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Trap emission by nanocrystalline anatase in visible range studied by conventional and synchronous luminescence spectroscopy: Adsorption and desorption of water vapor

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ABSTRACT

We report the spectroscopic study of adsorption and desorption of water vapor on nanocrystalline anatase in air under ambient conditions. We also report the energy level diagram of absorption and emission through the three electronic midgap states of different origin in anatase as determined by absorption spectroscopy, "conventional" PL emission spectroscopy and, for the first time, by synchronous luminescence spectroscopy at 25 °C. Under the extrabandgap photoexcitation, visible luminescence from nanocrystalline anatase contains peaks of "blue light" at ca. 450 nm and "green light" at ca. 500 nm due to the two different midgap states. Photoluminescence in visible range at 25 °C is quenched after water vapor adsorption with formation of "hydrated" anatase and increased in "dried" anatase after water desorption. For both "dried" anatase with strong emission of visible light and "hydrated" anatase with weak (quenched) emission, synchronous luminescence spectra are superior to "conventional" PL emission spectra in resolving characteristic emission peaks due to midgap states. Photoexcitation of self-trapped exciton (STE) as intrinsic electronic midgap state in anatase at 420 nm results in a strong emission of "green light" at 500 nm, which is preferentially quenched upon water vapor adsorption vs. "blue light" at 450 nm. Visible PL in anatase decreases when the average nanocrystal size increases within 5–30 nm range, suggesting participation of surface midgap states in water adsorption/desorption.

1. Introduction

Nanocrystalline titanium dioxide can be present as anatase, rutile or brookite, the least abundant and studied form of TiO_2. Rutile is thermodynamically the most stable phase of "bulk" titanium dioxide [1], so rutile is formed at high temperatures and is the most naturally abundant form of TiO_2. On the other hand, anatase is more stable than rutile as small nanoparticles ca. < 15 nm in size [1]. Nanocrystalline titania containing anatase has been studied as sorbent in aqueous [2] and non-aqueous [3] solutions, photocatalyst in aqueous [4] and non-aqueous [5] solutions, photocatalyst [6] and sorbent in the gas phase [7], as material for solar cells [8], electronic [9] and biomedical [10] devices, in chemical sensors [11] including humidity sensors [12], etc. For instance, the benchmark TiO_2 photocatalyst P25 Degussa aka Evonik consists of ca. 80% anatase and 20% rutile with average nanocrystal size of about 20 nm. Anatase in its "bulk" form has an indirect bandgap of 3.2 eV; anatase is considered photocatalytically more active than rutile, despite the smaller optical bandgap of the latter.

Electronic states in the bandgap of semiconductor (often termed "midgap states") participate in relaxation and transfer of excited charge which affects functioning of electronic devices [13], rates of photocatalytic reactions [14], etc. The midgap states affect rates of photocatalytic reactions via an improved absorption of visible light and an enhanced rate of electron-hole recombination [15]. "Engineering" of midgap states is promising for development of new functional materials; for example, nanocrystalline anatase was chemically reduced to "black titania" containing surface oxygen vacancies V(O) and Ti^{3+} sites [14], and the latter has shown an improved absorption of visible light and enhanced photocatalytic hydrogen generation rate.

The photoluminescence (PL) spectroscopy is one of the best methods to learn about electronic states in the nanocrystalline semiconductors and about midgap states in particular, due to its non-destructive character and high sensitivity. The PL from midgap states in semiconductors is often named "trap emission". Water molecule is a common adsorbate on metal oxides, and adsorption/desorption of water may strongly affect the properties of nanocrystalline functional materials. The increase or decrease (quenching) of the PL in nanocrystalline anatase after adsorption and desorption of water vapor was not reported, to our knowledge.

In the most frequently used "conventional" PL emission

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spectroscopy, the spectrum is obtained by scanning the emission wavelength λ_{emiss} under the photoexcitation at a chosen constant photoexcitation wavelength λ_{exc}. Unfortunately, the "conventional" PL emission spectra of nanocrystalline solids, including titanium dioxide are often poorly resolved at room temperature and feature a significant peak broadening [16] which makes interpretations difficult. For compounds in solution, it is usually possible to achieve a significant narrowing of emission peaks by using synchronous luminescence spectroscopy [17]. The experiment by synchronous luminescence spectroscopy is performed by varying simultaneously ("synchronously") *both* the photoexcitation λ_{exc} and emission λ_{emiss} wavelengths at a constant difference termed "the delta lambda parameter" $\Delta\lambda = \lambda_{emiss} - \lambda_{exc}$. Recently, synchronous fluorescence spectroscopy of compounds in solution has been critically reviewed [18,19]. To our knowledge, synchronous luminescence spectra of anatase were not reported.

Recently, we reported a mechanistic study of adsorption of aromatic and heterocyclic compounds in suspension using "conventional" PL emission spectroscopy [20–22]. Herein, we report characterization of nanocrystalline anatase by "conventional" in comparison to synchronous luminescence spectroscopy in visible range, at 25 °C in air under atmospheric pressure. We report the pathways of relaxation and recombination of excited charge in nanocrystalline anatase through the three specific electronic midgap states, some of which are strongly and preferentially modified by periodic adsorption/desorption of water. We also studied how visible photoluminescence in anatase changes when the nanocrystal size changes in the range of 5–30 nm.

2. Experimental

2.1. Materials

Nanopowders of anatase with average nanocrystal size of 30 nm (99.98% purity), 15 nm (99.5% purity) and 5 nm (99.5% purity) were obtained from the U.S. Nanomaterials. Sulfuric acid and hydrogen peroxide were obtained from Sigma.

