Photoluminescence of Laser-Synthesized Anatase Titanium Dioxide Nanopowders

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Abstract. Titanium dioxide (TiO_2) nanopowders were prepared by laser-induced pyrolysis. Raman scattering showed that prepared TiO_2 nanocrystals have anatase TiO_2 structure. Specific surface area of the powders varies from 84 to 110 m^2/g, while the grain size of nanoparticles is between 30 and 70 nm, depending on preparation conditions. We measured photoluminescence (PL) spectra of TiO_2 nanocrystals. Under laser irradiation with photon energy between 2.41 and 2.71 eV the TiO_2 nanocrystals displayed strong visible light emission, even at excitation power as low as 0.05 W/cm^2. The line shape and position of this broad luminescence band vary with excitation energy. As PL spectra of anatase TiO_2 can be attributed to three kinds of physical origins (self-trapped excitons, surface states and oxygen vacancies) in this paper we try to resolve which of them are dominant for different TiO_2 nanopowders of different grain size.

Introduction

Anatase TiO_2 nanocrystals have attracted much attention due to their unique dielectric, optical, and mechanical properties as well as numerous potential applications including photocatalysis, optical coating, and photoelectrochemical solar cells [1]. Photoluminescence spectroscopy as an important tool has been used to study the anatase phase of TiO_2 single crystals [2-8], thin films [9], polycrystalline powders [10], as well as nanocrystals [1, 11]. Under interband excitation, anatase TiO_2 exhibits a broad luminescence band with a large Stokes shift [3, 4, 7]. Most of the mentioned authors agree that the luminescence band can be assigned to radiative recombination of self-trapped excitons (STE). The STE are supposed to be localized on a TiO_6 octahedron, which is the unit structure of anatase TiO_2. However, the detailed mechanism of the luminescence process has not been well clarified [7]. On the contrary, Zhang et al. [1] examined the PL properties of TiO_2 nanocrystals (prepared by a hydrolysis process) excited by visible light with energy lower than the band gap of anatase TiO_2 (3.2 eV) [2] and concluded that the radiative recombination is mediated by localized levels within the forbidden gap related to surface defects residing in TiO_2 nanocrystallites. Besides PL, due to intrinsic STE and surface states, oxygen vacancies also can cause a luminescence as defect states in anatase TiO_2 [5]. This study deals with the examination of PL properties of laser-synthesized anatase TiO_2 nanopowders excited by visible light with photon energies between 2.41 and 2.71 eV.

Experimental procedure

Titanium dioxide nanopowders were synthesized by laser-induced pyrolysis, using titanium isopropoxide as a liquid precursor [12]. The produced powders were calcined in air at 500 ^{o}C for 4

hours. Specific surface area of as-produced nanopowders was measured by BET and for the samples labeled as TiS57 and TiS12 it was 110 and 84 m^2/g, respectively.

Raman measurements were performed at room temperature in the backscattering geometry using 514.5-nm line of an Ar^+ laser, Jobin-Yvon U1000 monochromator and photomultiplier as a detector.

Photoluminescence (PL) spectra were excited by six lines of Ar ion laser with photon energy between 2.41 and 2.71 eV using the same equipment as for Raman measurements. Beam power at the sample surface was between 0.05 and 0.8 W/cm^2. PL spectra were measured in air at room temperature.

