

ABNORMAL PHOTOLUMINESCENCE OF TiO₂ NANOCRYSTALS (NANOPARTICLES AND NANOTUBE ARRAYS)

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Abstract. *In this paper we report new abnormal photoluminescence results of TiO₂ nanocrystal particles and nanotube arrays. Photoluminescence spectra were recorded for TiO₂ nanocrystal particles and nanotube arrays that were synthesized by a wet chemical route and the electrochemical anodization, respectively. It was found that the TiO₂ nanocrystal with small size of 5-8 nm no emitted when excited by a laser beam of 325 nm, in contrary it emitted when excited by laser beam of 442 nm. The TiO₂ nanotube arrays exhibit a similar emission behavior. The nanotube arrays weakly emitted when excited by a laser beam of 325 nm and more strongly emitted when excited by a laser beam of 442 nm. The obtained results have been explained by a two-step exciting model and supposed to be related with the size effect of nanocrystal and it is an experimental evidence to believe that the TiO₂ nanoparticles and nanotube arrays are applicable for photo-catalysis under sun light.*

Keywords: TiO₂ nanocrystals, TiO₂ nanotube arrays, absorption, luminescence.

I. INTRODUCTION

Titanium dioxide TiO₂ has attracted the world-wide scientists and technologists because of its huge application possibilities in pigments, photocatalysis, solar cells, gas sensors, and water splitting [1–3]. It is well known that TiO₂ is a semiconductor having large energy band gap (3.2 eV, 3.0 eV for anatase and rutile phase, respectively). So TiO₂ is photoactive only to the light in the wave-length range shorter than 400 nm. It means this material has low photo-electronic efficiency under sun light due to the contribution of ultraviolet light is only about 5 % in total light power of the sun. On demand to improve the photo-electronic efficiency, a huge number of researches were focused on increasing absorption in the visible light region of TiO₂ by doping and/or co-doping appropriate elements [4–10]. Besides a large amount of researches were focused on incorporation of TiO₂ with the narrow band-gap semiconductor [11–13]. We know that the charge generation, charge separation and charge transfer have important contributions in the external efficiency of one photo-electronic device. In principle, a part of the photo-generated electron-hole pairs in the conduction and valence band can be separated and have to contribute in the external photo-current. The remaining part has lost itself due to electron-hole recombination, including the irradiative and non-irradiative processes. So the question going on our mind is that how to evaluate and to control

these processes in aim to manufacture the appropriate TiO₂-based materials responsive to visible light. In the irradiative recombination process the electron-hole pairs recombined and emitted photoluminescence light. The intensity of photoluminescence is a consequence of the competition between the irradiative and non-irradiative recombination's probabilities. So the photoluminescence spectroscopy (PL) can be used as an indicator of the optical energy conversion in materials. Dealing with the absorption and photoluminescence of the TiO₂ colloidal particles with sizes of 2.1 nm, 13.3 nm and 26.7 nm, Serpon and coworkers [14] reported an interesting result that they observed a non-linear dependence of luminescence intensity on size of particles. Nadica *et al.* [15] observed a wide band from 2.4 eV to 3.6 eV of the up-conversion photoluminescence (UCL) for the anatase and rutile TiO₂ nano-particles when excited by a laser beam light of 2.21 eV and 2.38 eV. Similar UCL spectra were also recorded for TiO₂ nanoparticle films using a He-Cd laser operating at 2.81 eV as an exciting light. The UCL reported results were explained as a result of irradiative transitions between the X and Γ energy states of 3d and 2p electrons of Titanium and Oxygen ions in the energy configuration suggested by Daude [16]. Wakabayashi and coworkers have observed luminescence of an anatase single crystal and attributed the photoluminescence in TiO₂ single crystal to the self-trapped exciton (STE). They also suggested an energy model for the excitation-relaxation processes in TiO₂ crystal and confirmed that the luminescence in TiO₂ crystal is due to only the recombination of STE [17].

In this report we present a two-step excitation model and an alternative explanation for the abnormal photoluminescence results recorded at room temperature of the TiO₂ nanoparticles and nanotube arrays under excitation of the light having energy smaller and larger than energy band gap of TiO₂.