2.2. Drying and hydration of nanocrystalline anatase

The as-obtained material was denoted asisAnatase. A quartz cuvette of 1.5 cc was cleaned with Piranha solution (sulfuric acid and hydrogen peroxide), rinsed well with distilled water, and dried. The asisAnatase with the given nanocrystal size was placed into a cleaned cuvette and dried at 110 °C in the oven in air overnight, resulting in a dried material denoted drAnatase. After drying, a cuvette with the specimen was removed from the oven, promptly closed with a polytetrafluoroethylene (PTFE) stopper, weighed, and sealed with Parafilm to protect the specimen from ambient moisture for the following spectroscopic measurements. Next, the obtained drAnatase was allowed to adsorb water vapor ("hydration") using a procedure recently reported by us [21]. Namely, the specimen in this cuvette has been placed above the water/air meniscus inside a tightly closed dessicator with liquid water, and kept in contact with water vapor at relative humidity RH ~ 100% at 25 °C overnight, yielding a "hydrated" material denoted hyd-drAnatase. When testing the stability of nanocrystalline anatase at the higher temperature (Table S1), the specimen was dried at 150 °C and hydrated as described above, and then dried again at 150 °C resulting in dr-hyd-drAnatase.

2.3. Sample characterization

The XRD patterns were obtained by using Rigaku SmartLab diffractometer with Cu K-alpha line at 0.15418 nm. The UV–Visible diffuse reflectance spectra (UV–Vis DRS) were collected in the reflectance mode at room temperature using Cary 5000 spectrophotometer which is equipped with Praying Mantis attachment (Harrick Scientific). A finely ground $BaSO_4$ of 99.998% purity (Alfa Aesar) was used as white reference. Chemical composition was verified by X-Ray Fluorescence (XRF) using the instrument MESA-50 (Horiba Scientific).

2.4. Measurements by "conventional" PL spectroscopy in the solid phase at 25 °C

The photoluminescence (PL) spectra were collected using spectrometer Fluorolog FL3-22 (Horiba Scientific). This instrument is equipped with dual monochromator gratings on the excitation and emission light paths. The instrument was calibrated daily using the Raman signal of liquid water [16] in quartz cuvette at 25 °C. To minimize optical artifacts due to primary and secondary absorption of light in solid specimen [16], all spectra were obtained in the Front Face (FF) geometry using the FL-1001 accessory (Horiba Scientific). To eliminate the consequences of fluctuations of intensity of the photoexcitation source, the emission signal S from the sample has been divided by the reference signal R generated by the excitation beam before reaching the sample, and the (S/R) ratio has always been used as an Y axis of the spectra. All PL spectra were collected at 25 °C with specimen packed into a cleaned and dried cuvette, closed with polytetrafluoroethylene (PTFE) stopper, and sealed with Parafilm tape to protect from ambient moisture. The photoexcitation wavelength λ_{exc} was varied from 340 nm to 500 nm at the 10 nm increments. The PL emission spectra were recorded with excitation and emission slits at 5 nm.

2.5. Measurements by synchronous luminescence spectroscopy in the solid phase at 25 °C

Synchronous luminescence spectroscopy measurements were conducted using at same Fluorolog FL3-22 spectrometer in the FF geometry described above. The (S/R) ratio was used to construct the Y axis of all synchronous luminescence spectra, and the specimen was in the same container and physical form as in "conventional" PL measurements. The $\Delta\lambda$ parameter, $\Delta\lambda = \lambda_{emiss} - \lambda_{exc}$ has been varied at the 10 nm increments. Synchronous luminescence spectra were recorded with excitation and emission slits set at 5 nm.

Numeric curve fitting was conducted with Microcal Origin 2015 program.

3. Results and discussion

3.1. Characterization of nanocrystalline anatase

In order to determine the bandgap in the nanocrystalline semiconductor, the Tauc plots are very useful. The Tauc formula is $(\alpha \times E)^{1/n} = E - E_g$ where E is the photon energy, E_g is the bandgap, α is an absorption coefficient, and n is the Tauc constant [23]. For the nanocrystalline semiconductors, the Kubelka-Munk (KM) function applies $F(R) = (1-R)^2/2R = k/s$, where R is optical reflectance $R(\lambda)$, k is an absorption coefficient, and s is the scattering constant. The Tauc plots can be conveniently obtained using the KM function $(F(R) \times E)^{1/n} = E - E_g$, where $n = 2$ is for an indirect optical transition with energy $E_g^{indirect}$. Anatase is commonly believed to be an indirect bandgap semiconductor, e.g. in recent reports by experiment [24] and density functional theory (DFT) calculations [25]. In contrast to direct transition, indirect transition requires lattice vibrations (phonons), so indirect bandgap is often found in optical experiments conducted at room temperature. The magnitude of quantum size effect in nanocrystalline anatase has been the topic of research. Some authors believed that there was no quantum size effect in anatase [26,27], while others found more recently weak quantum size effect based on measurements by optical spectroscopy [24,28]. Fig. 1 shows the Tauc plots to determine $E_g^{indirect}$ in anatase of different nanoparticle size. From Fig. 1, the following bandgaps were obtained: $E_g^{indirect}$ (5 nm) = 3.30 eV or 375 nm; $E_g^{indirect}$ (15 nm) = 3.28 eV or 378 nm, and $E_g^{indirect}$ (30 nm) = 3.22 eV or 385 nm. The obtained values are consistent with reported weak