Emission Spectra and Lifetimes of R6G Dye on Silica-Coated Titania Powder

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Introduction

Many molecular species adsorbed on semiconductor surfaces show photochemical reactivity. These photosensitization processes attract a lot of attention from a practical point of view for uses such as solar energy conversion.[1−3] The organic molecule is excited by light and injects an electron into the conduction band of the semiconductor. This allows conversion from visible light to electric current. The inverse process, that is, electrons at the semiconductor surface are scavenged by the ubiquitously present molecular oxygen, results in the degradation of the dye.[4] Since the electron transfer rate is much faster than the radiative lifetime, the fluorescence efficiency for emission is strongly reduced to a few percent. If a high fluorescence efficiency close to a semiconductor surface is required, the dye or the host solid must be shielded, for instance, by coating the semiconductor, such as titania (TiO_2) in the form of photonic crystals, with an insulating layer.

Photonic crystals are three-dimensional composites of dielectric materials with a periodicity on length scales of the wavelength of light. Due to the periodic variation of the refractive index, the crystals possess a photonic band structure, which can lead to a photonic band gap: a frequency range for which light will not propagate in any direction because of Bragg diffraction. Currently, these crystals receive a lot of attention for the possibility to completely control spontaneous emission and the propagation of light.[5−7] An advantageous way to make photonic crystals is to use artificial opals as a template.[8,9] An inverted structure is made which consists of interconnected air spheres in a solid backbone also called inverse opals or air-sphere crystals.[10,11] To observe the effect of the photonic band gap, an emission source must be placed inside such a photonic crystal and the dielectric material should exhibit a high refractive index. Examples of emission sources are quantum dots, rare earth ions, or (laser) dyes. These compounds have to meet severalrequirements to be useful as an emission probe in a photonic crystal.[12,13] They should have a high quantum efficiency and a broad inhomogeneous emission spectrum and be bleachable. Because organic laser dyes such as rhodamine 6G (R6G) meet all of these requirements, they are suitable light sources. In solution, R6G has a quantum efficiency of 95% almost independent of solvent and temperature.[14,15] To create a high refractive index contrast, we have developed an inverse opal of titania, that has a refractive index[10] of $n = 2.7$ and is in crystalline form transparent at visible wavelengths. To put the light source inside our crystals, we adsorb them on the internal titania−air interfaces.[16,17] But dye on a titania surface is not an efficient emitter. Because of the fast electron transfer, the quantum efficiency of the dye is reduced, which precludes an absolute determination of the radiative decay rate that probes the photonic band gap. To prevent the electron transfer, we should find a way to shield the dye from the semiconductor surface.

Titania is also used in the paint industry, because of its white appearance. Due to its high refractive index and small grain size, it scatters light strongly. Here, a major concern is photodegradation of pigments adsorbed on titania, which takes place under ultraviolet and visible light illumination. To improve the weathering resistance of the pigments, the titania usually undergoes surface treatment. The particles are coated with an insulating layer like silica (SiO_2), alumina (Al_2O_3), or a polymer.[18−20] This insulating layer shields the dye from the titania surface and thus reduces the electron tunneling probability. Van Dyk and Heyns[18] showed that treating titania powders with alumina and silica reduces the photoactivity and improves dispersion stability. Kamat and co-workers[19] have investigated the coating of semiconductor powders with a polymer in order to prevent the electron transfer. Here, it appeared that the dye dissolves into the polymer matrix and therefore comes close to the titania surface, where the tunneling probability increases and electron transfer can easily take place.

In this article, we present measurements of fluorescence emission spectra and fluorescence lifetimes of R6G dye adsorbed on titania that is coated with silica. Since coating titania air-sphere crystals, porous materials with a confined geometry, is a challenge to materials science and chemistry, we first study titania powders coated with silica. The coating of titania can be achieved by the use of tetraethoxysilane, a precursor that reacts with water under basic conditions to yield silica. Similar to this technique, zirconia, maghemite, and gold colloids can be

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coated with silica.[21−23] An interesting method to coat with silica in confined geometries has recently been demonstrated by Vossen and colleagues.[24]

The titania powders are characterized with electron microscopy. After adsorbing the dye on the powders, we measure the lifetimes and spectra of the dye to infer the fluorescence properties of the light sources.