II. EXPERIMENTAL

The TiO₂ nanoparticles doped Cu with concentration of 0, 6, 8 and 13 wt% were manufactured by using a wet chemical processing. Titanium isopropoxide (Ti(i-OC₃H₇)₄) (TPOT), acetone C₅H₈O₂ (ACT), Cu(NO₃)₂·3H₂O of Aldrich company were used as starting materials in synthesis of TiO₂ and TiO₂ doped with Cu nanocrystal samples. The size of the nanoparticles was estimated by using field emission scanning electronic microscope images (FESEM) and X-ray diffraction patterns. It was found that the manufactured TiO₂ nanoparticles have size of about 5 nm. The detail of the experimental procedure can find in our previous paper [18].

TiO₂ nanotube arrays were grown by anodic oxidation at room temperature of high purity (99.7%) Ti foil in an ethylene glycol solution containing 2 wt% deionized (DI) water and several different concentrations of NH₄F for 3h. Pt sheet was used as a counter electrode. The distance between the anode and cathode electrodes was kept of about 1.2 cm. The anodization was carried out by varying the constant potential from 10 V to 60V. The anodization current was monitored by using a Keithley 2000 multimeter. The experimental setup is shown in Fig. 1. Before anodization, Ti foil surface and Pt sheet were ultrasonically cleaned in ethanol for 20 minutes, in DI water for 10 minutes, and finally dried at 50 °C in air. After finishing the anodization process, TiO₂ nanotube samples were immediately washed in DI water to remove residual ion F⁻, and then precipitates covering the surface of TiO₂ nanotube arrays were removed by ultrasonication in ethanol for 10 minutes and subsequently dried in air. A typical anodized sample was annealed at 450 °C for 3h (ramp 5 °C/min) to completely transfer the TiO₂ into anatase crystalline phase.

The morphology of all the samples was evaluated by using a Hitachi SEM S4800. The crystalline structure of typical TiO₂ nanotube array membrane were investigated by using an X-ray diffractometer Siemen D 5000 with Cu K α radiation ($\lambda = 1.5406\text{\AA}$). The optical absorption and luminescence of all the samples at room temperature were carried out by using an UV-Vis Cary 5000 and a high-resolution luminescence spectrometer, respectively.

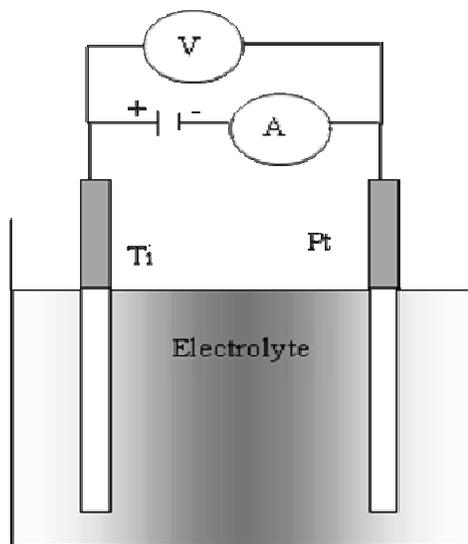


Fig. 1. A modelling schema of the electrochemical anodization setup used to grow TiO₂ nanotube arrays with the electrolyte containing ethylene glycol added NH₄F of various concentrations and 2 wt% of deionized water.

III. RESULTS AND DISCUSSION

III.1. Experimental Results

Fig. 2 presents luminescence spectra of TiO₂ nanocrystal doped with Cu with the excitation light of 325 nm and 442 nm. No emission was observed for all the samples excited by a light of 325 nm wave-length. In contrary, strong wide emissions in a range of 450-900 nm were observed when excited by a light of 442 nm wave-length. Similar luminescence results were obtained for TiO₂ nanotube arrays manufactured by the electrochemical anodization as presented in Fig. 3. This recorded experimental luminescence result is an unordinary one. So appears a question that how to explain it?

IV. DISCUSSIONS

It is well known that the excitation by a light (325 nm wave-length ~ 3.78 eV) having energy greater than the band gap of TiO₂ (~ 3.0 eV), then electrons have been excited directly from valence band to conduction band and consequently yielded free charge-pairs of electron and hole in conduction and valence bands, respectively. These photo-excited electrons have two competitive ways to come back to the initial states as shown in Fig 4 and Fig. 5. By one of

