Temperature Dependence of the Luminescence of TiO$_2$ Powder

L. Forss, M. Schubnell

Paul Scherrer Institut, Würenlingen-Villingen, CH-5232 Villingen PSI, Switzerland (Fax: +41-56/98 23 27)

Abstract. The temperature dependence of the luminescence quantum yield of powdered titaniumdioxide in vacuum, nitrogen, and water vapor, respectively, was measured in the temperature range 300 K to 800 K. The observed luminescence is attributed to luminescence from surface states. We find that the luminescence is thermally quenched, as predicted by a simple model. Furthermore, the luminescence is shifted towards shorter wavelengths with increasing temperature. We also observed that the luminescence in vacuum is weakly quenched in the presence of nitrogen or water vapor.

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Direct conversion of solar energy into chemical energy has been the goal of much research for the last twenty years. One can think of two principally different ways to achieve this, thermochemically or photochemically. One could also consider a combination of both. To decide whether a chemical reaction occurs photochemically, one can think of several criteria that have to be fulfilled:

• The reaction should only occur when the light is on. This criterion is not sufficient especially for a solid-state reaction running in solar concentrators in which very high temperatures can occur. Direct irradiation of particular sytems can heat up the particles to a considerably higher temperature than the surrounding medium and thus lead to thermochemical reactions. To make an accurate statement about whether the reaction occurs photochemically in such a system one would have to know the temperature on the surface of the particles.
• A photochemical reaction should depend on the exciting wavelength as a photochemical system must have a band gap and should therefore only react when the energy of the photons is greater than the band gap.
• A photochemical system that is able to store solar energy should also show a certain degree of luminescence, as a fraction of the excited states must decay radiatively [1].

This paper is concerned with the last point.

Ries and Smestad [2] have shown that the chemical potential of the excited states can be calculated if the luminescence quantum yield of the system is known. When the band gap is larger than kT (i.e., the Wien approximation holds) the chemical potential can be calculated according to

$$\mu = kT_0 \ln \frac{J_{\text{Abs}}(T_0)}{J_{\text{BB}}(T_0)} + kT_0 \ln \Phi(T_0). \tag{1}$$

T_0 is the temperature at which the reaction occurs, J_{Abs} is the number of absorbed photons, J_{BB} is the number of absorbed photons absorbed from black-body radiation at T_0, μ is the chemical potential of the excited states compared to the chemical potential of the ground state, and Φ is the photoluminescence quantum yield. Ries and Smestad calculated the potential one can expect for some semiconductor electrodes and photovoltaic cells from their luminescence properties and found excellent agreement. They also predicted the luminescence quantum yield of silicon and pyrite from their open cell voltages.

The predicted decrease of photoluminescence with applied potential on photoelectrodes has been observed on photoelectrodes of GaAs, CdS, CdTe, and ZnO [3, 4]. In the same paper results are shown which give evidence that the photoluminescence on cadmiumsulfide electrodes is independent of the applied potential. However, it is also observed that the photocurrent hardly changes with applied potential, i.e., the created potential within the bulk is not sufficient to overcome some resistance between the bulk and the surface and therefore cannot be converted. This demonstrates that photoluminescence is required for a system to be able to convert light into storeable Gibb's free energy, but is not a sufficient criterion. On the other hand, if we do not observe any photoluminescence the loss processes are high. In this case we therefore expect the conversion efficiency of solar radiation to be small.

According to (1) the maximum free energy gain that can be obtained by a photochemical process at any temperature can be estimated by measuring the photoluminescence quantum yield. No luminescence would mean no chemical

potential. However, the luminescence quantum yield may be very low for large band gap systems that are still capable of producing a considerable chemical potential.
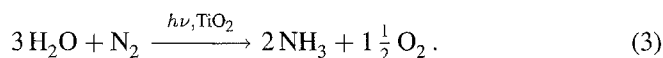
Titaniumdioxide has been used in many reactions proposed for solar energy conversion [5–12].
The two reactions that interest us most are:

- Photoconversion of water to hydrogen and oxygen [6, 10–12]

$$H_2O \xrightarrow{h\nu, TiO_2} H_2 + \frac{1}{2}O_2. \tag{2}$$

- Photoconversion of nitrogen and water to ammonia and oxygen [12]

$$3 H_2O + N_2 \xrightarrow{h\nu, TiO_2} 2 NH_3 + 1\frac{1}{2}O_2. \tag{3}$$

This reaction has also been done with Fe_2O_3 as a photocatalyst [13].

