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Carrier recombination dynamics in anatase TiO_2 nanoparticles

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ABSTRACT

We present an experimental study of the radiative recombination dynamics in size-controlled TiO_2 nanoparticles in the range 20–130 nm. Time-integrated photoluminescence spectra clearly show a dominance of self-trapped exciton (STE) emission, with main features not dependent on the nanoparticle size and on its environment. From picosecond time-resolved experiments as a function of the excitation density and the nanoparticle size we address the STE recombination dynamics as the result of two main processes related to the direct STE formation and to the indirect STE formation mediated by non-radiative surface states.

1. Introduction

TiO_2 nanoparticles (NPs) have recently attracted much attention due to their properties in view of applications such as photocatalysis, optical coating, solar cells [1] and as high refractive-index encapsulant for light-emitting diodes [2]. While rutile TiO_2 has been extensively investigated, being rutile the stable phase at high temperature, the investigations concerning the electronic structure and physical properties of anatase leave open several questions and among those the role of surface states in ruling the carrier dynamics. Carrier capture in surface states has been considered as the mechanism that accounts for the extraordinary photocatalytic action of titania nanoparticles and a growing interest in anatase appears as a consequence of successful application of colloidal NPs for environmental purification and in solar cells, provided that the NPs synthesis with different techniques is a low cost procedure. Nevertheless, despite the success of some applications of anatase NPs, the understanding of electron transport and recombination in nanostructured TiO_2, a critical issue in view of device realization and optimization, is still incomplete. In particular the studies addressing the dependence of titania NPs on the size and the environment where the nanoparticles are dispersed focus onto specific aspects and a comprehensive understanding has not been reached. In this contribution we present a study of the self-trapped exciton (STE) recombination dynamics in anatase TiO_2 NPs by means of time-integrated and time-resolved photoluminescence (PL) in a set of samples where TiO_2 NPs, produced by polyol synthesis, are dispersed in water or prepared on a quartz substrate. By comparing the spectra and the PL decays we identify different processes for the STE formation and we discuss the role of particle size on the exciton recombination.

2. Experimental

TiO_2 NPs were prepared by polyol-mediated synthesis [3], which is quite a different process for NPs production in respect to the more common used procedures for industrial production. This technique has been used to prepare nanosized metal and alloy particles and allows an accurate and reproducible control of the mean diameter of the particles in a broad size range and the mixing of the reactants at molecular level.

The samples with different particle sizes were prepared in water "aging" the sol 0, 2 and 8 h. Particle size was examined by dynamic light scattering (DLS, Zetasizer–Nanoseries, Malvern). DLS measurements reveal that the particle size of the three synthesized samples is 24, 67 and 127 nm (from here in we will call these systems NP24, NP67 and NP127 respectively), with size dispersion $\leq$20%. The NPs were dispersed in aqueous solution, with pH = 1

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and concentration of 6%. We also studied a sample obtained by a spin coating deposition of the titania solution on a fused quartz window (we will call this sample Q).

The samples were mounted in a closed cycle cryostat and the measurements were performed in the temperature (T) range 10–300 K, but in this paper we will discuss only the low T data. Time Integrate (TI) and Time Resolved (TR) photoluminescence (PL) spectra were obtained after excitation with the second harmonic of a R6G dye laser synchronously pumped by a frequency doubled Nd:YAG mode-locked laser. The excitation wavelength was 300 nm (that ensures a full absorption in the samples, as it results from transmission measurements not reported here) and the pulse duration was 5 ps. The laser beam was focused onto the sample to form a spot of $\sim 1 \cdot 10^{-4}$ cm^2. The PL was collected and dispersed through a single grating monochromator with 50 cm focal length and detected by a microchannel photomultiplier followed by a photon counting apparatus for TI-PL measurements (spectral resolution of 1 nm) and a time-correlated single-photon counting setup providing an experimental time response with a full width of 100 ps for TR-PL experiments, allowing to resolve time constants of the order of 20 ps.

3. Results and discussion

In Fig. 1a we report the TI-PL spectra, normalized at their maximum intensity, of the different samples measured at 12 K. The spectra are broad structureless bands centered at 2.2 eV, with a full width of about 0.6 eV, red shifted respect to the absorption edge of anatase TiO_2. Similar PL bands have been reported in literature both for bulk anatase TiO_2 [4], TiO_2 films [5] and nanosized structures [6]. PL spectra as a function of temperature have been also reported in Ref. [7]. We do not observe PL emission near the band edge arising from the radiative recombination of free excitons. The spectral TI band shape turns out to be independent on particle size and particle environment. Moreover, as shown in Fig. 1b for NP67 sample, we find that, for all the samples, in the range of investigated intensity (from 0.1 W/cm^2 to 100 W/cm^2) the PL band shape does not change. These experimental findings strongly support the attribution of the PL band to the radiative recombination of self-trapped excitons (STEs), due to strong lattice deformations in anatase [4], and/or to the recombination of excitons bound to oxygen vacancies [8] or Ti^{3+} states [9].

