now carried out a detailed diffuse reflectance study to gain insight into the surface photochemical processes that lead to the oxidation of C_{60} on TiO_2 surface.

Experimental Section

Materials and Sample Preparation. High-purity (99.9%) C_{60} samples were obtained from SES Research, Houston, and were used as supplied. Particulate TiO_2 (particle diameter 30 nm, surface area 50 m^2/g) and Al_2O_3 (particle diameter 20 nm, surface area 100 m^2/g) were obtained as gift samples from Degussa Corp. (Product name P-25). C_{60} adsorbs poorly on TiO_2. Hence, we chose to prepare C_{60}-coated TiO_2 samples by dispersing 1 g of TiO_2 powder in a toluene solution containing a known amount of C_{60}. The solution was stirred for 2 h, and then the solvent was evaporated off in a rotovap. Typically, a sample of 0.09 mmol of C_{60}/g of TiO_2 is considered to yield a monolayer coverage. This estimate is made with the assumption that each C_{60} molecule occupies approximately 100 Å and is spread evenly on the TiO_2 surface. A similar procedure was also adopted for preparing the C_{60}/Al_2O_3 sample. The opaque powder sample was then transferred to an optical cell and was degassed by connecting it to a vacuum line.

Optical Measurements. The diffuse reflectance absorption spectra of TiO_2-coated C_{60} samples were recorded using Milton-Roy Spectronic 3000 diode array spectrophotometer equipped with a Labsphere diffuse reflectance attachment. The diffuse reflectance laser flash photolysis experiments were carried out in a vacuum-tight $3 \times 6 \times 40$ mm^3 rectangular cell using Nd: YAG laser (Quanta Ray DCR-1) as the excitation source and the xenon lamp as the monitoring source. The diffusely reflected monitoring light from the sample was collected and focused onto a monochromator which was fitted with a photomultiplier tube (PMT). The PMT signals were digitized with a Tektronix 7912A digitizer. The details of the experimental setup are described elsewhere.[38,39] Before triggering each laser pulse, the sample was shaken to expose a fresh surface for excitation. Air-equilibrated samples were obtained after exposing the previously degassed samples to air for about 30 min.

Diffuse Reflectance FTIR Experiments. All FTIR experiments were performed with the samples exposed to air. The diffuse reflectance spectra of these air-equilibrated samples were measured in the region $4000-400$ cm^{-1}, at a resolution of 8 cm^{-1} using a Bio-Rad FTS 175 FTIR spectrometer and the Bio-Rad diffuse reflectance accessory. In most cases, no enhancement in spectral features was observed when the resolution was increased from 8 to 4 cm^{-1}. Hence, the spectra were all obtained at 8 cm^{-1} resolution with TiO_2 being used as the background. Because of strong absorbance by oxides, TiO_2, spectral data below 1100 cm^{-1} for the adsorbed species were not measurable. Similarly, information above 2500 cm^{-1} was also difficult to obtain because of adsorbed water or surface hydroxyl groups. The diffuse reflectance FTIR spectra of the C_{60} adsorbed on TiO_2 were monitored while undergoing steady state photolysis using visible light from a Fiber-Lite Model 190 fiber-optic illuminator.
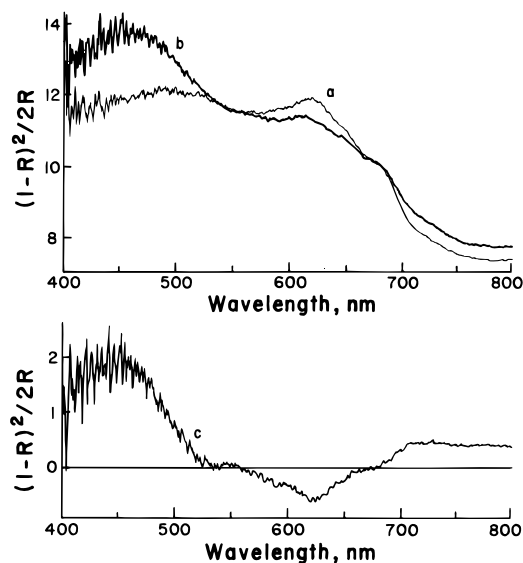
Figure 1. Diffuse reflectance absorption spectra of C_{60}-coated TiO_2 particles (0.09 mmol/g of support) recorded (a) before and (b) after the photolysis with 532 nm laser for 3 min. Spectrum c is the difference between spectra a and b.