Experimental results

Micrographs obtained by scanning electron microscope (SEM) for two TiO_2 powder samples are presented in Fig. 1. Mean particle diameter is about 30 nm for sample TiS57, while the dimension of particles of TiS12 sample is between 50 and 70 nm, as can be seen in Fig. 1(a) and (b), respectively.
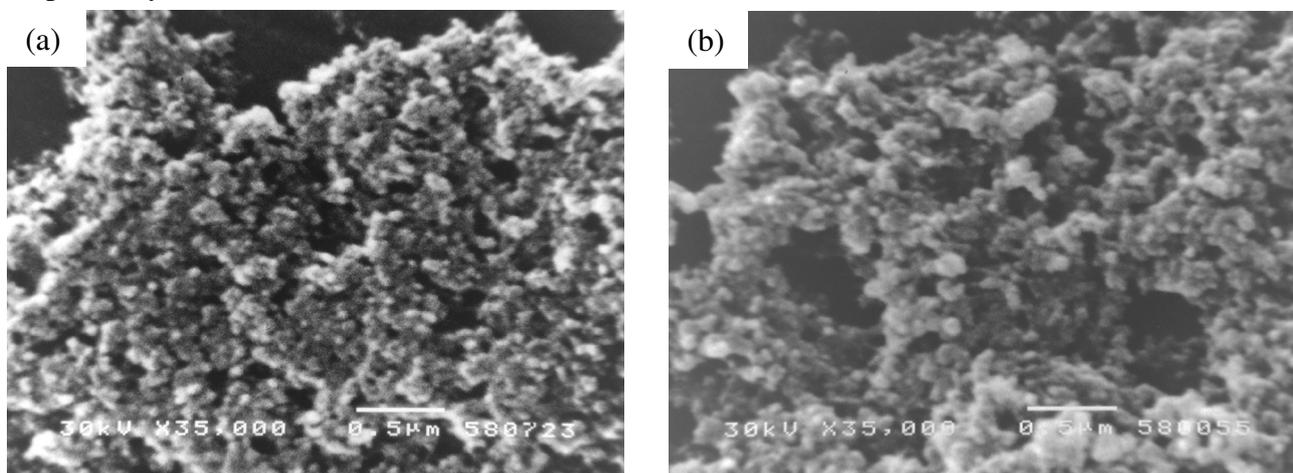
Fig. 1 Scanning electron micrographs of TiO_2 nanopowders: TiS57 (a) and TiS12 (b).
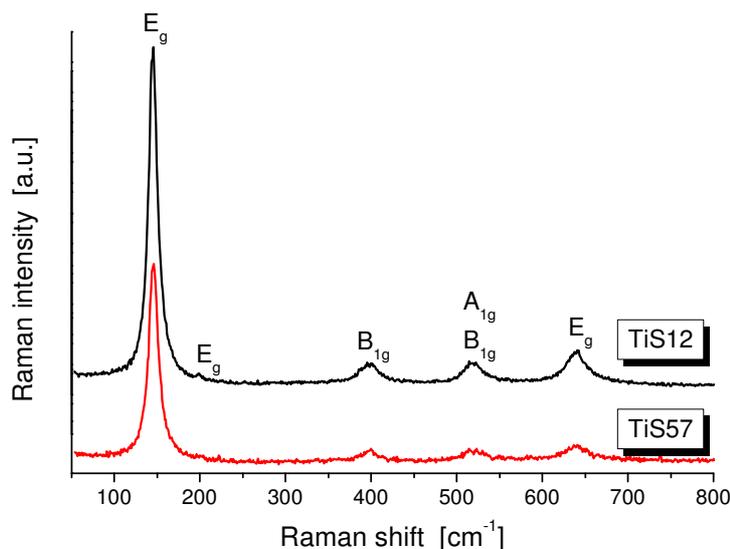
Fig. 2 Raman spectra of TiS57 and TiS12 nanopowders.

Raman spectra of TiS57 and TiS12 samples presented in Fig. 2 show that these TiO_2 nanopowders are in anatase phase. Namely, all observed Raman modes could be assigned to the Raman spectra for anatase single crystal: ~145 cm^{-1} (E_g), 197 cm^{-1} (E_g), 399 cm^{-1} (B_{1g}), 513 cm^{-1} (A_{1g}), 519 cm^{-1} (B_{1g}), and 639 cm^{-1} (E_g) [13]. Although the spectra were measured under the same experimental conditions it is obvious that the Raman modes for the TiS12 sample are more intense than those for TiS57. This is a consequence of the grain size differences in these samples. Namely, it is well known that a decrease in grain size of TiO_2 nanocrystals causes shifting and broadening of the Raman modes [13].

Laser-synthesized anatase TiO_2 nanopowders excited by visible light with photon energy between 2.41 and 2.71 eV exhibit a broad luminescence band with a maximum between 2.00 and 2.35 eV. Shape, position and intensity of this band strongly depends on the grain size and nanocrystal preparation conditions, as well as on measuring conditions (laser power and photon energy, temperature, duration of irradiation, ambient – vacuum or air, pressure).