Experimental Section

Ethanol (99.5%) and ammonia solution (31.5%) were obtained from Merck. Tetraethoxysilane (99%) was purchased from Fluka. Titania powder in the anatase crystal structure, with a mesh size of −325,[25] was obtained from Aldrich. R6G (99%) was obtained from Lambda Physik, and the solutions in ethanol were made freshly each time. Silica powder consists of 60 nm spheres prepared via a microemulsion technique.[26] The scanning electron microscope (SEM) images were taken with an ISI DS-130 scanning electron microscope, after sputtering the samples with a thin layer of gold.

Coating. The coating reaction was performed in plastic centrifuge tubes to prevent nucleation on a glass wall. Titania (1 g) was suspended in 10 mL of ethanol. Ammonia (1.5 mL) was added, and the suspension was stirred for 15 min. Three portions of 1.86 mL (8.3 mmol) of tetraethoxysilane were added, with intervals of 20 min, under vigorous stirring, and the suspension was stirred gently overnight. The amount of tetraethoxysilane was varied from 0 to 3.71 mL/1 g titania. This corresponds to an amount of 0−1 g silica/1 g titania. The next morning, the suspension was first centrifuged and then decanted before the slurry was resuspended in fresh ethanol. This procedure was repeated four times, and finally the powder was dried in an oven at 50 °C for more than 10 h.

Doping. Coated or uncoated (0.25 g) titania powder or pure silica powder was suspended in 5 mL of R6G solution (10^{-7} M in ethanol). The suspension was stirred for 30 min before it was centrifuged and resuspended in ethanol once. The coated or uncoated titania powder was dried in an oven at 50 °C for several hours.

Emission Spectra. Samples were placed on a glass slide, and all measurements were done at room temperature. Fluorescence spectra were obtained by exciting the dye with a 532 nm laser beam obtained from a frequency-doubled pulse-compressed mode-locked Nd^{3+}:YAG (Spectra Physics) laser. The spectra were collected with a Carl-Leiss prism spectrometer, equipped with a photomultiplier tube protected against stray light by a Schott OG570 filter. The emission spectrum is recorded from 11750 to 18350 cm^{-1}. The spectral resolution was 100 cm^{-1}. Self-absorption of the dye is excluded because of the very low dye concentration used.

Lifetime Measurements. The emission lifetimes of the dye adsorbed on the powders were obtained using a time-correlated single-photon counting technique.[27] The dye was excited with a frequency-doubled pulse-compressed mode-locked Nd^{3+}:YAG laser emitting 3 ps pulses at 12.5 ns intervals. The excitation spot size is 0.3 mm in diameter. The fluorescence was detected at the peak fluorescence with a Hamamatsu R3809U Micro Channel Plate detector (MCP). The signal from the MCP is amplified and fed to a constant fraction discriminator, time to amplitude converter, and multichannel analyzer (MCA). The time difference between the MCP signal and the excitation pulse was recorded by the MCA. With this setup, a time resolution of 55 ps is achieved.