In Fig. 2a the decay curves for different particle size are shown in a logarithmic scale, detecting the PL at the peak energy for each sample, at low excitation intensity (0.3 W/cm^2) and at 12 K. In the inset we show the typical risetime of the PL signal, which turns out to be of the order of few tens of ps, indicating a fast capture in the STE states. The decay profiles are not exponential, revealing the presence of a complex dynamics, and the overall dynamics becomes faster with increasing the particles size. Similar decay profiles have been already observed in TiO_2 systems [10–12], strontium titanate [13] and in several systems as semiconductor nanocrystals of CdSe [14], disordered systems [15] and polymeric films [16]. Nevertheless most of the works report fits to the experimental data with a stretched exponential function, with no physical information on the processes that give rise to such dynamics. Recently a detailed study on silica-based nanostructures [17] proposes a model where a strong interplay arises between STE states and a transfer mechanism involving the surface states. It is well known that the main application field of TiO_2 NPs (photocatalysis) is strictly related to the presence of surface states that can easily capture free carriers on a sub picosecond scale. The PL decays reported in Fig. 2 show a significant fastening of the overall dynamics with increasing the NPs sizes and the excitation density. In order to clarify the origin of the complex dynamics that rules the recombination processes in TiO_2 NPs, we phenomenologically analyze the decay profiles using the following simplified expression (neglecting the rise of the PL signal):

$$I = I_1 + I_2 = Ae^{-\left(\frac{t}{\tau_1}\right)} + Be^{-\left(\frac{t}{\tau_2}\right)^{\beta}}. \quad (1)$$

We suppose the presence of two main contributions I_1 and I_2 characterized by two time constants τ_1 and τ_2. The experimental data of Fig. 2a are well reproduced by Equation (1) with $\tau_1 \approx 500$ ps and $\tau_2 \approx 100$ ns with $\beta = 0.5$, typical of diffusive process. We observe that, while these time constants are almost independent on the particles size, the ratio of the two contributions changes significally with the particle diameter, in particular the slow process I_2 becomes more important for smaller particles. These results suggest that the fast component I_1 can be associated to volume STE recombination, while the slow component I_2 to recombination mediated by surface states, in agreement with [12,13,16]. This interpretation is further supported by the dependence of the decay profiles on the excitation density, as shown in

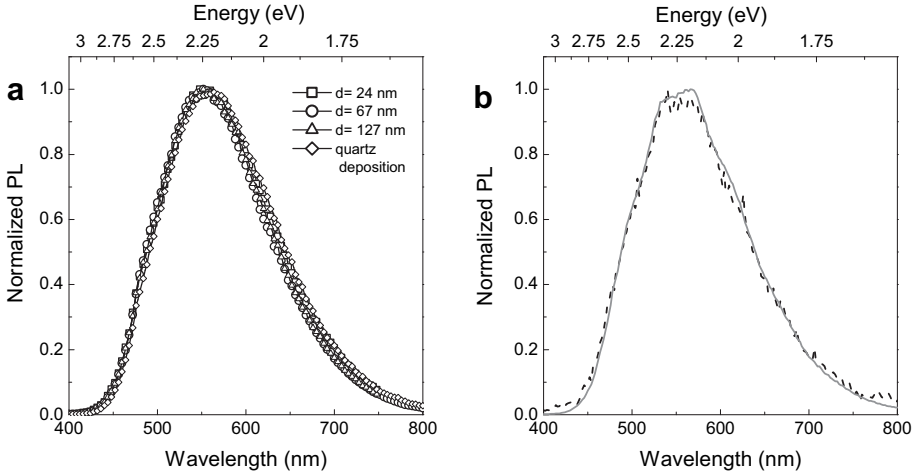

Fig. 1. TI-PL spectra at 12 K, normalized at the maximum of each spectrum: a) Comparison between nanoparticles dispersed in water with different diameters d ($d = 24$ nm open squares; $d = 67$ nm open circles; $d = 127$ nm open triangles, respectively) and deposition on quartz (Q, open diamonds); b) Comparison between normalized spectra of sample NP67 for different excitation intensities, black dashed line 0.3 W/cm^2 and gray solid line 100 W/cm^2, respectively.