Surface Plasmon Enhanced Luminescence from Au covered Titania Nanotubes burned in a Methane Flame

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Abstract — **It is shown that coating by Au layers with thickness of 5 – 10 nm of titania nanotubes with anatase structure produced by burning the as-electrochemically-prepared nanotubes in a methane flame leads to the increase of the green photoluminescence intensity, while the effect of Ag coatings is insignificant. Titania nanotubes with average outer diameter of 150-200 nm and wall thickness of 60 nm were produced by anodization of Ti foils in an ethylene glycol based electrolyte containing a mixture of HF and H_3PO_4. The enhancement of the green emission is believed to be due to the effect of surface plasmons in Au coatings. This suggestion is supported by calculations of dispersion relations of surface plasmons at the Au/TiO_2 interface and by the measurement of the transmission spectra of uncoated and metal coated titania nanotubes.**

Index Terms — **luminescence, optical absorption, surface plasmons, titania nanotubes, dispersion relations.**

I. INTRODUCTION

In addition to the traditional utilization of Titania (TiO_2) as pigments, recently it became widely used in sensors, electrocatalysis, and Graetzel-type solar cells (e.g. [1] and references therein). Among titatia nanostructures, titania nanotubes (TiO_2 NTs) have improved properties for application in photocatalysis, sensing, photoelectrolysis, photovoltaics, lithium ion batteries, and biomedical applications [2]. Recently, titania also gained interest as a material used in photonic band gap crystals for the visible spectrum of light due to its high index of refraction and low absorption [3]. Optical properties of TiO_2 NTs, particularly luminescence, are very important for photonic applications. In a recent work, the spectral distribution of cathodoluminescence from a cluster of nanotubes clearly demonstrated the formation of resonator modes [4].

Among the methods used for the preparation of TiO_2 NTs, electrochemical anodization of titanium foils is a cost-effective approach for the growth of highly ordered structures [5].

Taking into account the possibility of doping porous titania templates with rare earth and transition metal ions and the morphology controlled light scattering properties, one can expect that luminescent materials prepared on porous TiO_2 templates are prospective for random laser applications [6]. The development of methods for enhancing the luminescence efficiency from titania nanotubes is an important task. One way for enhancing the optical properties, and particularly the luminescence intensity, is to make use of plasmonic effects in metallo-dielectric structures. Enhancement of the emission due to surface plasmons was observed in some metal-semiconductor systems such as Ag/ZnO films [7], Ag (or Al)/InGaN quantum wells [8]. It was shown recently that the near-bandgap photoluminescence intensity (in the region of 380-440 nm) from anatase titania nanotubes produce by annealing at 300 ^{o}C in a furnace is increase by covering with thin Ag films [9].

In this work, we demonstrate that the green emission from titania nanotubes produced by burning in a methane flame can be enhanced by the deposition of Au films due to the excitation of surface plasmons.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Technological conditions for the preparation of porous TiO_2 layers with controlled morphology and porosity on the basis of Ti foils include rinsing and sonicating in isopropyl alcohol, drying and anodizing. The investigated samples were anodized in a mixture of HF (1 ml) and H_3PO_4 (10 ml) in ethylene glycol (100 ml) under 100 V during 2 hours. This treatment results in the fabrication of TiO_2 nanotubes with outer diameter around 150-200 nm and the wall thickness of 60 nm as illustrated in Fig. 1. The samples were subjected to burning in a methane flame during several seconds to several minutes after anodization. Ag and Au coatings were deposited onto titania nanotubes by means of a Cressington magnetron sputtering coater.

A VEGA TESCAN TS 5130 MM scanning electron microscope (SEM) was used for morphological characterization of the samples.

Photoluminescence (PL) was excited by 325 nm line of a He-Cd laser and analyzed through a double spectrometer at low temperature (10 K). The samples were mounted on the cold station of a LTS-22-C-330 cryostat.