Figure 3 shows the PL spectra for TiS12 nanopowder under 2.71 eV excitation at several beam powers. The peaks appearing at the high-energy side of the curves belong to the Raman signal of the sample. The PL signal is obviously intensified with increasing excitation power. However, the PL spectral shape does not change evidently with increased excitation power. Dependence of the PL peak intensity (I_{PL}) on the excitation power (P) and its approximation by a power-law function $I_{PL} \approx P^\gamma$ [1] are shown in Fig. 4. At lower excitation powers, a linear relationship is observed ($\gamma =1$), whereas at higher powers it becomes sublinear ($\gamma \sim 0.2$).
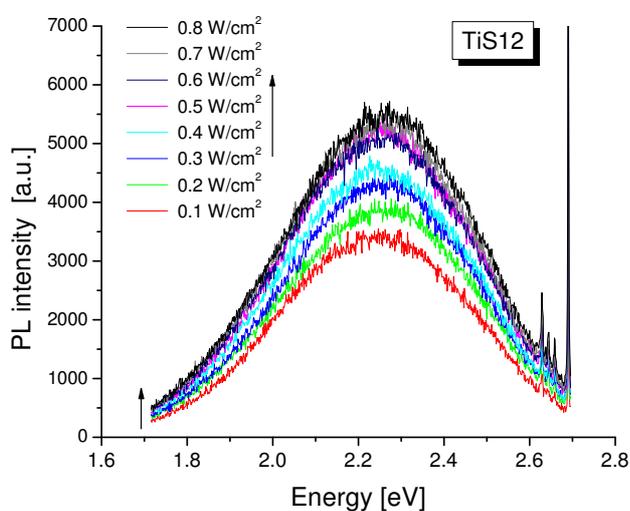
Fig. 3 PL spectra of TiS12 nanopowder at several excitation powers between 0.1 and 0.8 W/cm^2 (E_{ph}=2.71 eV).
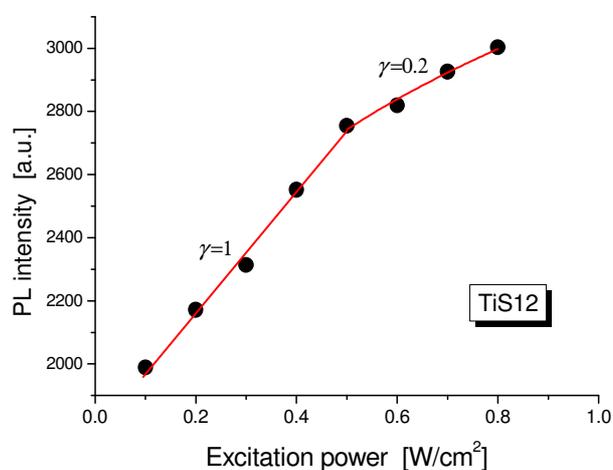
Fig. 4 PL peak intensity as a function of excitation power for TiS12 nanopowder (E_{ph}=2.71 eV).
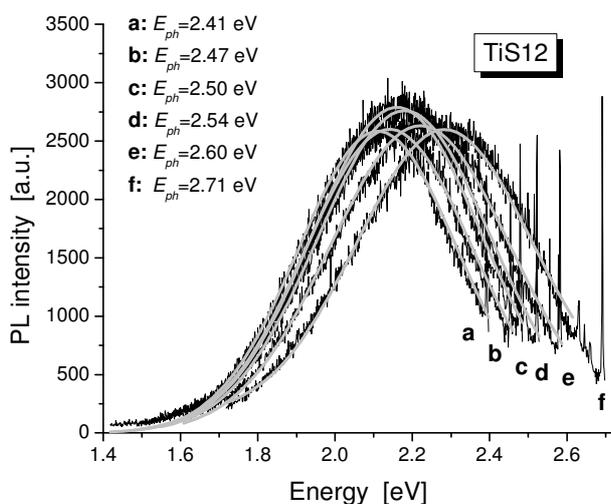
Fig. 5 PL spectra of TiS12 sample excited by several excitation photon energies between 2.41 and 2.71 eV and the same beam power.
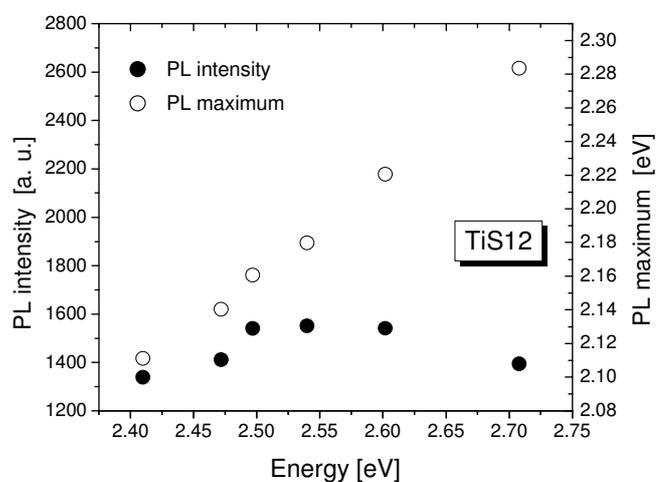
Fig. 6 Dependence of PL maximum (*open circles*) and PL intensity (*solid circles*) on excitation photon energy for TiS12 sample.