Results and Discussion

Absorption Characteristics and Laser Photolysis of C_{60} on TiO_2. The diffuse reflectance absorption spectrum of C_{60} on TiO_2 is shown in Figure 1 (spectrum a). The purple sample exhibits broad absorption in the visible region ($400-750$ nm). As compared to the solution spectrum, this absorption band is relatively broad and exhibits a maximum absorption around 620 nm. Similar broadening of the absorption band has been observed for several organic dyes adsorbed on oxide surfaces (see for example refs 37 and 49). Interaction between the adsorbed dye and the support material has been shown to alter the energetics of the electronically excited molecule.

Although close packing of C_{60} could lead to aggregation effects, we did not observe such effects on TiO_2 particles. The characteristic absorption band at 620 nm and the possibility of forming monomer triplets with visible excitation (see next section) indicated that most of the C_{60} dispersed on TiO_2 particles exist in the monomeric form. A similar monomeric distribution of C_{60} has also been achieved in polymer thin films.[12,22,50] It should be noted that the aggregates show distinctively different absorption bands compared to the monomeric form as observed in the case of Langmuir–Blodgett films and mixed solvents, and their photoactivity significantly differs from that of the monomers.[36]

Upon excitation of an air-equilibrated sample of C_{60}-coated TiO_2 with a diffused 532 nm pulsed laser beam ($2-3$ mJ, 10 MHz, Nd:YAG laser), the sample changed its color. The absorption spectrum recorded after laser photolysis of the sample for a period of 3 min is shown in spectrum b (Figure 1). The decreased absorption in the 620 nm region and an increased absorption in the 400 nm and IR region indicates that irreversible changes are occurring on the TiO_2 surface. The difference between the two spectra recorded before and after the photolysis is highlighted in spectrum c. Similar susceptibility of C_{70} to photodegradation on the TiO_2 surface to photodegradation was noted in our preliminary communication.[48]

Spectral changes similar to those in Figure 1 were also observed during UV oxidation of fullerenes in oxygenated benzene or toluene solutions with UV light irradiation.[43–45] These photochemical changes were considered by these researchers to arise from epoxide formation. We attribute the

spectral changes in the present experiments (Figure 1) to the formation of epoxide type chemical species on the TiO$_2$ surface since these are similar to those observed with UV irradiation experiments.[43−45] Our assignment is further supported from the work of Anpo and co-workers,[46] who characterized C$_{60}$O formation on oxide surfaces using EPR and XPS techniques. Please note that bulk C$_{60}$ is chemically stable to visible light irradiation. Thin films or solutions of C$_{60}$ exhibit relatively negligible degradation under similar excitation with visible light. Thus, the experiments described in the present study show that the photooxidation of adsorbed C$_{60}$ is influenced by the semiconducting support material (TiO$_2$) by directly participating in the photocatalytic process.

Diffuse Reflectance Laser Flash Photolysis Studies. It has been shown earlier that singlet excited states can be readily generated in solutions and polymeric films upon excitation of C$_{60}$ with UV or visible light.[1,2] These molecules are weakly fluorescent with characteristic emission bands in the red-IR region. Efficient intersystem crossing (>95%) results in the population of triplet excited states. The long lifetime (100−250 μs) of the triplet excited states facilitates reaction with electron donors and acceptors.

We employed a diffuse reflectance laser flash photolysis to study the photochemistry of C$_{60}$ on the TiO$_2$ surface. The design of the cell employed in this study is illustrated earlier.[41] The cell had the provision to degas the sample by connecting it to the vacuum line. The cell was then transferred to the laser flash photolysis setup to carry out transient absorption measurements. The transient absorption spectra recorded following the 532 nm excitation of degassed and air-equilibrated TiO$_2$/C$_{60}$samples are shown in Figure 2, A and B, respectively.