Raman spectra were measured at room temperature with a Confocal MonoVista CRS spectrometer.
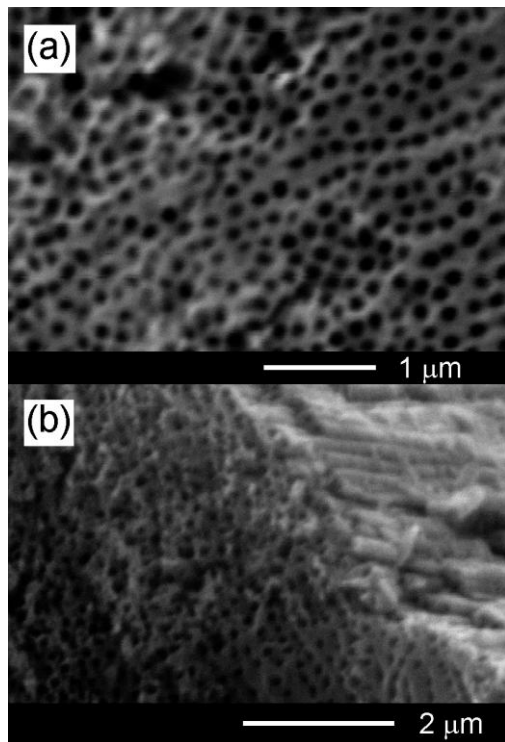
Fig. 1. Top view SEM image (a) and oblique view (b) of TiO_2 nanotubes produced by etching Ti foils in a mixture of HF and H_3PO_4 in ethylene glycol.

III. RESULTS AND DISCUTIONS

Figure 2 presents the PL spectra of TiO_2 nanotubes with the morphology illustrated in Fig. 1 subjected to different thermal treatment procedures. One can see that the luminescence of TiO_2 NTs annealed at 300 ^{o}C in a furnace during 30 minutes (curve 1) is dominated by the near bandgap emission which includes two narrow lines at 371 nm (3.34 eV) and 372 nm (3.33 eV) followed by several phonon replica with phonon energy equal to 50 meV, while the luminescence of samples burned in an methane flame is dominated by a green PL band.
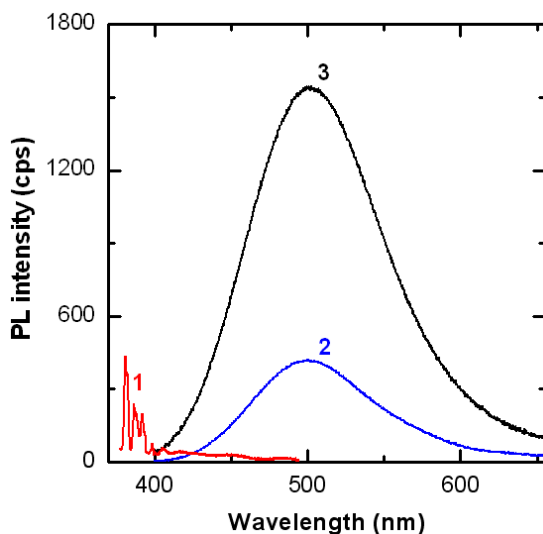

Fig. 2. Low temperature (10K) PL spectra of TiO_2 NTs subjected to annealing in a furnace at 300 ^{o}C during 30 minutes (1), to burning in a methane flame during 3 seconds (2) and 1 minute (3).

