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Light-induced charge separation and storage in titanium oxide gels

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We report on the interaction of light with a particular class of media—wet gels, which in contrast to sols of nanoparticles possess a macroscopic bulk structure, and which differ from conventional solids by the existence of the internal liquid-solid interface. We show, taking an absorption cross section of trapped electrons from Safrany, Gao, and Rabani [J. Phys. Chem. B **104**, 5848 (2000)], that a separation of charges with quantum efficiency as high as 46% appears under the band-gap irradiation of titanium oxide gels: electrons are stored in the gel network as Ti^{3+} centers, whereas holes are stored in the liquid phase. Under a prolonged UV-laser irradiation, more than 14% of Ti^{4+} centers can be converted into Ti^{3+}. Their lifetime can be extremely long and exceeds months at room temperature. The trapped electrons are responsible for a "dark" absorption continuum covering the spectral range from 350 nm to 2.5 μm.

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I. INTRODUCTION

Charge carrier dynamics under the band-gap illumination of solids is of fundamental importance. A wealth of information regarding band electronic structure, elementary excitations in solids, and charge and energy transfer processes has been extracted from spectroscopic studies with energy and time resolution [1,2]. It has long been known that free charge recombination can proceed through a localization process. If an electron and a hole are trapped by the same impurity center, they undergo annihilation, which can be accompanied by the emission of a photon. On the other hand, the recombination could be delayed if the traps for opposite charges are distant. In homogeneous solids with no or little defects, charges can be localized due to a self-trapping process (localization of themselves due to self-induced lattice distortion). These are polarons. The density of such isolated and long-lived charged states in the solid volume is rather low. Distant trapped charges in semiconductors enable nonexponential radiative recombination process. Moreover, free opposite charges can produce free and self-trapped excitons, which decay radiatively. In finite solids and near the surface, the light-induced charges can be trapped in surface sites, which is fundamental to photocatalysis. When the separation efficiency and the trap density are high, the solids may be considered for information or energy storage applications.

In this article, we report on an observation on the efficient charge separation in a particular class of media—wet gels, which in contrast to sols of nanoparticles possess a macroscopic bulk structure, and which differ from conventional solids by the existence of the liquid-solid bulk interface. The effect is induced by the UV light band-gap illumination above 3.24 eV [3] of the titanium oxide gels confined in a hermetically closed cell. The existence of an extremely large contact area S between solid (gel) and liquid (solvent), $S \propto m$ (where m is the gel mass), may allow an efficient separation and conservation of charges at high densities (electrons in the solid and holes in the liquid), which recombination through the interface can be controlled. We recently began to explore this domain of the gel interaction with a laser light and we have observed a strong photoinduced darkening [4]. In the following, we will give arguments for its assignment to photoinduced trapped electrons and we will describe optical properties of these media and the charge separation kinetics.

II. EXPERIMENT

The experiments were carried out using a pulsed nanosecond master optical parametric oscillator laser (Spectra Physics) tunable over a 0.22–1.7 μm spectral range. The laser delivers energy of $\leqslant 10$ mJ in a pulse of 5 ns duration in the UV spectral range with a repetition rate of 10 Hz. The spectral width of the laser line in the visible is 0.2 cm^{-1}. The output laser beam is directed to hermetically closed quartz optical cells filled with the gel. Samples were exposed to different laser intensities at different wavelengths. The laser energies (J/pulse) incident and transmitted through gel were permanently monitored by a two-channel energy meter (Coherent). The absorption spectra of the irradiated gels were measured *in situ* by an optical fiber probe using spectroscopic UV/visible/IR light continuum sources. The fiber transmits the signal to a monochromator (grating 150 l/mm, $f=30$ cm, slit 20 μm) coupled to a CCD detector (Princeton). The signal is also sent to an H20 filter-monochromator (Jobin Yvon–Spex) equipped with a fast-integrated photomultiplier (Hamamatsu). The signal is displayed by a 500 MHz TDS510 digitizing oscilloscope (Tektronix), which