The spectrum recorded immediately after laser pulse excitation ($\Delta t = 1.5$ μs) shows a maximum absorption around 390 and 720 nm and a bleaching in the region of 480−620 nm (Figure 2A). The spectrum recorded at longer times shows a little change in the position of the absorption bands but no net bleaching in the 480−620 nm region. Similarly, the presence of oxygen has little effect on the transient absorption. These spectral properties are quite different than those observed after laser pulse excitation of C$_{60}$ dissolved in aromatic solvents[7,10,51] or in nonreactive polymer films.[2,12,22] (³C$_{60}$* is the only detectable transient in the microsecond−millisecond time domain when excitation is carried out in toluene or benzene solutions. This transient is readily quenched by oxygen.) We also compared the excited state behavior of C$_{60}$ on a neutral surface such as alumina. The transient absorption spectrum recorded following 532 nm laser pulse excitation of the degassed sample of C$_{60}$/Al$_2$O$_3$ shows the formation of triplet excited state as the major transient (spectrum a in Figure 3). Upon exposure to air, most of the transient is readily quenched (spectrum b in Figure 3). The sensitivity of the transient absorption to the presence of oxygen in the Al$_2$O$_3$ sample is thus different than in the TiO$_2$ sample.

At low coverage, the transient absorption spectra of both degassed and air-equilibrated samples of C$_{60}$/TiO$_2$ are similar (Figure 2, A and B). This lack of sensitivity to oxygen suggests that the contribution of the triplet excited state to the overall transient absorption is relatively small on the TiO$_2$ surface. ³C$_{60}$* if present on the TiO$_2$ surface would decay rapidly in air as it is quenched by oxygen.[1,52] Also, the difference absorption spectrum of ³C$_{60}$* shows a positive absorption at wavelengths greater than 385 nm. However, a distinct bleaching at 620 nm (both in degassed and in air-equilibrated samples) is observed in the spectra presented in Figure 2A,B. The stability of the transient in air suggests that C$_{60}$ undergoes oxidative degradation
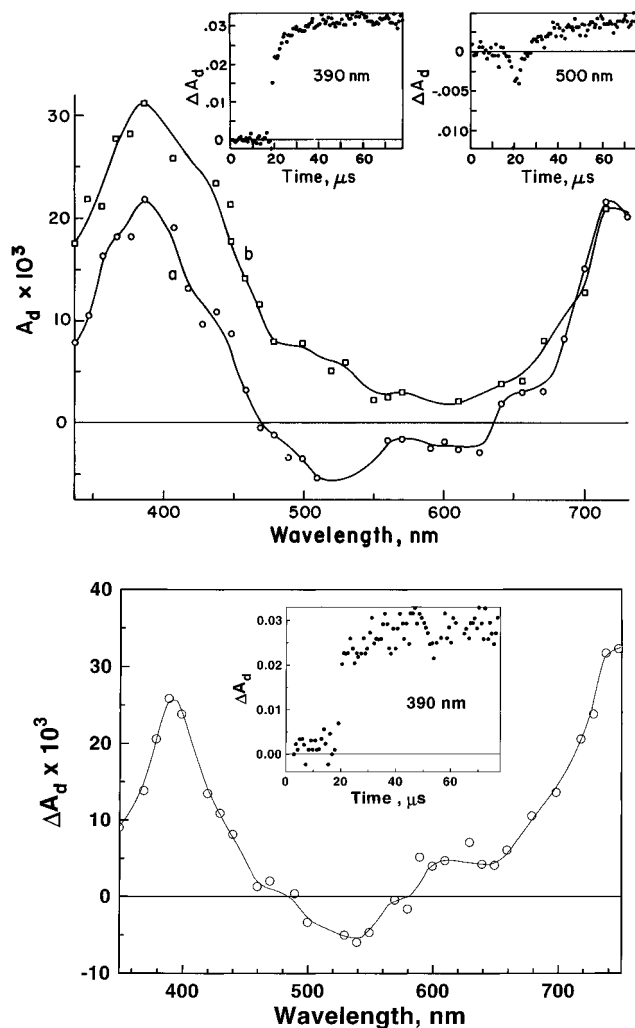
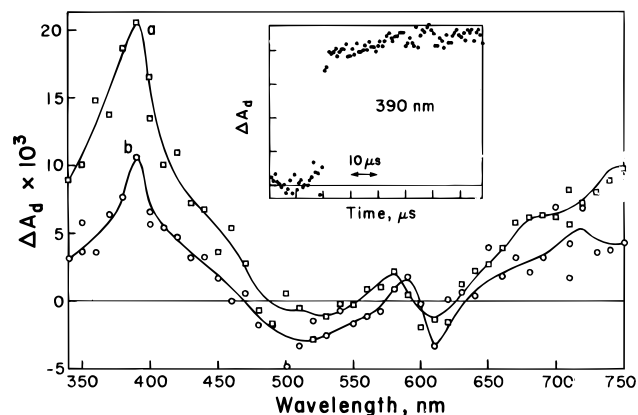**Figure 2.** (A, top) Time-resolved difference absorption spectra recorded after 532 nm laser pulse (∼2 mJ) excitation of degassed C$_{60}$/TiO$_2$ sample (0.09 mmol/g of TiO$_2$). This surface coverage of C$_{60}$ corresponded approximately to a monolayer. The difference absorption spectra were recorded at (a) 1 6 and (b) 50 μs after laser pulse excitation. (B, bottom) Time-resolved difference absorption spectra recorded after 532 nm laser pulse (∼2 mJ) excitation of air-equilibrated C$_{60}$/TiO$_2$ sample (0.09 mmol/g of TiO$_2$). The difference absorption spectrum was recorded 20 μs after laser pulse excitation.
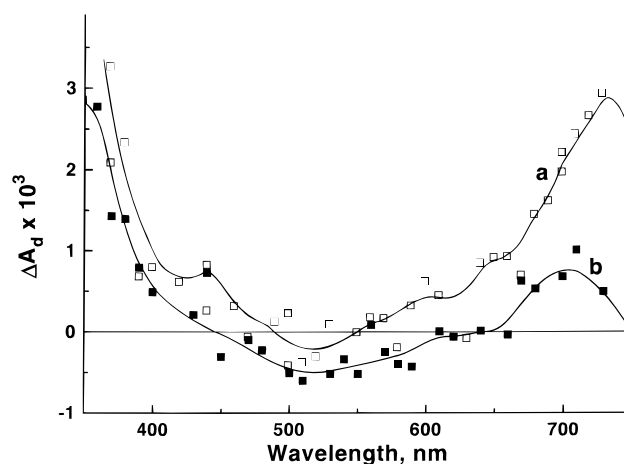
Figure 3. Time-resolved difference absorption spectra recorded 10 μs after 532 nm laser pulse (∼2 mJ) excitation of (a) degassed and (b) air-equilibrated C$_{60}$/Al$_2$O$_3$ sample (0.09 mmol/g of Al$_2$O$_3$).