The luminescence comes from the anatase phase of titania as demonstrated by the Raman spectrum presented in Fig. 3. Anatase is tetragonal, with two TiO_2 formula units (six atoms) per primitive cell. The space group is D_{4h}^{19} (I4/amd). The 18-dimensional reducible representation generated by the atomic displacements contains the zone-center (*k=0*) modes: 3 acoustic modes and 15 optical modes. The irreducible representations corresponding to the 15 optical modes are $1A_{1g} + 1A_{2u} + 2B_{1g} + 1B_{2u} + 3E_g + 2E_u$. Three modes are infrared active, the A_{2u} mode and the two E_u modes. The B_{2u} mode is silent. The remaining six modes corresponding to symmetries $A_{1g} + 2B_{1g} + 3E_g$ are Raman active. The Raman shift for these phonons is 514 cm^{-1} for the A_{1g} mode, 399 cm^{-1} and 514 cm^{-1} for the B_{1g} modes, and 144 cm^{-1}, 197 cm^{-1} and 639 cm^{-1} for the E_g modes [10]. Therefore, the A_{1g} and one of the B_{1g} modes overlap, while all other modes are observed in the spectrum from Fig. 3.
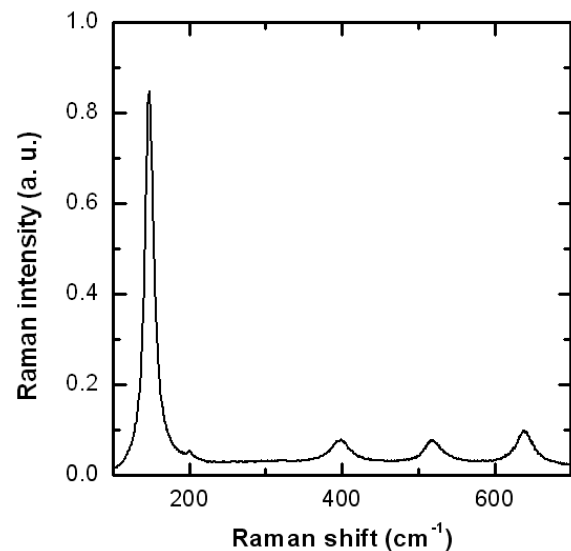

Fig. 3. Raman spectrum of TiO_2 NTs burned in a methane flame during 3 sec. measured at room temperature.

As concerns the nature of the observed PL bands, previously two sharp lines peaking at 3.31 and 3.37 eV have been observed in the near bandgap PL spectra of anatase titania [11]. These lines were interpreted as defect-trapped-exciton related although the free-exciton origin of the 3.31 eV peak was also argued. Apart from this possible nature of the PL lines at 3.34 eV and 3.33 eV observed in our samples, their relation to free-to-bound transitions can not be excluded [12]. As concerns the green PL band observed in samples burned in a methane flame, a green luminescence band is frequently observed in luminescence spectra of titania and is attributed to radiative recombination of selftrapped excitons localized on TiO_6 octahedra [13-17]. Selftrapped excitons are reported to be stable in anatase TiO_2, whose structure is based on a network of TiO_6 octahedral units. Excitons in such structures result from the interaction of conduction band electrons essentially located on Ti 3d states with holes essentially on oxygen 2p states [14]. One can see from Fig. 2 that the intensity of the green emission increases with increasing the duration of burning from 3 seconds to 1 minute.
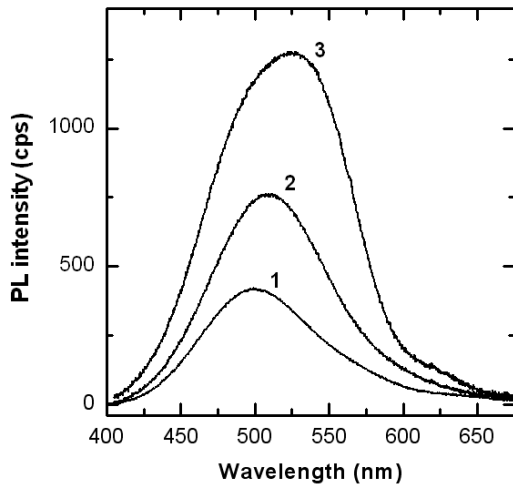
Fig. 4. PL spectra of TiO_2 NTs burned in a methane flame during 3 sec. (1) and covered with Au films with thickness of 5 nm (2), 10 nm (3) measured at 10 K.