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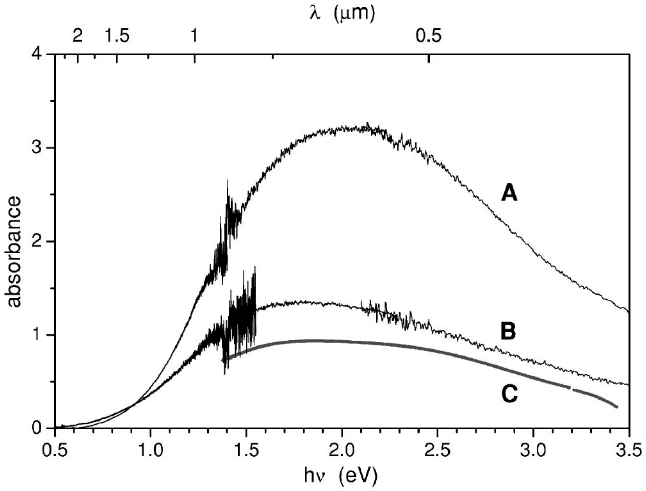

FIG. 1. Laser-induced absorption spectra of the gels with HCl (A) and with HNO_3 acids (B) (1-mm cell, $\lambda_L = 355$ nm, dose ~ 10 J/cm^2), and of the colloidal TiO_2 nanoparticles from Ref. [9] (C).

enables the absorption kinetics analysis. The data acquisition is controlled using LABVIEW software.

Titanium oxide gels are bushy polymerlike structures with a general formula $TiO_a(OH)_b(OR)_{4-2a-b}$. The primary gels are formed owing to hydrolysis-polycondensation reactions in alcoholic solutions after a relatively long period known as the induction period (t_{gel}) [5]. Moreover, the gels continue densifying over a period $\sim 40 t_{gel}$ that is called the aging stage. Formation kinetics of titanium oxide gels has been recently followed by elasticity [6] and optical [3] measurements. A metalorganic molecule, such as titanium tetra-isopropoxide [$Ti(OR)_4$ or TTIP], is generally used as a precursor. The chemical transformation of TTIP is not complete ($2a+b<4$), and the presence of residual organic groups and liquid alcohol is essential for the bulk gel stability. Drying of the titanium oxide gels and/or their thermal treatment breaks their structure and transforms them into a powder.

The gels were prepared under a dry atmosphere in the ethanol solution containing TTIP, water, and acid (H^+) at the room temperature of 22 ± 1 °C and under continuous stirring during the reagent mixing process. Most of experiments discussed below were carried out with the mixtures of $TTIP/H_2O/HCl/EtOH = 1/3/0.1/18$ (Molar ratio), which show the gelation time of 12 min. The titania concentration in these gels is fixed to 4.3×10^{20} cm^{-3}. The wet gels are noncolored, transparent, and stable over a month. We have used TTIP of 98% purity by Acros Organics, ethanol provided by Interchim, and distillated water. The gels were exposed to a laser light after $t \geqslant 40 t_{gel}$, when their formation is almost accomplished [3].

III. RESULTS AND DISCUSSION

The laser-induced absorption spectrum of the gel (prepared with HCl) is shown by curve A in Fig. 1. It is extremely broad with a full width at half maximum of 1.9 eV and covers all the visible and partially UV and IR spectrum ranges. The line shape was not specific to the mixture composition. Nevertheless, the maximum is slightly shifted by ~ 0.2 eV to short energies when nitric acid (curve B in Fig. 1) is used instead of HCl. No significant change in the spectral line shape is observed with the increase of the gel absorbance $\int_0^l \alpha(x)dx$ from 0.2 to 5.0 (~ 700 nm) in the 1-mm optical cell. Here α is the absorption coefficient and l is the cell width.