on the TiO$_2$ surface. Blank experiments carried out with TiO$_2$ alone at a comparable laser intensity did not yield any detectable transient absorption. Some irreversible change was also seen

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Figure 4. Time-resolved difference absorption spectra recorded at 1 μs following the 532 nm laser pulse ($\sim$2 mJ) excitation of (a) degassed and (b) air-equilibrated C_{60}/TiO_2 sample (0.18 mmol/g of TiO_2). This surface coverage corresponds approximately to 2 $\times$ monolayer.

on the Al_2O_3 surface, but this fraction was small compared to the C_{60}/TiO_2 sample. The higher yields of the oxidation product observed on the TiO_2 surface is attributed to the greater reactivity of the semiconducting support material.

The inserts in Figure 2A show the absorption−time profiles at 390 and 500 nm. Although some of this absorption is prompt, a growth in the absorption could still be seen following 532 nm laser pulse excitation. This shows that the net photoreaction extends for a period of about 10 μs. (Interference of light scatter prevented us from obtaining a better time resolution.) This transient was stable in both degassed and air-equilibrated samples and exhibited no observable decay during the monitoring period of 150 μs. In fact, its spectral feature closely resembles the difference spectrum in Figure 1c and hence confirms the fact that the oxidation product formed immediately after the laser pulse excitation is stable for a long period of time.

Figure 4 shows the transient absorption spectrum recorded with TiO_2/C_{60} sample at a higher coverage. The absorption bands at 390 and 720 nm in the degassed samples are sharper, and a significant decrease in these absorption bands is seen in air-equilibrated samples. This we attribute to the increased contribution from the triplet excited state in the higher coverage sample. Since the C_{60} coverage is more than a monolayer, not all the C_{60} molecules can interact with TiO_2 surface, thus yielding some $^3C_{60}^*$ in degassed samples.