The data presented in Fig. 4 demonstrate that covering of TiO_2 NTs with Au films with thickness of 5 and 10 nm leads to increased luminescence intensity and to the shift of the PL band to longer wavelengths. However, the increase of the film thickness beyond 20 nm results in a decrease of the luminescence intensity (not shown in this graph). This decrease can be attributed to the increased absorption in the metal film of both excitation and emission light. As concerns the increase of the luminescence intensity with Au films, it is suggested to be due to the enhancement of both the excitation field and the green emission via surface plasmons in the Au film, the second effect being stronger, since the excitation wavelength (325 nm) does not match the surface plasmon (SP) resonance. Fig. 5 shows the dispersion relations of surface plasmon polaritons (SPP) on Au/TiO_2 and Ag/TiO_2 surfaces calculated by the dielectric functions. For a single interface between a metal and a dielectric the dispersion relation can be derived from Maxwell's equations and boundary conditions [18]:

$$k_{SPP}(\omega) = \frac{\omega}{c} \sqrt{\frac{\varepsilon_d(\omega) \cdot \varepsilon_m(\omega)}{\varepsilon_d(\omega) + \varepsilon_m(\omega)}} , \qquad (1)$$

with $\varepsilon_m(\omega)$ and $\varepsilon_d(\omega)$ being the permittivity of the metal and the dielectric, respectively (c is the speed of light).
Therefore, the SP frequencies of Ag/TiO_2 and Au/TiO_2 are calculated as ~3 eV and ~2.3 eV, respectively, and the density states of the SP mode become dramatically larger with approaching these frequencies.
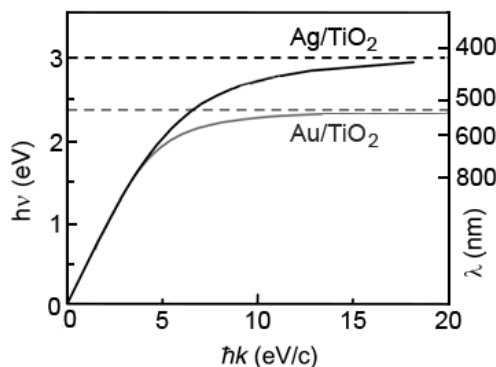

Fig. 5. Dispersion relations of the SPP at Ag/TiO_2, and Au/TiO_2 interfaces.

One should note that the emission intensity from samples coated with Ag films is not influenced with film thicknesses up to 20 nm, it being decreased by thicker films. These data are corroborated by measurements of the optical transmission in Ag and Au coated TiO_2 NTs (Fig. 6). Absorption bands are observed around 420 nm and 520 nm in Ag and Au coated samples, respectively.
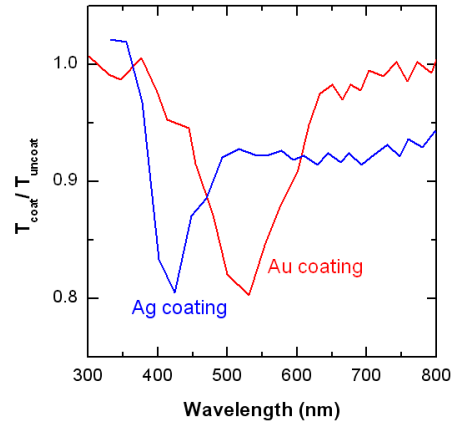

Fig. 6. Transmission curves of Ag and Au coated TiO_2 NTs. The transmission of coated samples (T_{coat}) is divided by the transmission of uncoated ones (T_{uncoat}).

IV. CONCLUSION

The results of this study demonstrate the enhancement of the green luminescence from titania nanotubes burned in a methane flame via coating with metal films. The enhancement is due to the effect of surface plasmons in Au coatings.

ACKNOWLEDGMENTS

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