Figure 5 shows the PL spectra of TiS12 sample excited by different photon energies with the same power. All spectra (thin black lines) have similar shape and can be fitted by a Gaussian function (thick gray lines). Dependence of the PL maximum and PL intensity on the excitation photon energy is presented in Fig. 6. As the excitation photon energy was increased from 2.41 to 2.71 eV, the PL maximum was blueshifted from 2.11 to 2.28 eV, while PL peak intensity exhibits small variations.

PL spectra of TiS57 nanopowder measured under the same conditions as for TiS12 sample show considerably different behavior. Namely, dependence of their intensity on excitation power does not obey any power-law function. The reason for such irregular behavior could be found in the fact that PL intensity for TiS57 decreases rapidly with irradiation time. The dependence of PL intensity (I_{PL}) on irradiation time (t) is shown in Fig. 7 and it obeys exponential decay law.

PL spectra of TiS57 sample excited by several photon energies between 2.41 and 2.71 eV and the same beam power are shown in Fig. 8. All spectra (thin black lines) are fitted by the Gaussian function (thick gray lines), as for TiS12. However, the shape and intensity of the PL spectra for TiS57 change with increase in photon energy. This is especially pronounced for the highest excitation photon energy of 2.71 eV. For this energy, the fitting curve composed of only one Gaussian type function does not coincide well with the experimental data. This implies that PL spectra for TiS57 at higher photon energies must be fitted by a sum of Gaussian functions and it will be done in the next paragraph with appropriate explanation.

Fig. 7 Dependence of PL intensity on irradiation time for TiS57 (E_{ph}=2.71 eV).

It should be emphasized that PL band at ~ 1.95 eV assigned to oxygen vacancies in anatase TiO_2 [5] does not exist or has a very small intensity in the presented PL spectra. This indicates that both nanopowders are almost stoichiometric.
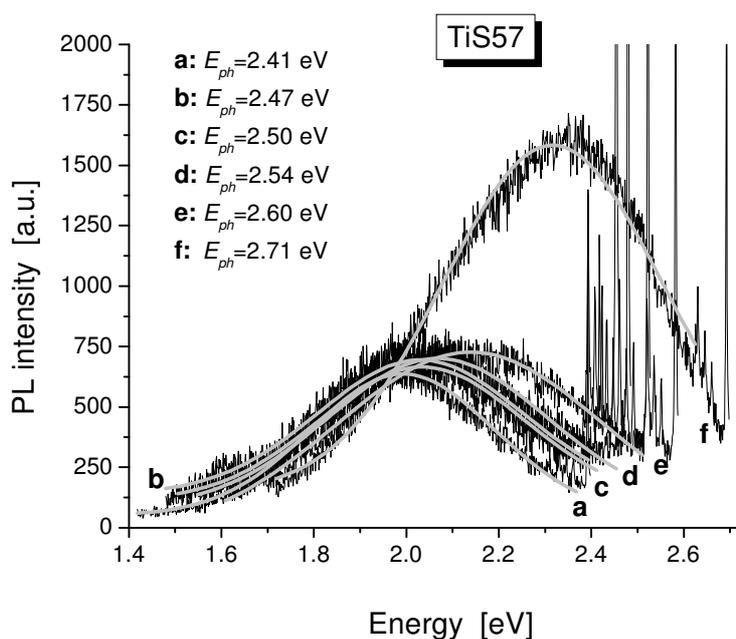
Fig. 8 PL spectra (*black lines*) of TiS57 sample excited by several excitation photon energies between 2.41 and 2.71 eV and the same beam power. All spectra are fitted by one Gaussian function (*thick gray lines*).

Discussion

Presented experimental results show that two laser-synthesized TiO_2 nanopowders with different grain size exhibit different PL properties under the same measuring conditions.

TiS12 sample has PL properties similar to the ones described by Zhang et al. [1]. The sublinear dependence of PL intensity on higher excitation power indicates that the recombination is mediated by some localized centers, which saturate at high excitation powers and thus let charge carriers recombine via competing nonradiative channels. Since no change in the spectral shape of the band with excitation power is observed, excitonic recombination in quantum dots cannot be the origin of observed luminescence. Also, the visible emission observed in TiS12 should not be explained as self-trapped exciton luminescence due to a small energy difference between the excitation photon energy and the emission maximum. With increase in excitation photon energy from 2.41 to 2.71 eV, the PL maximum blueshifts from 2.11 to 2.28 eV while the PL peak intensity has small variations. This indicates that a series of localized levels within the forbidden gap have a distribution and are suitable for luminescence, and that these levels might have nearly the same luminescence efficiency [1].