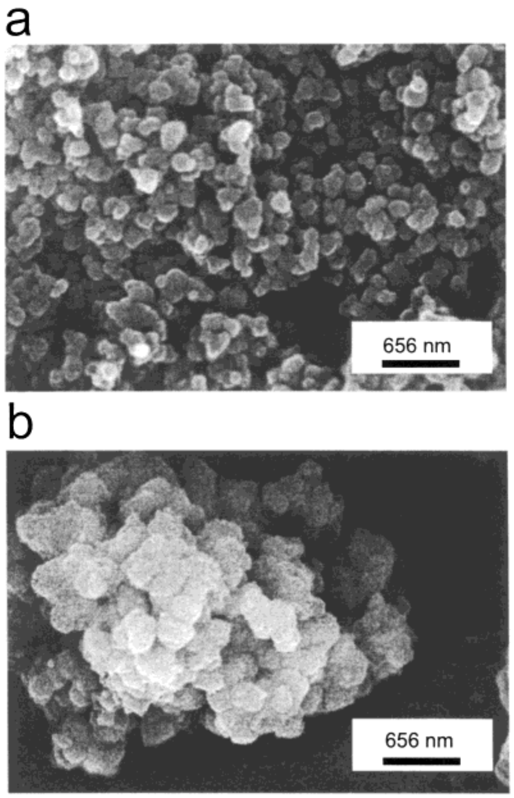

Figure 1. Scanning electron micrographs of (a) uncoated titania powder and (b) titania powder coated with 1 g of silica per gram of titania. The particle size of the uncoated titania is about 100−250 nm in diameter. The diameter of the coated titania particles is about 200−400 nm, and the particles seem more clustered together by the silica.

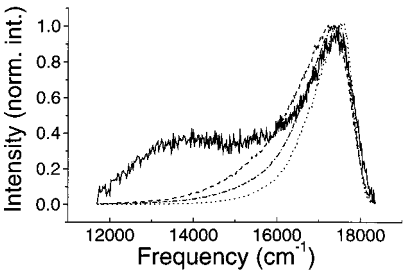

Figure 2. Fluorescence spectra of R6G adsorbed on coated titania, uncoated titania, and silica. The solid curve is uncoated titania, the dashed curve is 0.02 g silica/1 g titania, the dotted curve is 0.5 g silica/1 g titania, and the dashed−dotted curve is pure silica.

Results and Discussion

Images a and b of Figure 1 show SEM pictures of uncoated titania and titania coated with 1 g of silica per gram of titania, respectively. The difference between both powders is clearly seen, since they are at the same scale. The particles of the uncoated titania are about 100−250 nm in diameter. The diameter of the coated titania particles is larger, about 200−400 nm. The coated titania particles appear to be clustered together. Possibly, the silica coating encloses more than one titania particle and covers groups of particles.

The emission spectra of R6G are shown in Figure 2. The spectra are normalized to the peak intensity. For comparison, the spectra and lifetimes of R6G adsorbed on

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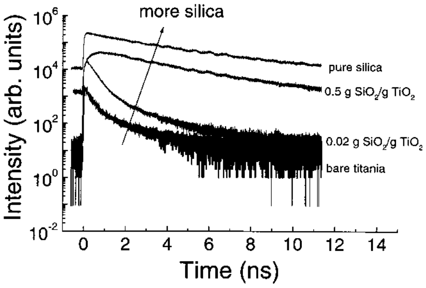

Figure 3. Time-resolved fluorescence of R6G adsorbed on uncoated titania, titania coated with 0.02 g silica/1 g, titania coated with 0.5 g silica/1 g, and pure silica. An arrow indicates the increasing amount of silica. The lines are offset for clarity.

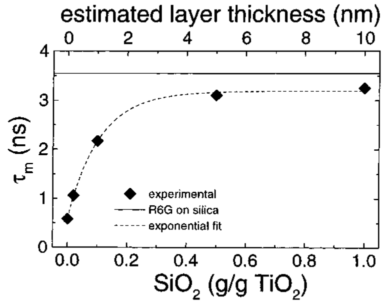

Figure 4. Mean lifetime of R6G, obtained from Figure 3, versus the amount of silica coating represented as diamonds. An exponential fit through the data points, with a 1/e value of ~2 nm, is indicated with a dashed curve. The straight line at 3.55 ns is the lifetime of R6G on pure silica. On the upper axis, the estimated layer thickness in nanometers is displayed.

pure silica are measured; they resemble those of R6G in solution. With decreasing layer thickness, especially for the uncoated titania, there is relatively more fluorescence intensity in the red. Kay and Grätzel[28] ascribed such a shift to the interaction of the dye with the polar titania surface. It has also been suggested that the red fluorescence band is the result of a new emitting species.

