Anti-Stokes photoluminescence in TiO_2 nano-particle films at room temperature

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Anti-Stokes photoluminescence (ASPL) or photoluminescence upconversion is a phenomenon in which the photon energy of PL output is higher than that of the excitation source. ASPL has attracted much attention [1–7] because of its observation in high purity bulk semiconductors [1], semiconductor heterojunctions [4], and quantum dots [2, 3, 7] with high efficiency under cw-excitation. This effect has been previously reported for both doped and high purity bulk semiconductor. For up-conversion, the proposed mechanisms involve (i) Auger recombination that ionizes carriers to the higher band gap region where they undergo radiative recombination, (ii) two-photon absorption (TPA) process via real or virtual states, and (iii) an interaction with the thermally populated phonon modes as in the anti-Stokes Raman shifts.

In this letter, we report anti-Stokes PL at moderate excitation intensity in quantum confined TiO_2 nano-particle films; the up-conversion is very efficient, and we propose a mechanism based on surface state. In contrast to Ref. [2] where micro-PL measurements on a self-assembled InAs/GaAs QDs sample reveal the existence of a strong PL up-conversion arising from single QDs and also from the InAs wetting layer, the up-conversion of TiO_2 QDs originates only from the QDs states.

TiO_2 nano-particle films coated with sodium dodecylbenzenesulfonate (CF) (sample 1) and those not coated with CF (sample 2) have been prepared by forced hydrolysis and magnetron sputtering respectively. First, solid powder of TiO_2 was prepared by forced hydrolysis from $TiO(NO_3)_2$ followed by centrifuging and drying. TiO_2 nano-particles with diameters from 30 nm to 50 nm were formed after annealing at 800 °C for 2 hr. In order to prevent the glomeration of crystalline particles and maintain the scale of TiO_2 nano-particles, surfactant CF was used to coat the TiO_2 nano-particles. The TiO_2/CF was mixed with deionized water in the volume ratio of 1:2, and stirred the mixture for 10 min, then deposited it for at least 12 hr. The mixture was turned into three layers: on the top was dilute TiO_2 solution; at the bottom were large clusters exceeding nanometer scale. We collected the mixture in the middle and dripped it onto the glass substrate and made it into TiO_2 nano-particle films coated with CF. TiO_2 nano-particle (not coated with CF) films have been also prepared by magnetron sputtering.

PL measurements were performed at room temperature. The excitation beam, provided by a cw He-Cd laser, was focused on the sample. The luminescence was dispersed by a monochromator and detected with a photomultiplier. The output power of laser was 70 mW and excitation wavelength was 441.6 nm.

The PL spectra of samples 1 and 2, under excitation energy which is below the TiO_2 band gap, are shown in Figs 1 and 2 respectively. The two figures are very similar. From 400 nm to 470 nm, a broad line is observed that cannot be found in the bulk structure at room temperature. These are properties of nanometer materials. The weak emission peak around 415 nm corresponds to electron–hole pairs recombination at the band edge of TiO_2. This emission has been found in TiO_2 nano-particle before. It is interesting that a sharp and intense up-converted line at about 429.8 nm newly appears in both kinds of samples. In order to exclude the emission of CF in sample 1, we measure the PL spectrum of CF at the same conditions. No emission occurred, so the narrow line is not induced by CF.

The measurements were performed at room temperature, so the up-conversion is not involved by an interaction with the thermally populated phonon modes as in the anti-Stokes Raman shift. From the comparison of two samples' PL spectra, the UCPL line appears at the same position, so influence of exogenous impurity is not in consideration.

As we know, when the scale of the TiO_2 crystalline particles is comparable to its de-Broglie wavelength, novel properties are induced by size quantization effects. Firstly, there are many unsaturated chemical bonds and defects, thus some additional energy levels are formed between conduction band and valence band. The quantity of atoms near the surface of nano-particles is so large that influence on emission by surface states plays a crucial role as in Ref. [6], the observation of anti-stokes PL in InP QDs and CdSe QDs is due to surface states and phonon process. Secondly, because of size quantization effects, the probability of exciton formation is great and some exciton energy levels exist near the bottom of the conduction band. These intermediate states provide great possibility in up-conversion process. In light of the above experimental results, we propose the following mechanism based on surface states.