These reactions were all performed at one sun or at laboratory conditions. We, on the other hand, are interested in the conversion of concentrated solar light, i.e., irradiance in the order of $3\,MW\,m^{-2}$ and temperatures above $1000\,K$.

As mentioned above, a system that luminesces should be able to convert solar photons into chemical energy. The purpose of this study was to investigate the effect of increasing temperature on the luminescence of a system that has been shown to convert solar energy at 300 K.

TiO_2 has been widely used for experiments related to solar energy conversion [8, 14, 15]. Furthermore, TiO_2 has been shown to luminesce at room temperature or below under various conditions [16–18]. The luminescence has been described as transitions from surface states and is sensitive to adsorption of gases such as oxygen or water that quench the luminescence [19]. Titaniumdioxide also shows electroluminescence [20, 18] with a spectral distribution below the band gap, i.e., luminescence also occurs from levels within the bandgap. The quantum efficiency in these experiments was very low, suggesting efficient nonradiative recombination. As far as we know there have been no studies about the temperature dependence of the luminescence of powdered TiO_2 at temperatures above 300 K. In [19] Hashimoto et al. described that the intensity increased steadily with decreasing temperature and became almost constant below 77 K. They also observed an excitation spectrum that extended up to 600 nm and corresponds to the luminescence spectrum from the surface states.

In this paper we investigate the temperature dependence of the photoluminescence of TiO_2 powder in the temperature range from 300 K to 800 K.

Experimental

250 mg TiO_2 (anatase), as obtained from FLUKA, was suspended in 10 ml water and sonicated for 5 min. 200 μl of this suspension was dropped onto a round 1 cm diameter quartz disk and let dry slowly for two days. In this way one obtains a homogeneous film of TiO_2 on the quartz disk. The procedure is similar to the one used by Calzaferri et al. [21].

The TiO_2 was irradiated by the third harmonic of a Q-switched Nd:YAG laser (355 nm) with pulses of 10 ns
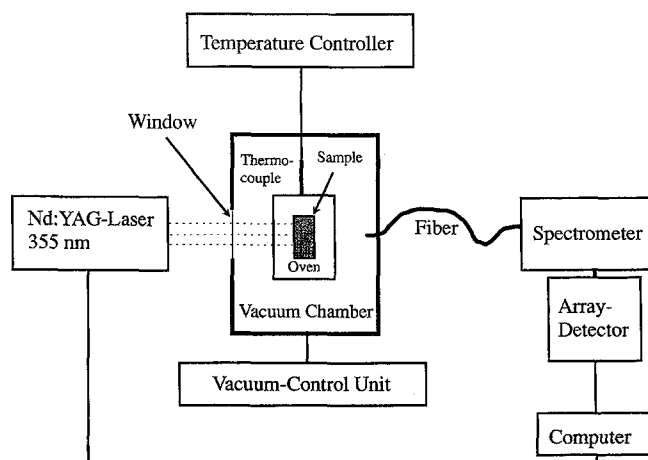

Fig. 1. Experimental setup to measure luminescent radiation

and an energy of about 1 mJ per pulse. The luminescent radiation is collected with a quartz fiber, diffracted in a 25 cm spectrometer and detected with a cooled optical multichannel analyzer (OMA). The laser excitation light was cut off with a band edge filter. Detection of the luminescent radiation started synchronously with the laser pulse and lasted for 10 ms. The thermal noise was recorded 50 ms later, again during 10 ms. The net signal is then calculated by subtracting the counts collected in the second time period from the counts collected in the first interval. The UV-radiation absorbed by the TiO_2 sample was measured as the difference to a calibrated reference reflectance standard (Spectralon). The sample compartment is a vacuum chamber that can be flushed with various gases. The sample is mounted in a cavity of a copper block that can be heated electrically up to 800 K. The temperature of the sample is controlled with a PT100 resistance thermometer, The experimental setup is shown schematically in Fig. 1. Details of the used apparatus were described in [22].