Although, these gels are fundamentally different from titanium oxide solids, certain similarities of their properties may exist. Firstly, the band-gap energy of the gel $E_{gel} = 3.24$ eV [3] is very close to that of the solid phases anatase and rutile: $E_{sol} = 3.2 - 3.0$ eV. The absorption of a photon results in the electron transition from the valence band due to the O^{2-} $2p$ orbital to the conduction band due to the Ti^{4+} $3d$ orbital [7]. An effect of the visible darkening has been previously observed in TiO_2 colloids with a quantum yield below 0.16 [8]. A comparison could be made of our measured spectrum with those earlier observed in titanium oxide colloidal nanoparticles ($D \approx 1.5$ nm) charged by electrons in pulsed γ-radiolysis experiments [9]. One example is shown in Fig. 1 by the curve C (we remark that the complete spectrum of the trapped electrons from UV to IR has not yet been reported).

Optical measurements in the spectral range between the fundamental absorption edge and the lattice absorption are of fundamental importance for an understanding of the traps nature. IR studies earlier evidenced a small polaron absorption band at ~ 0.8 eV [10] in the rutile crystalline phase, whereas the TiO_2 colloids have been studied above 1.5 eV. Our measurements show no specific IR-absorption bands in the gels. The spectrum C in Fig. 1 has a maximum at ~ 1.8 eV and a shoulder at ~ 2.5 eV. According to several authors [11], the short- and long-wavelength bands in the visible absorption spectra correspondingly belong to trapped h^+ and e^-, whereas this point has been revised later. The authors of [9,12] based on their experimental data proposed to identify these spectral features with the absorption of free conduction-band electrons with a small contribution from the trapped electrons (as Ti^{3+} centers). Although the trapped holes can be disregarded in the alcoholic solutions because of rapid radical producing reactions [8,13] ($h^+ \rightarrow H^+, Cl^\bullet$ in our case), the conclusive solution of this problem has not been yet given.

Our measured spectra are similar to that of C in Fig. 1 and can be assigned to the trapped electrons. First, recombination of free charges is very rapid and a trapping occurs on the ns time scale [8,11,14]. Secondly, our complementary EPR measurements (at $T = 77$ K) and a comparison of the results with [15,16] evidence a strong resonance due to Ti^{3+} with $g_\perp = 1.924$ and $g_\parallel = 1.878$. The EPR experiments, which second objective is to measure the extinction coefficient of Ti^{3+} in these gels, are in progress and will be discussed elsewhere [17]. Moreover, the red cutoff of our spectra of 0.5 eV corresponds to the binding energy of the electron in the Ti^{3+} traps [12].

Ti^{3+} can appear as stable surface defects under UV irradiation of TiO_2 solids. This process is known to saturate at laser doses about 360 J/cm^2 in the spectral range 3.4 eV $\leqslant h\nu \leqslant 4.7$ eV and it has a low quantum efficiency of

5×10^{-7} [18]. The defect production and healing are related to the surface reaction $Ti^{4+}:O_2^{-}\leftrightarrow Ti^{3+}+O_2$. Apparently, this mechanism cannot account for the photodarkening in titanium oxide gels. First, this effect is observed in the bulk material. The gel initially contains no such defect sites after preparation. These sites may be progressively accumulated under the laser irradiation. However, no difference in Raman and IR spectra between fresh and UV-treated samples has been remarked. Moreover, the gel darkening kinetics does not differ for fresh and UV-treated samples too. In this case, the Ti^{3+}-defect healing would require a two-stage charge-transfer reaction, which reconstructs the Ti-OR bounding.

Residual organic groups are essential for the bulk gel stability. A direct breakage of the Ti–OR bonds seems to require higher photon energy. This has been observed in our laser experiments with $h\nu_L\geqslant 4.4$ eV by the appearance of a white residue (TiO_2 powder) at the point of the laser impact with the gel. This process of the gel transformation into TiO_2 under irradiation by UV lamps has already been studied in Refs. [19–22]. The localization of the conduction-band (CB) electron on Ti^{4+} may be followed by the residual OR-group dissociation: $e_{CB}^{-}\cdots O_{1.5}^{2-}Ti^{4+}(OR)^{-}\rightarrow\cdots O_{1.5}^{2-}Ti^{3+}+OR^{-}$. This would require lower photon energy of $h\nu_L\geqslant E_g=3.24$ eV. However, whatever the process considered, it results in the Ti–OR bond breakage, which is accompanied by a formation of powder. This mechanism can be disregarded because no powder formation is observed at the gel irradiation with photon energies between 3.24 eV and 4.1 eV. The localization of the CB electron on Ti^{4+} seems to proceed in the $\cdots$-Ti-O-Ti-O-$\cdots$ 1D chain and involves the small polaron mechanism.