Dependence of Surface Coverage on the Photoproduct Yield. From the diffuse reflectance laser flash photolysis we attempted to compare the relative yields of the photoproduct formed at different coverages of C_{60}. As shown earlier,[53−55] if the exciting light is totally absorbed by the sample, the intensity of the diffused monitoring light from the sample can be used to estimate the fractional absorption, A_d, of the transient formed at the surface: $A_d = \ln(I^0_a/I_t)$ where I^0_a and I_t are the incident and unabsorbed fraction, respectively, of analyzing light intensities at the solid sample. For small fractional absorption ($A_d \ll$ 1), A_d is proportional to the concentration of the transient formed after the laser pulse excitation. The transient absorption at 390 and 740 nm was monitored in degassed and air-equilibrated samples (Figure 5). In degassed samples both triplet excited C_{60} and the photoproduct contribute to A_d. On the other hand, in the air-equilibrated samples only the photoproduct survives.

Two points are evident from the dependence of 390 nm absorption on the C_{60} coverage in Figure 5. (i) A_d increases with increasing coverage as more and more of the C_{60} molecules absorb the incident laser pulse but tends to attain saturation at very high coverages. (ii) The absorption of the air-equilibrated
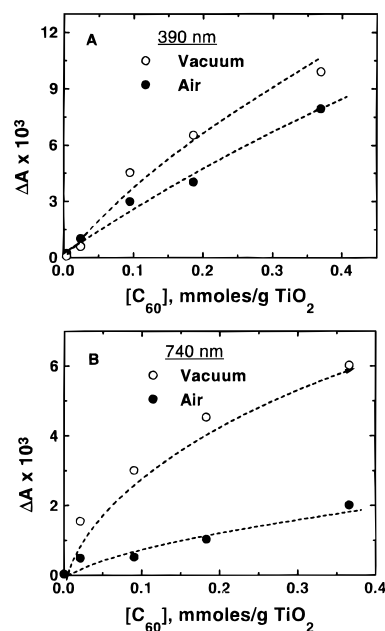

Figure 5. Dependence of transient absorbance at (A) 390 and (B) 740 nm observed following 532 nm laser pulse excitation of the C_{60}/TiO_2 sample. The experiments were performed under degassed and air-equilibrated conditions.
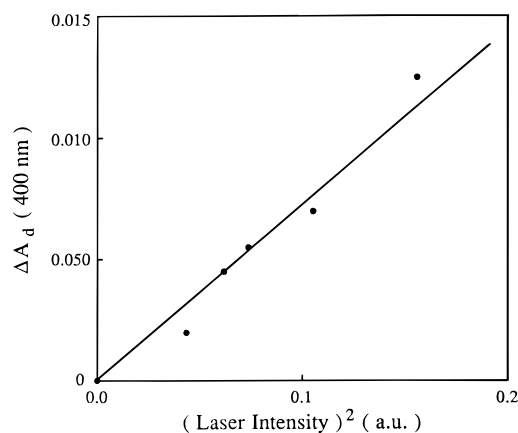
Figure 6. Dependence of photooxidation yield on the laser intensity. The relative yield of the photooxidation was determined from the maximum transient absorbance at 400 nm. The transient absorption was recorded after excitation (532 nm) of C_{60}-coated TiO_2 sample (0.09 mmol/g of TiO_2) at different laser intensities.

sample is lower than the degassed samples at all coverages. At higher coverages, the difference between the two absorption values (degassed and air-equilibrated samples) is also larger. This is especially significant for the A_d values at 740 nm, at which $^3C_{60}^*$ has absorption maximum. This increased difference in A_d at 740 nm with greater coverage essentially shows the enhanced contribution of the triplet excited state under these conditions. These results further confirm the observation made in the previous section that only a fraction of C_{60} molecules that are in direct contact with the TiO_2 surface undergo oxidative phototransformation.

Dependence on the Excitation Laser Intensity. The dependence of the yield of this product on the excitation intensity was monitored by varying the laser intensity and recording the maximum absorption at 390 nm. The linear dependence of maximum absorption on the square of the laser dose (Figure 6) shows that the formation of this oxidation product is a biphotonic process. At higher laser intensities the singlet excited state ($^1C_{60}^*$) can absorb another photon during the laser pulse duration of 6 ns and generate higher excited