Results

In Fig. 2 we show the luminescence spectra of TiO_2 at 10^{-5} mbar at temperatures between 300 K and 750 K. The peak at 2.3 eV is a reflection of the second harmonic of the Nd:YAG Laser. We could not observe the expected band edge luminescence at about 400 nm. The observed broad luminescence band between 2 eV and 3 eV is in agreement with others [19] thought to be luminescence from surface states. With increasing temperature the luminescence clearly decreases.

A more detailed analysis of the temperature dependence reveals that the luminescence spectrum at high temperature is shifted to the blue, as seen in Fig. 3. In Fig. 4 we show an energy-level diagram with that we try to explain this effect. With increasing temperature the absorption edge of the semiconductor is red-shifted as the vibrational levels above the valence band become occupied. The temperature distribution in the excited surface states also becomes broader and thus occupies higher states that contribute to the shift of the luminescence spectrum toward shorter wavelengths.
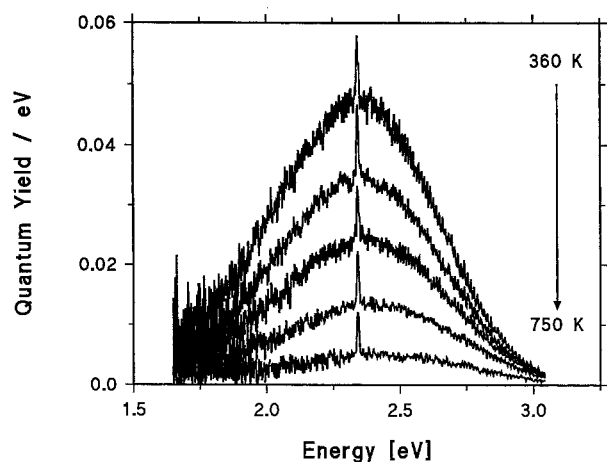
Fig. 2. Luminescence spectra of TiO$_2$ in vacuum (10^{-5} mbar) at different temperatures (Excitation: 355 nm). The peak at about 2.3 eV is a weak reflection of the second harmonic of the Nd:YAG laser
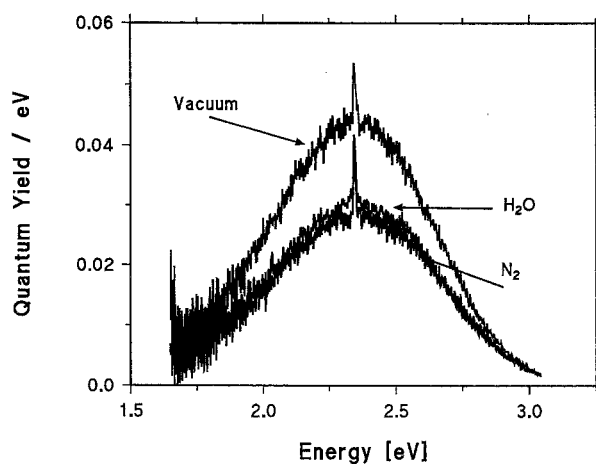

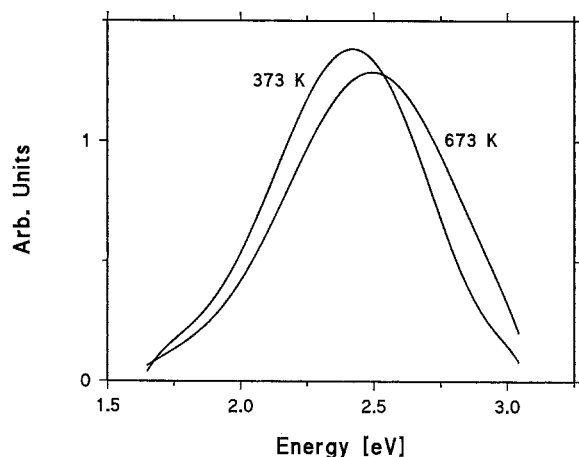**Fig. 5.** Luminescence of TiO$_2$ at 400 K under vacuum, N$_2$ and H$_2$O