Additional experiments were conducted with the liquid solutions before gelation at $t<t_{gel}$, which were exposed to the laser light in the electrochemical cell. When darkening appears, the laser beam was switched off and a voltage of $U=35$ V/cm was set on the electrodes. The dark cloud in these conditions is related to short polymer chains, which grow and invade the cell volume at $t=t_{gel}$ in the absence of UV irradiation. Because these chains are free, they can move in the electric field if charged. We indeed observed that the dark cloud in the cell center rapidly disappears and concentrates toward the positively charged electrode, whereas gas bubbles appear at the negatively charged electrode (reaction $2H^{+}+2e^{-}\rightarrow H_2\uparrow$). This confirms that the darkening is related to negatively charged oxopolymers, and that the holes leave the polymer network for the liquid phase.

Possible attribution of the electron localization mechanism to polarons requires a comment. The Ti 3*d* band-gap states are suggested to be polaronic in nature [23]. However, the line shape of the observed absorption band excludes large polarons (weak electron-phonon coupling). Moreover, the Holstein model of small polaron (strong coupling), although it predicts the bell-like line shape [24], does not fit our spectra well. The reason for that may be related to an inhomogeneous broadening [25]. Indeed, free electrons may be trapped at different Ti^{4+} sites bound in the gel structure by one, two, or three oxygen bridges. This may change the electron affinity of the titanium center and consequently the electron binding energy. We specify that our spectra differ from those previously measured in colloidal nanoparticles by the absence of the short-wavelength shoulder. This discrepancy may reveal a particularity of the electronic traps in the gel structure.

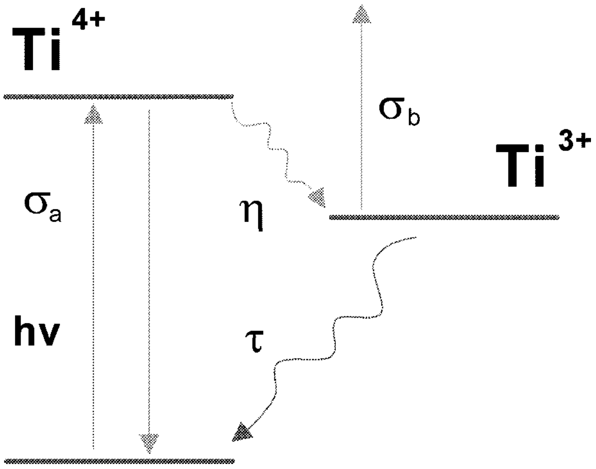

FIG. 2. The schema of the relevant processes in the titanium oxide gels induced by UV laser photons.

A basic model describing the kinetics of the induced charges in the gel involves the interband laser light absorption, charges separation and trapping, and relaxation [4]. The schema of the relevant processes is shown in Fig. 2. A mathematical formalism has been developed in Ref. [26],

$$\partial b/\partial t=\eta(a_0-b)\sigma_a I-b/\tau, \tag{1}$$

$$\partial I/\partial x=-(\sigma_a a+\sigma_b b)I. \tag{2}$$

Here $a=[Ti^{4+}]$ is the number density of Ti^{4+} ions, $b=[Ti^{3+}]$ is the number density of Ti^{3+} ions, I is the laser intensity, $a_0=a+b=[Ti^{4+}]_0$ is initial value of a, σ_a and σ_b are cross sections of initial and induced absorption correspondingly, and τ is the time of relaxation of induced absorption. In [4], the simplest set of Eqs. (1) and (2) has been used to address the main features of UV laser darkening of titania gels prepared using HNO_3 acid. Kinetic curves (transmission of the cell versus irradiation dose) for different laser intensities go together at small doses and then diverge in such a way that higher intensity provides deeper modification (less transmission) at the same irradiation dose. The kinetics at small fluences demonstrates the photochemical nature of the modification addressed by the first term in the right part of Eq. (1), whereas the kinetics at high fluences is dominated by the second, relaxation term. Detailed analysis of the laser-induced darkening kinetics of gels prepared with nitric acid will be published elsewhere [27]. This kinetics appeared to be quite complicated and is accompanied by chemical changes in the sample composition.