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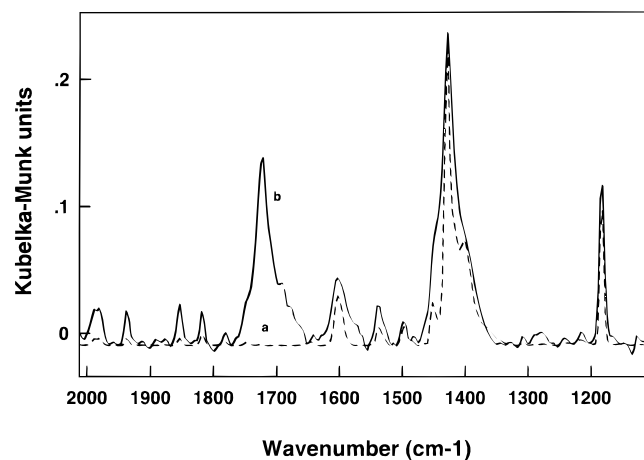
Figure 7. Diffuse reflectance FTIR spectra in the region $1100-2000$ cm^{-1} of C_{60} on TiO_2 (0.09 mmol/g of TiO_2). The spectra were recorded (a) before photolysis and (b) after steady state photolysis with a 30 W halogen lamp for 72 h.

singlet states. Since these higher singlet states (S_n) are more energetic, they are more reactive on the TiO_2 surface than the S_1 state.

Diffuse Reflectance FTIR. In order to probe the surface photochemical events of the C_{60} adsorbed on TiO_2 powder and to identify the photoproduct rising from such a self-sensitized degradation, a diffuse reflectance FTIR study of the powders was carried out at various irradiation times.

The FTIR spectrum of C_{60} as reported in the literature[56] shows only four strong absorbance bands at 1429.0, 1182.7, 575.9, and 526.9 cm^{-1}. The literature spectrum of C_{60} shows no defining features above 1600 cm^{-1}, consistent with the absence of C−H or C−O bonds. The FTIR spectrum of C_{60} on TiO_2 recorded before photolysis (spectrum a in Figure 7) is consistent with the above prediction. Since the absorption of the TiO_2 background precludes the observation of any vibrational bands below 1000 cm^{-1}, only two strong peaks are observed at 1432 and 1184 cm^{-1}. Several smaller bands are also observed with the prominent one at 1590 cm^{-1}, which possibly arises from a coadsorbed solvent impurity. We do not consider these peaks as significant since the peak at 1590 cm^{-1} is significantly lower than the two major vibrations at 1184 and 1432 cm^{-1}

The IR spectra of C_{60} on TiO_2 was recorded following steady state photolysis at various time intervals. Under steady state illumination conditions the photodegradation of C_{60} on TiO_2 surface occurred slowly. Changes are observed upon extended photolysis ($\sim$72 h) of the TiO_2 sample. The FTIR spectra of C_{60} on TiO_2 following photolysis is shown in Figure 7b. Consistent with the structure of the C_{60} molecule and the relatively clean IR spectrum, no changes are observed in the vibrational bands at 1429 and 1184 cm^{-1}. However, after prolonged photolysis, a new peak appears at 1720 cm^{-1}. This peak seems to arise from the C−O stretch, which is characteristic of a carbonyl or carboxylic type functional group. These results indicate the formation of oxygenated C_{60} derivative on the TiO_2 surface. These observations are also consistent with the previous UV oxidation of C_{60} in benzene solutions.[44]

Mechanism of Photooxidation. There are two major possible pathways for the photodegradation of C_{60} on TiO_2 surface: (i) interaction of C_{60} with the singlet oxygen produced via triplet energy transfer and (ii) photoejection of electrons (surface-induced photoionization) from excited C_{60} into TiO_2 particles followed by the irreversible oxidation. The former possibility is unlikely. If this was true, C_{60} photooxidation would not have occurred under degassed conditions. The

SCHEME 2: Energy Level Diagram Illustrating the Charge Injection from Excited C_{60} into TiO_2 Particles
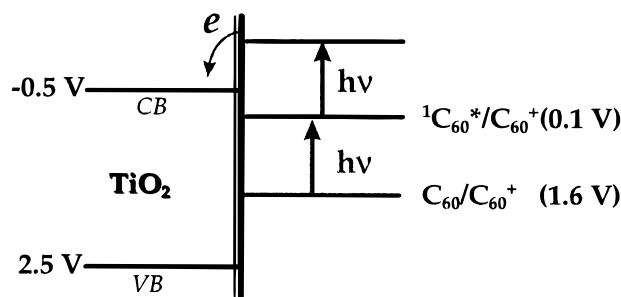
stability of fullerenes to singlet oxygen has also been noted in earlier studies.[1,7,8,52,57] Therefore, we consider the second possibility, viz., photoejection of electrons from excited C_{60} into TiO_2 particles, as the primary step responsible for photooxidation.