On the other hand, PL spectra of the TiS57 sample have similar shape and intensity only for lower photon energies (E_{ph}<2.61 eV), while the spectrum excited by 2.71 eV has different shape and much higher intensity (2-3 times). This spectrum is fitted by a sum of two Gaussian peaks as presented in Fig. 9. The first peak has a maximum at ~2.16 eV, while the maximum of the second
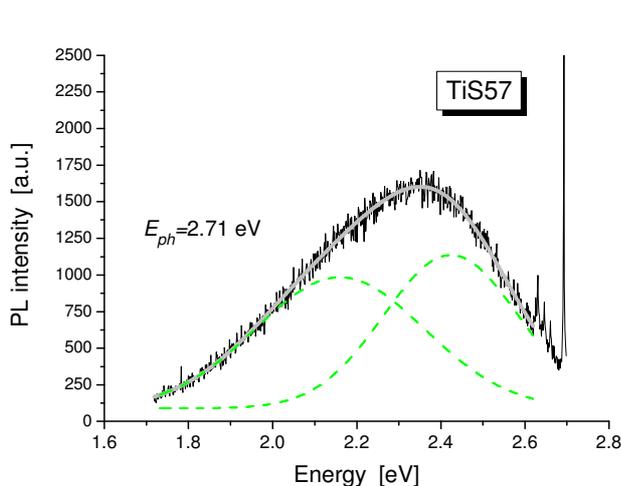
Fig. 9 PL spectrum of TiS57 (*black line*) excited by 2.71 eV. Fitting curve (*thick gray line*) is obtained as a sum of two Gaussian-type peaks (*dashed lines*).

Fig. 10 Dependence of positions and intensities of peaks on excitation photon energy for TiS57 obtained by fitting with one (*circles*) and two (*triangles*) Gaussians.

one is at ~2.43 eV. Note that the fitting curve from Fig. 9 agrees much better with the experimental results than the one from Fig. 8 obtained by fitting with one Gaussian peak. Figure 10 shows dependence of peak position and intensity on excitation photon energies in the case of fitting by one (*circles*) and two (*triangles*) Gaussian peaks. As can be seen from the figure, the position of the first Gaussian peak (in the case of fitting by two Gaussians) changes from 2.00 to 2.16 eV when the excitation photon energy changes from 2.41 to 2.71 eV. (Note that its position for E_p<2.61 eV coincides with the position of PL maximum in the case of fitting by one Gaussian.) Such a variation is very similar to the variation in the position of PL maximum for TiS12 that implies that the second

PL band in spectra of TiS57 could arise from a radiative recombination of electrons via intrinsic surface states in TiO_2 nanoparticles. On the other hand, position of the second PL band is about 0.9 eV lower than the value of the energy gap estimated from the UV transmittance measurement for this sample (3.3 eV). This allowed us to conclude that this band originates from the visible luminescence due to emission of self-trapped excitons. Namely, the STE emission is caused by strong lattice relaxation and small exciton bandwidth in anatase TiO_2, and has a large Stokes shift of about 0.9 eV [2, 9].

It is worth mentioning that the luminescence of TiS57 exhibits a large intensity decay with irradiation time because under laser irradiation, the surface composition and structure of the sample might be damaged due to the effect of overheating leading to the luminescence efficiency decay [1]. This effect is much more pronounced in the samples with smaller grain size, as they are more sensitive to laser beam irradiation.

Conclusion

We have studied the PL properties of laser-synthesized anatase TiO_2 nanopowders excited by visible light with energy lower than band gap. It is observed that the PL spectra of nanopowders with larger grain size are dominated by a radiative recombination of electrons via intrinsic surface states for all applied excitation photon energies. On the contrary, excitation of the sample with smaller nanoparticles by higher photon energies (close enough to the energy band gap) activates self-trapped exciton luminescence in anatase TiO_2 nanocrystals. Presented PL spectra of both samples did not exhibit significant presence of the PL band related to oxygen vacancies. Much larger PL intensity decay with irradiation time is observed for the samples with smaller grain size. These results show that anatase TiO_2 nanopowders possess interesting luminescence characteristics depending on preparation conditions. Therefore, knowing their luminescence properties is necessary for their potential application in photocatalysis, optical coating and photoelectrochemical conversion using visible light.

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