In the present communication, we focus on the entirely reversible laser modification induced in the titania gel prepared with hydrochloric acid. As we will see from the following, the measured kinetic curves in this case are entirely dose-dependent. For this reason, the second relaxation term in Eq. (1) can be omitted. Moreover, in the range of intermediate doses, the proposed basic model is not valid and should

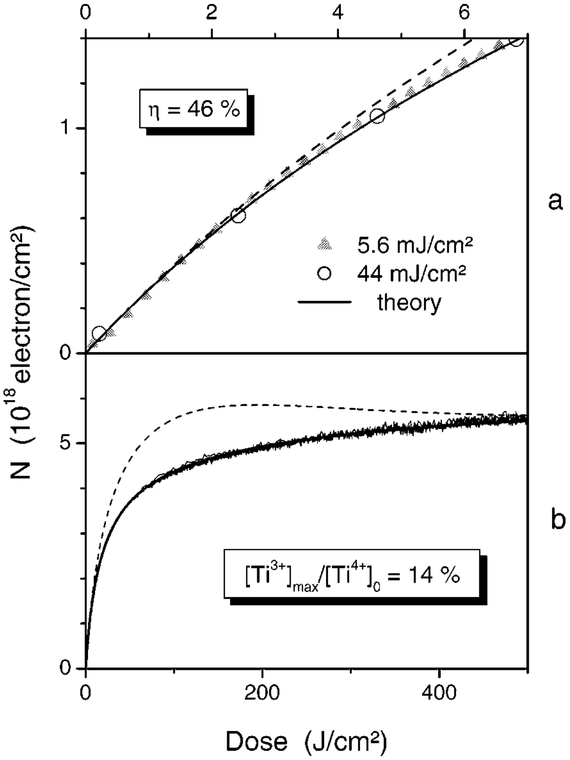

FIG. 3. Electron loading kinetics in the gel (HCl acid, 1-mm optical cell) at small (a) and large (b) doses. The theoretical modeling is presented by the solid curve. The dashed curve is calculated using Eqs. (1) and (2), without taking into account the intensity-dependent relaxation.

be completed by new dose-dependent relaxation terms. Below, we discuss our new experimental observations and we apply numerical treatment of the physical model to discuss the darkening kinetics on the entire time scale at different laser fluences.

In the current experiments, titanium oxide gels were confined in the optical cell of $l = 1.0$ mm width and irradiated at $\lambda_L = 355$ nm. The absorption coefficient $\alpha_1 = 4.6$ cm^{-1} has been measured directly in the gel with $a_0 = [\mathrm{Ti}^{4+}]_0 = 4.3 \times 10^{20}$ cm^{-3}. This results in $\sigma_a = 1.1 \times 10^{-20}$ cm^2. The electron absorption cross section in the maximum at 700 nm $\sigma_{\mathrm{el}} = 1.80 \times 10^{-18}$ cm^2 has been taken from Ref. [9] as the most relevant to our case. The contribution of this laser-induced absorption continuum at the laser wavelength is taken $\sigma_b = \sigma_{\mathrm{el}}/3$. The kinetics curves were measured at 430 nm where the electron absorption cross section is taken $\sigma_2 = \sigma_{\mathrm{el}}/1.5$. The number of electrons (per unit cross section) in the cell $N_{\mathrm{electrons}} = \int_l [\mathrm{Ti}^{3+}](x)dx$ is shown in Fig. 3 as a function of the laser dose $h\omega_L \int I_L(t)dt$ in the range of small (a) and large (b) laser doses. Two presented data sets correspond to different laser fluences of 44 mJ/cm^2 and 5.6 mJ/cm^2. The important information about the trapped electron yield η and the relaxation time τ can be obtained from these experiments.