$$C_{60} + h\nu \rightarrow {}^1C_{60}^* \rightarrow {}^3C_{60}^* \tag{1}$$

$$(C_{60}/TiO_2) + nh\nu \rightarrow C_{60}{}^{\bullet+} + TiO_2(e) \tag{2}$$
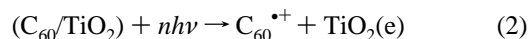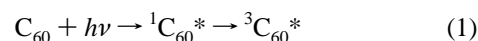
In the presence of oxygen the back electron transfer between the injected electron and $C_{60}{}^{\bullet+}$ is suppressed as the oxygen scavenges electrons.

$$O_2 + TiO_2(e) \rightarrow O_2{}^{\bullet-} + TiO_2 \tag{3}$$
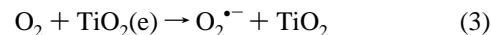
It has been shown in our earlier studies that the intrinsic semiconducting property of the support material plays an important role in controlling the fate of the excited substrate. Support materials such as TiO_2 are large bandgap semiconductors (conduction band energy -0.5 V vs NHE) that promote the oxidation of an adsorbed dye by directly accepting an electron from the excited state. If the oxidation potential of the excited molecule is more negative than -0.5 V, it can inject electrons into the TiO_2 particles (Scheme 2). This excited state property is the basis of photosensitization process that is widely employed in imaging science and photochemical solar cells. In the present case the oxidation potential of C_{60} is around 1.6 V vs NHE. Since the oxidation potential of $C_{60}^*(S_1)$ is 0.1 V vs NHE ($E_s = 1.5$ eV), we would not expect singlet excited C_{60} to directly inject electrons from its S_1 state into TiO_2 particles. Therefore, more than a single photon is necessary to induce the photoinjection process. The higher excited states created at higher laser intensities will be energetic enough to inject electrons into the TiO_2 particles. The pulse duration of the laser pulse (6 ns) is sufficiently long enough for the S_1 state to get excited into higher electronic states by reabsorbing another photon. The biphotonic dependence observed in Figure 6 supports such an argument. Under steady state photolysis, the photodegradation occurs with a very slow rate. An extended period (several hours) of visible light illumination is necessary to induce noticeable spectral changes.

The photoejection of electrons into TiO_2 particles is likely to be followed by the interaction of $C_{60}{}^{\bullet+}$ radical with either the lattice oxygen (of TiO_2) or chemisorbed oxygen that results in the formation of an epoxide type species (reaction 4).

$$C_{60}{}^{\bullet+} TiO_2 \rightarrow (C_{60}O\cdots O) \tag{4}$$
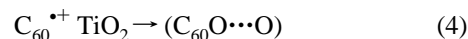
Alternatively, the reduced oxygen can also interact with C_{60} to yield similar epoxide (reaction 5)

$$C_{60}^{\bullet+} + O_2^{\bullet-} \rightarrow C_{60}O_x \qquad (5)$$
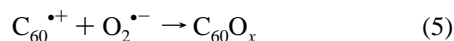
Since similar photochemical changes are observed in both degassed and air-equilibrated samples, we consider reaction 4 as the major route for epoxide formation. On the other hand, the neutral surfaces such as Al$_2$O$_3$ promoted this photooxidation to a lesser extent.

Prior to photolysis, C$_{60}$ can be extracted readily from the TiO$_2$ surface by washing with toluene. However, following the photolysis the photoproduct strongly adheres to the surface of TiO$_2$, and it is not possible to extract with either polar or nonpolar solvents. The difficulty in extracting the oxidation product by conventional methods suggests a strong binding of the epoxide to the TiO$_2$ surface. Formation of EPR-active species on oxides such as TiO$_2$ was recently observed by Anpo and co-workers.[46] These researchers found C-centered radicals to be the likely precursor intermediates for the epoxide formation. The distinct stability of these radicals is attributed to the large π-system of fullerenes. In the present experiments, the carbon-centered radicals generated via a biphotonic process act as a precursor for the epoxide formation on the TiO$_2$ surface.

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