The influence of the electron transfer from the excited state of the dye to the conduction band of titania can be probed by the excited-state lifetime, as displayed in Figure 3. An arrow indicates increasing amounts of silica. The lifetime of R6G on pure silica, the upper curve, is obtained from a single-exponential fit and is 3.55 ns. Comparing this value with a lifetime of 3.62 ns measured for R6G in ethanol,[15] we conclude that R6G on silica has a high quantum efficiency (93%) as expected, since silica is considered an insulator.[2] The decay of R6G on bare titania is fast and not single exponential. We obtain a mean lifetime for this sample of 0.58 ns.[29] The curve for the sample that was coated with 0.02 g silica/1 g titania still shows a fast decay component, but the sample with 0.5 g silica/1 g titania resembles the R6G on pure silica. Although there is a peculiar ingrowth in this curve that is not yet understood, the mean lifetime of 3.11 ns almost matches the lifetime of R6G on pure silica. Coating the titania with silica shows that the lifetime increases with increasing amount of silica.

In Figure 4, the relation between the mean decay time and the amount of silica relative to titania is given. The error bars for the data points are comparable to the symbol size. The straight line at the top of the graph is the lifetime of R6G on pure silica. The dashed line is an exponential fit through the measured data points with a 1/e value of ~0.2 g silica/1 g titania. The lifetime tends to the value of R6G on silica with increasing amount of silica. This exponential behavior is expected if we assume that the insulating silica layer acts as a barrier for the electrons and the tunneling probability decays exponentially with the layer thickness.

On the upper axis, the estimated layer thickness is shown. These values are calculated by assuming that the yield from the reaction of tetraethoxysilane to silica is 100%. We estimate the specific surface area, which manufacturers do not specify, to be 50 m^2/g.[30] We suppose that the silica forms a homogeneous layer on the titania surface. With these values, we can calculate the thickness of the silica layer. The 1/e value of the exponential fit corresponds to a thickness of ~2 nm.

Because the adsorption of R6G on titania is different from the adsorption of R6G on silica-coated titania, the emitter concentration is different for each sample and therefore determining the rate constants from the fluorescence intensities is a challenge. If we then make the hypothesis that the radiative decay rate stays constant and the lifetime for R6G in ethanol corresponds with an efficiency of 95%, we can deduce the quantum efficiency for the different powders. This corresponds to quantum efficiencies of R6G on bare titania of 15%. For 5 and 10 nm coated titania powders, quantum efficiencies of nearly 85% are obtained. The latter values are very close to the ideal case where there is no quenching. From these results, we can conclude that a 5 nm layer (or 0.5 g silica/1 g titania) is thick enough to prevent electron transfer.

Recently, Tada et al.[31] have observed that a monolayer of silica, ~0.2 nm, has a promoting effect on photochemical reactions at titania surfaces of R6G in solution.[31] The thin silica layer significantly increases the adsorption of the organic species, while the electron transfer is enhanced because the concentration of the dye near the titania sites is higher relative to the solution concentration. In a dry condition, however, where there is no diffusion, they demonstrated that R6G on coated titania behaves similar to the coated powders of our experiment.

Conclusion

We have shown that it is possible to shield a dye from a semiconductor surface by coating this surface with an insulating layer. By coating titania particles with an insulating silica layer, we recover the quantum efficiency by suppressing the electron transfer from the excited state of R6G to the conduction band of titania. The titania particles are coated with silica by the use of a sol−gel technique, and the coated titania particles appear to be bigger in diameter than the uncoated particles. The decay of R6G on bare titania is not single exponential and has a very short decay time of 0.58 ns corresponding to a quantum efficiency of ~15%. With an increasing amount of silica and so an increasing thickness of the silica layer, the lifetime of the R6G increases. We were able to achieve a lifetime of 3.25 ns for R6G on titania coated with 1 g silica/1 g titania, almost resembling the lifetime of R6G on pure silica. This 10 nm thick silica layer on titania yields a quantum efficiency of 85% that is approaching the 95% for R6G in ethanol.

With this result, we are now working on coating the inner surface of our photonic titania air-sphere crystals.

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After adsorption of the dye on the surface, we are in an excellent position to investigate inhibited emission lifetime effects.

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