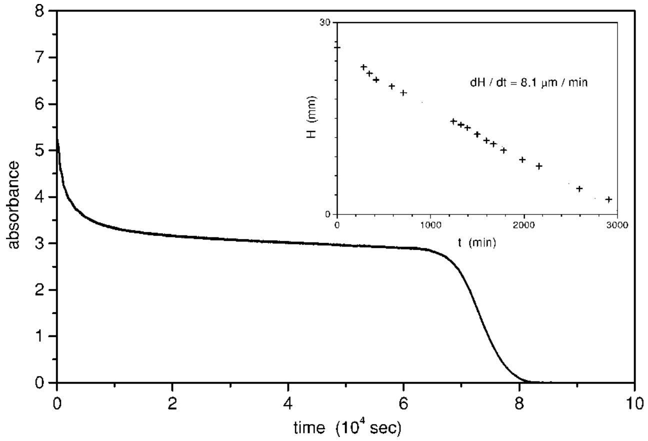

FIG. 4. Relaxation kinetics of the photoinduced visible absorption in gels (HCl acid, 0.6-mm optical cell, observation at $\lambda = 700$ nm). A decrease of the dark column height H in the cell with time is shown in the inset of the figure.

The analysis of the set of equations (1) and (2) shows that this model successfully fits the experimental data at relatively small doses [see the dashed curve in Fig. 3(a)]. In the limit of small light doses and a low charge loading the efficiency of the charge separation process can be obtained from the initial slope of the experimental curve $\eta = (1-T)^{-1} \cdot dN_{\mathrm{electrons}}/dN_{\mathrm{photons}}$, where $T = \exp(-\alpha_1 l)$ is the initial sample transmission. This extrapolation applied to experimental data in Fig. 3(a) results in a high value of the trapped electron quantum yield of $\eta = 0.46 \pm 0.04$. This can be compared to the electron yield in TiO$_2$ colloids, which is below 16% [8]. In the nanosized particles, the recombination of free charge carriers dominates because of the space confinement effect. The gels composed of macroscopic polymer-like chains pose fewer restrictions on elementary charge movement. For this reason, the probability of the free electron-hole pair annihilation immediately after creation is expected to be lower in these gels than in the colloids. However, the structural disorder decreases the electron-hole mobility, which favors recombination [28]. This may explain the fact that $\eta < 1$. Another factor, which may affect η, is the free hole lifetime relative to trapping: the shorter the lifetime, the higher is η. Inserting efficient hole scavengers in the gel structure is a way to increase the quantum yield of the electron trapping. The structural disorder as well as the hole removal efficiency apparently reflect the local gel nanostructure and depend on the preparation conditions. A study is underway to verify this assumption.

Figure 3(b) shows experimental results in the range of large laser doses. The two-parametric (η, τ) theoretical model fitted to the initial slope and the maximum $N_{\mathrm{electrons}}$ (related to the cell absorbance at long irradiation times) is also presented in this figure by a dashed curve. One can see that this theoretical curve does not agree with the experiment at intermediate times. Moreover, the relaxation time τ, obtained from this fit, appeared to be much shorter than the experimental value, measured when the laser beam is switched off (see Fig. 4 and the discussion below).

It is remarkable that kinetics curves in Fig. 3 corresponding to significantly different laser intensities coincide over a wide range of irradiating doses, i.e., the creation of trapped electrons is a pure photochemical process depending on irradiating dose rather than on intensity and irradiation time separately. This signifies that the right-hand side of Eq. (1) is linear with respect to intensity and the relaxation term b/τ can be omitted. Equation (1) then reads

$$\partial b/\partial t = \eta(a_0 - b)\sigma_a I. \tag{3}$$

To complete the general model (2) and (3), we have considered two hypotheses: (a) at high electron concentrations (long irradiation), fast electron-hole recombination in gels decreases the yield of the trapped charges, and (b) absorption of laser photons in the dark continuum induces losses of the trapped electrons.