Since the measurements were performed at moderate excitation power densities, the efficiency of direct

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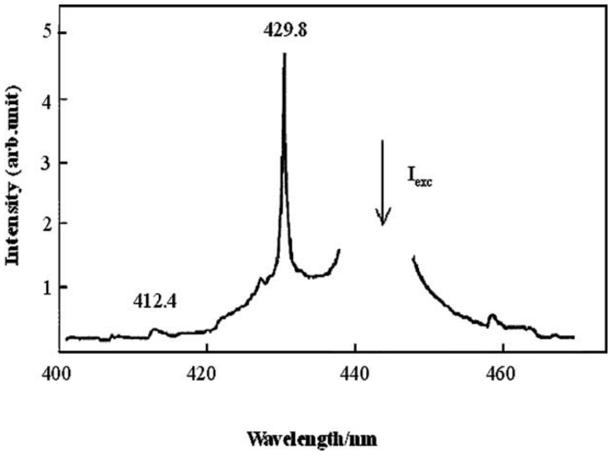

Figure 1 Up-converted photoluminescence of TiO_2/CF nano-particle films CF with the excited wavelength 441.6 nm at room temperature.

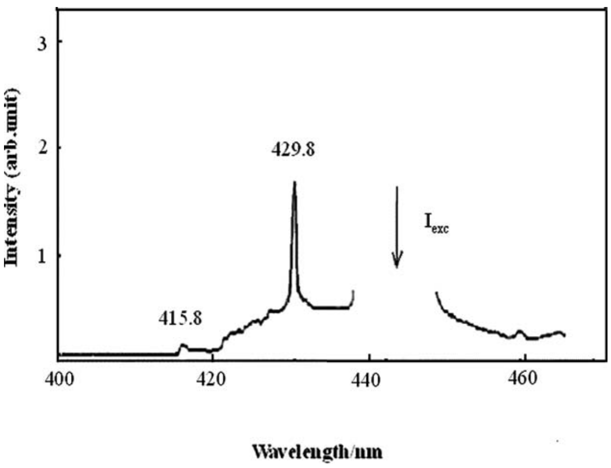

Figure 2 Up-converted photoluminescence of TiO_2 nano-particle films at the same experimental conditions as Fig. 1.

two-photon absorption is low and can be disregarded. Auger process or two-step two- photon absorption (TS-TPA) can be involved to explain this nonlinear phenomenon. For TS-TPA, the up-conversion process starts with the creation of electron–hole pairs in the excited states of QDs. Then the electron–hole pairs relax to form excitons. These excitons have a very limited spatial extension due to the confinement in QDs and can survive long enough to be excited by another photo. These excitons recombining give rise to the ASPL. The Auger process recombination in QDs can also be considered as a possible mechanism for the ASPL. Electron–hole pairs in the excited states recombine by transferring the excess energy immediately to another electron or hole. At higher excitation energies, the excited states of QDs can also participate as an initial state for the second excitation process. Because the energy level structure of nano-particle is a function of QD size, only those particles whose intermediate states are resonant with the excitation energy contribute to the up-conversion signal and quantum efficiency is relatively high.

In conclusion, TiO_2 nano-particle films coated with and without CF have been prepared by forced hydrolysis and magnetron sputtering respectively. The broad photoluminescence has been observed under below-band-gap excitation at room temperature. A sharp and intense up-converted line at 429.8 nm newly appears in two kinds of samples. The large interface roughness of the nano-particles is responsible for the appearance of surface states localized between conduction band and valence band. These intermediate states provide great possibility to observe a rather strong up- conversion photoluminescence signal. The most possible mechanism for this up-conversion process is a two-step two-photon absorption or Auger process. This first observation of ASPL of TiO_2 nano-particle demonstrates the influence on the QD properties induced by the deep electronic states located at the surface of QDs and will make prospects for the further application of TiO_2 in catalysis, photocatalysis and especially dye- sensitized solar cells.

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