Fig. 3. Comparison between the luminescence spectrum of TiO$_2$ in vacuum at 373 K and at 673 K. The spectra were smoothened and normalized to equal area to show the difference more clearly
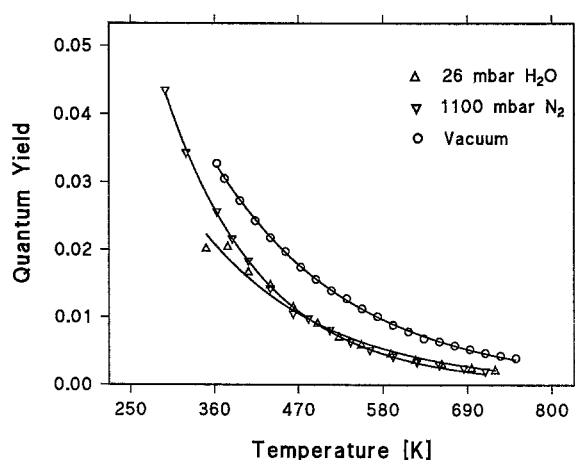

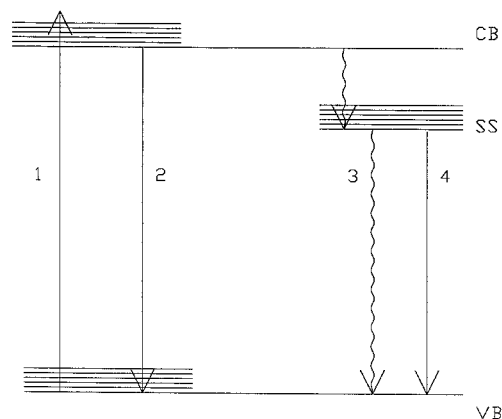**Fig. 6.** Temperature dependence of the quantum yield of powdered TiO$_2$ (Excitation: 355 nm)

Fig. 4. Energy level diagram to explain the wavelength shift of the luminescence at high temperature. Absorption (1) becomes shifted to longer wavelengths as the vibrational levels of the valence band (VB) become occupied, whereas the luminescence (4) becomes shifted to shorter wavelengths as higher lying surface states (SS) become occupied. In our experiments we did not observe any luminescence (2) from the conduction band (CB)

Therefore, we conclude that as the absorption spectrum is red-shifted with increasing temperature the luminescence should become blue-shifted, which makes sense, as it is well known that the luminescence should behave mirror-symmetrically to the absorption spectrum [23, 24].

In Fig. 5 we compare the luminescence spectra of TiO$_2$ at 370 K in vacuum, in a 1100 mbar N$_2$ atmosphere, and in 26 mbar H$_2$O. The location and the shape of the luminescence spectra are independent of the ambient atmosphere. As already mentioned, the luminescence of TiO$_2$ occurs from surface states that are very sensitive to adsorbed molecules. We can thus explain that the quantum yield is significantly lower in N$_2$ and H$_2$O atmosphere than in vacuum as adsorbed molecules can change the surface state density and maybe react with excited electrons. One is tempted to explain the quenching of the luminescence by water with photocatalytic reduction of water by excited electrons in the conduction band of TiO$_2$. To prove this further experiments are necessary.

In Fig. 6 the integral quantum yield is plotted against temperature. The quantum yields for the TiO$_2$ luminescence

under N_2 and H_2O are almost identical whereas the quantum yield under vacuum is higher, i.e., both N_2 and H_2O quench the TiO_2 luminescence. The temperature dependence of the photoluminescence quantum yield can be explained by a model proposed by Mott and Seitz [25], and Collins and Paul [26] for the temperature dependence of the luminescence quantum yield in solids. They found that the thermal quenching of the photoluminescence can be described by

$$\Phi = \frac{1}{1 + A \exp\left(\dfrac{-\Delta E}{kT}\right)} . \tag{4}$$

In this equation ΔE is the activation energy for thermal deactivation of excited states and A is the corresponding Arrhenius constant divided by the temperature-independent rate constant for luminescent recombination.

The observation by Hashimoto [19] that the luminescence becomes constant below 77 K is consistent with this formula.

Conclusions

It has been shown that TiO_2 luminesces at temperatures up to 800 K. TiO_2 should therefore, in principle, be able to convert solar energy at temperatures up to 800 K although the photochemical conversion efficiency will decrease. We estimate that the chemical potential of the excited states in illuminated TiO_2 drops from 2 eV at 300 K to 1 eV at 800 K relative to the valence-band edge.

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