(a) We consider the first hypothesis. According to Refs. [8,11,29–31], the electron-hole recombination proceeds rapidly on the picosecond-to-nanosecond time scales in titanium oxide nanoparticles. This process, not significant in the beginning of the irradiation process, may occur in gels at higher charge loadings. However, the recombination of free charges can be excluded because this is a feature of a single excitation event and its rate does not depend on the irradiation time and on the dose. Indeed, because each laser pulse creates the same number of e^-/h^+ pairs in the gel, the recombination of the free charge carriers may only decrease the quantum yield η of the trapped electrons. On the other hand, recombination of free holes generated during the laser pulse with already trapped electrons may increase with the irradiation time. It can be shown that this process is described by substitution of η by $\eta(1+b/b_C)^{-1}$ in Eq. (3), where b_C stands for the critical concentration of the filled traps, and η is for the low-dose trapped electron yield.

(b) Next we consider the second hypothesis. From Fig. 1, we see that the trapped electrons absorb UV laser photons. This results in the liberation of traps. The reexcited electrons possess a high kinetic energy, which is much higher than that of the newly excited conduction-band electrons. These energetic electrons may leave the gel structure and be solvated. This process results in a decrease of the broad continuum absorption. The dose-dependent relaxation term can be expressed as $-\eta_q\sigma_b bI$, where η_q stands for the electronic trap depopulation yield.

With the above assumptions, the kinetic equation (3) then becomes

$$\partial b/\partial t = \eta\sigma_a I(a_0 - b)/(1 + b/b_C) - \eta_q\sigma_b bI. \tag{4}$$

Although both terms in Eq. (4) depend on intensity, their functionalities are different. Detailed analysis of the experimental data shows that the second hypothesis of the trap liberation by absorption of UV photons allows us to explain the experimental darkening kinetics. The numerical solution of Eqs. (2) and (4) with $b \ll b_C$ and $\eta_q=0.043$ is shown by the solid curve in Fig. 3. The absorptions cross sections σ_a and σ_b were measured separately and used in the model, as well as the initial titania concentration $a_0=4.3\times10^{20}$ cm^{-3}, as fixed parameters. The theoretical curve is in very good agreement with the experiment. This result shows that ~4.3% of the trapped electrons are lost after absorption of 3.5-eV photons.

The experiment ascribes to the trapped electrons a long lifetime. There is a strong indication that this relaxation process is due to the solvated oxygen, which is known as an efficient electron scavenger. Elimination of oxygen involves a radical chemistry, which completely restores the gel transparency. The basic reactions are

$$e_{tr}^- + O_2 + H^+ \rightarrow HO_2,$$

$$e_{tr}^- + HO_2 + H^+ \rightarrow H_2O_2.$$

At high electron loadings, an additional reaction can appear,

$$e_{tr}^- + 1/2H_2O_2 + H^+ \rightarrow H_2O.$$

As a result of the oxygen consumption, after a prolonged UV-light illumination, the gel relaxation time can progressively increase. A representative relaxation curve after the UV irradiation is presented in Fig. 4. In this experiment, the 0.6-mm quartz optical cell has been filled with the gel of $a_0=4.3\times10^{20}$ cm^{-3} and irradiated at 355 nm until the absorbance at ~700 nm reaches 5.3. After that, the laser was switched off and the sample absorbance was measured. Detailed analysis of the relaxation process is beyond the scope of the present communication. Here we only briefly describe its main features. Bimodal relaxation kinetics can be evidenced from Fig. 4. The initial relatively rapid nonexponential decay component seems to be of a recombination nature. This relaxation is not complete and terminates on a plateau at a relatively high absorbance level. The subsequent decay is very slow and corresponds to the lifetime of $\tau_e > 10^6$ s. In the absence of oxygen, this slow decay of the visible absorption dominates at long times. Ti^{3+} centers in these conditions are conserved for many months. On the other hand, if oxygen diffusion into the gel structure is allowed, the relaxation is faster. A stepwise decrease of the absorbance at $t\approx7\times10^4$ s in Fig. 4 is due to the atmospheric oxygen, which enters the cell through a nonhermetically fitted cover. As a result, the gel bleaching was observed propagating downward of the cell. This change in the height H of the dark column versus time is shown in the inset of Fig. 4. We note that the characteristic relaxation time in these gels is found much longer than that reported in Ref. [4]. The reason is that the nitric acid has been previously used for the gel preparation.