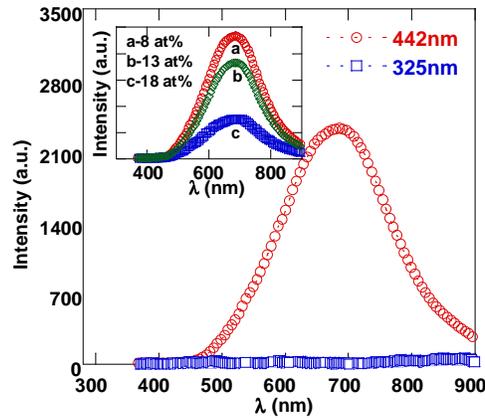


Fig. 2. Luminescence spectra of TiO_2 doped Cu in concentration of 8 at% excited by a laser beam with wave-length of 442 nm and 325 nm. The inset presents luminescence spectra of TiO_2 doped Cu in concentration of 8, 13 and 18 at% excited by a laser beam with a wave-length of 442 nm.

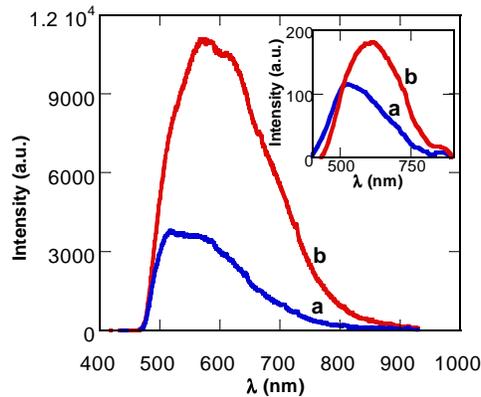


Fig. 3. Photoluminescence spectra of the nanotube arrays excited by laser beams of 442 nm and 325 nm (inset): a) the as synthesized, b) annealed at 450 °C for 2h.

these ways the photo-excited electrons can relax first to the intermediate states lying closely under conduction band. In case of TiO_2 these intermediate states are conducted to the 3d states of Ti^{3+} ions that depend on oxygen deficiency in TiO_2 . After that they relax and/or transfer to the exciton-traps in band gap and subsequently relax to valence band by the irradiative transitions via trapped exciton recombination. The other way is the non irradiative transitions via lattice phonons and/or surface states. In TiO_2 nano materials the surface states play as the redox centers. Based on the report of [17] the nature of these relaxation processes happen in TiO_2 nanocrystal can be illustrated as in Fig. 4.

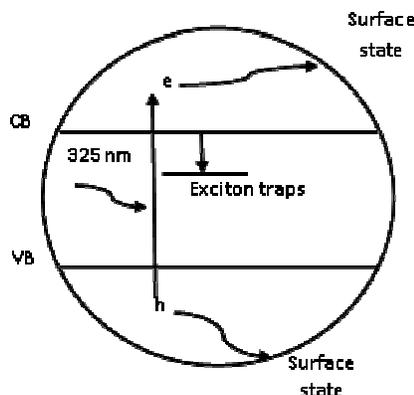


Fig. 4. The configuration of the possible transitions happen in Cu-doped TiO₂ nanocrystals excited by a light of 325 nm wave-length

a) Excitation with the light having energy larger than band gap

According to report of Wakabayashi [17], in case of the crystal having size larger than the free diffusion length of charge (electron and hole in conduction and valence bands), the photo-excited electrons can move freely in conduction band and effectively step by step relax to the intermediate states, then transfer to exciton traps and finally emitted luminescence via the trapped exciton recombination. Many authors [15, 17] recorded a broad luminescence band about of 2.2-2.3 eV for anatase TiO₂ single crystal under the uv-light irradiation. This emission was known as the self-trapped exciton (STE). In our case as presented in Fig. 1 for anatase Cu-doped TiO₂ nanocrystal with crystal size of about 5 nm. No emission was observed when excited with a light with wavelength of 325 nm. The detail explanations for this case can be seen in our previous paper [16]. From Fig. 1 and Fig. 2 we easily recognized a difference between photoluminescence spectra of Cu-doped TiO₂ nanoparticles and nanotubes. The Cu-doped TiO₂ nanoparticles completely no emitted, but TiO₂ nanotubes weakly emitted. This difference is reasonably related with the divergence of nanocrystal size of two materials. From XRD patterns and FESEM images we have known that the Cu-doped TiO₂ nanocrystal has particle size of about 5 nm, but in contrary the nanotubes have the wall thickness and length of 12 nm and 21 μ m, respectively. The no emission of Cu-doped TiO₂ nanocrystals is rather related with the very small size of TiO₂ nanoparticles so that the diffusion length of photo-excited electrons is longer than the size of nanoparticles. Finally it is believed that the no emission of Cu-doped TiO₂ nanocrystals excited by a light having energy larger than the band gap of TiO₂ is reasonably related to the less relaxation of the photo-excited electrons to the exciton traps in band gap. It means the photo-excited electrons rather trapped to the surface redox states and the Cu-doped TiO₂ nanocrystals and nanotube arrays with small size are expected to be an active photocatalysis.