Gels, in contrast to solids, are very elastic compounds. Moreover, because of its polymer nature, the gel can be considered on a microscopic scale as a linear object. The free particle state is always unstable in the 1D potential, which promotes relaxation toward the self-induced distorted lattice minimum. In this sense, the filled traps O^- (h^+) and Ti^{3+} (e^-) may be considered as small 1D polarons. This may explain the efficient trapping and slow recombination of charge carriers.

Our results show that the critical trapped electron concentration [in terms of Eq. (3)] is higher than $b_C/a_0 > 0.2$. In this last case, the mean distance between two Ti^{3+} centers is less than three Ti^{4+}-O-Ti^{4+} distances. The conduction-band electron in titanium oxide solid is heavier than the valence-band hole and its localization is expected to proceed faster [32]. The hole, on the other hand, may move over a longer distance in the gel structure. We estimate a free path length of a newly created hole before it is trapped. Because the distance Ti-O is 0.177 nm (terminal OR groups), 0.203 nm (with two

Ti-O bridges), and 0.223 nm (with three Ti-O bridges) [33,34], we estimated this distance as $l_h \leqslant 1$ nm (we considered that $l_{\text{Ti-Ti}} = 2l_{\text{Ti-O}}$). It can be shown that l_h is considerably smaller than a free hole displacement during a typical electron-phonon relaxation time of $\sim 1-10$ ps. Supposing that a free hole moves by the diffusionlike process (that is, making N steps it distances by $\sqrt{N}$ from the starting point), the free hole is trapped after no more than four scattering events. This indicates an extremely high degree of the structural disorder in gels.

Finally, the limiting concentration of the trapped electrons b^* in the gel solid structure can be estimated. In fact, trapped electrons are nonhomogeneously distributed in the sample and their mean concentration $\overline{b} = (1/l)\int_l b(x)dx$ is smaller than the maximal local concentration. For the measured absorbance of 9.0 ($\sim$700 nm, $l=1$) in gels with $[\text{Ti}^{4+}]_0 = 4.3 \times 10^{20}\ \text{cm}^{-3}$ using Eqs. (2) and (4), we have calculated the maximal local electron loading of 0.14 e^-/Ti^{4+}. The limiting concentration of the trapped electrons is then $b^* \geqslant 6 \times 10^{19}\ \text{cm}^{-3}$. This is an order of magnitude higher than the limiting electron loading of titanium oxide sols of the finest nanoparticles ($2R = 1.5$ nm) calculated as 0.012 e^-/Ti^{4+} in Ref. [9].

Earlier, electron trapping on Ti(IV) sites has been reported in monolithic titanium dioxide gels with a lower efficiency of 1% [35]. Apparently, this effect is very sensitive to a particular method of the sample preparation. An efficient scavenging of holes may strongly decrease the fluorescence intensity due to free charges recombination and increase the trapped electrons yield. We remark that in contrast to [35], no fluorescence has been observed under the band-gap irradiation in our samples. Moreover, EPR and electron absorption spectra of our samples, as well as the band-gap energy, are different from that reported in Ref. [35], which suggests different gel microstructure.

IV. CONCLUSION

In conclusion, we report on the light interaction with a new class of media—wet gels. The separation of charges with a quantum efficiency of 46% appears under the band-gap illumination of titanium oxide gels (absorption cross section of trapped electrons is taken from Ref. [9]): the electrons are stored in the gel network as small polarons, Ti^{3+} centers, whereas the holes are stored in the liquid phase as H^+ ions or radicals ($\text{Cl}^\bullet$). The gel structure possesses a very large number density of the electron traps. Under a prolonged UV-laser irradiation, more than 14% of Ti^{4+} centers can be converted into Ti^{3+}. Their lifetime can be as long as several months in the absence of oxygen. The trapped electrons are responsible for a "dark" absorption continuum in the spectral range from 350 nm to 2.5 μm. The observed effect may be particularly interesting for optical memory and micromachining applications.

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