b) Excitation with the light having energy smaller than band gap

In the previous paragraph we have suggested that the photo-excited electrons relax less to the exciton traps in band gap of Cu-doped TiO₂ nanocrystals. In aim of to prove this suggestion

we have taken other second experiment to measure photoluminescence with an exciting light of 442 nm in wavelength (~ 2.78 eV – it is smaller than the band gap of TiO_2). In contrast to the case of 325 nm excitation, all the samples emitted a wide luminescence band from 450 nm to 900 nm with the excitation of a light of 442 nm wave-length. This photoluminescence result confirms that the exciton trapped recombination rather is allowable transition in our Cu-doped TiO_2 nanocrystals. So the no emission of TiO_2 nanoparticles under an excitation by a light of 325 nm is an experimental evidence to prove that the photo-induced electrons do not relax to the exciton trap states. So for understanding and explaining this obtained result we use a modified two-step energy configuration as presented in Fig. 5.

In this model we used a two step excitation configuration. First electrons were excited to certain impurity states in band gap. In case of TiO_2 nanoparticles doped with Cu the impurity states have been created by doping Cu. In case of TiO_2 nanotube array manufactured by the electrochemical anodization the impurity states are related with the oxygen deficiency that evidenced by a long tail in its optical absorption spectra as shown in Fig. 6.

In the next step electrons have been excited from these impurity states to conduction band. Therefore a part of the photoinduced electrons in the first step remains in impurity states and transferred later into the exciton traps, which have contribution in luminescence emission. So the luminescence emission generally is weak, but it confirms again that the no emission is a consequence of the relaxation-less of the photo-excited electrons from conduction band to the exciton traps. It means the electrons excited to conduction band in the second step have been trapped into the surface states, acting as the redox centers being active in photo-catalysis. In principle the stronger luminescence is the weaker photocatalytic material. So the Cu-doped TiO_2 nanocrystals having grain size of about 5 nm and TiO_2 nanotube arrays are an expected photocatalytic material working in visible light.

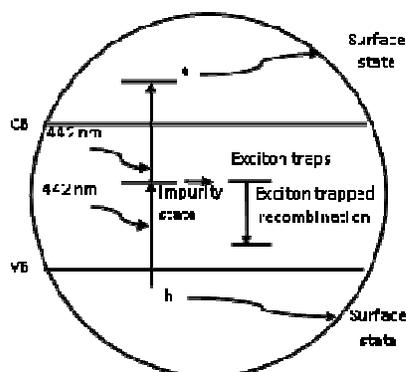


Fig. 5. Configuration of the possible transitions happen in Cu-doped TiO_2 nanocrystals excited by a light of 442 nm wave-length.

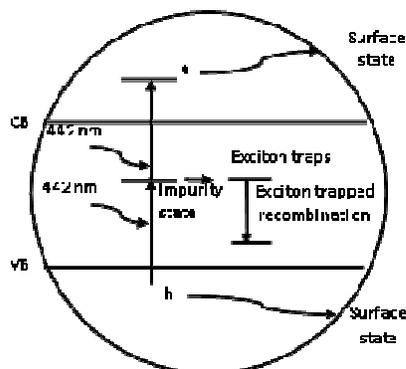


Fig. 6. The absorption spectra of the as synthesized TiO_2 nanotube array (a) and the TiO_2 nanoparticle thin film synthesized by spin coating from a solution containing TiO_2 nanoparticle synthesized by sol-gel method (b).

V. CONCLUSIONS

The observed photoluminescence of the Cu-doped nanoparticles and nanotube arrays excited by the light having energy larger and/or smaller than band gap energy is evidence related to the energy-transfer processing happened in the nanomaterials. A two-step exciting model related with the size effect and the impurity states concerning with Cu doping and oxygen deficiency was used to explain the photoluminescence results recorded for the TiO₂ nanocrystals. It is believed that the TiO₂ nanoparticles doped with Cu and nanotube arrays are expected active photocatalytic materials working under the visible light.

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