Surface Plasmon Enhanced Luminescence from Ag covered Anatase Titania Nanotubes

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***Abstract* – We show that coating of titania nanotubes by Ag layers with thickness of 5 – 20 nm leads to the increase of the near-bandgap photoluminescence intensity by one order of magnitude, while the effect of Au coatings is insignificant. Titania nanotibes with average outer diameter of 250 nm and wall thickness of 70 nm with anatase structure were produced by anodization of Ti foils in an ethylene glycol based electrolyte containing a mixture of HF and H_3PO_4 followed by annealing at 300 ^oC. The enhancement of the band-edge emission is believed to be due to the effect of surface plasmons in Ag coatings. This suggestion is supported by calculations of dispersion relations of surface plasmons at the Ag/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 nanotuves, dispersion relations.**

I. INTRODUCTION

Titania (TiO_2) is widely used as a pigment, 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].

Titania nanotubes have been produced by a variety of methods including deposition into a nanoporous alumina template, sol–gel transcription using organo-gelators as templates, seeded growth, and hydrothermal processes [1,2]. However, among all methods, electrochemical anodization of titanium is a cost-effective approach for the growth of highly ordered TiO_2 NTs [4].

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 [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. 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].

In this work, we demonstrate that the band-edge emission from titania nanotubes produced by electrochemical anodization of titanium can be enhanced by the deposition of Ag films. This enhancement is due to the excitation of surface plasmons in Ag.

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 (Aldrich) 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 (11 ml) in ethylene glycol (120 ml) under 120 V during 2 hours. This treatment results in the fabrication of TiO_2 nanotubes with outer diameters around 250 nm and the wall thickness of 70 nm, as illustrated in Fig. 1. The samples were annealed at 300 ^oC during one hour 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 351 nm line of an Ar^+ SpectraPhysics laser and analyzed through a double spectrometer at low temperature (10 K). The resolution was better than 0.5 meV. 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.

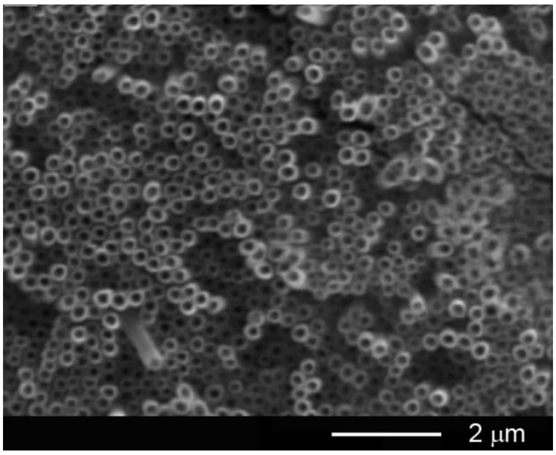

Fig. 1. SEM image of TiO_2 nanotubes produced by etching Ti foils in a mixture of HF and H_3PO_4 in ethylene glycol.

III. RESULTS AND DISCUTIONS

Figure 2 presents the PL spectra of TiO_2 nanotubes (with the morphology illustrated in Fig.1) subjected to annealing at 300 °C and covered with Ag films of different thicknesses. The luminescence measured in the spectral range from 370 to 500 nm 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.

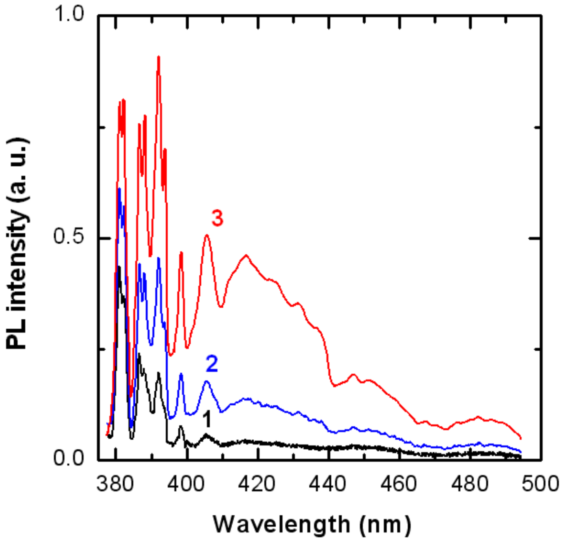

Fig. 2. PL spectra of TiO_2 NTs covered with Ag films with thickness of 5 nm (1), 10 nm (2) and 20 nm (3) measured at 10 K.

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 [9]. Therefore, the A_{1g} and one of the B_{1g} modes overlap. The two E_g modes at 144 cm^{-1}, 197 cm^{-1} are outside of the range of measured Raman shifts.

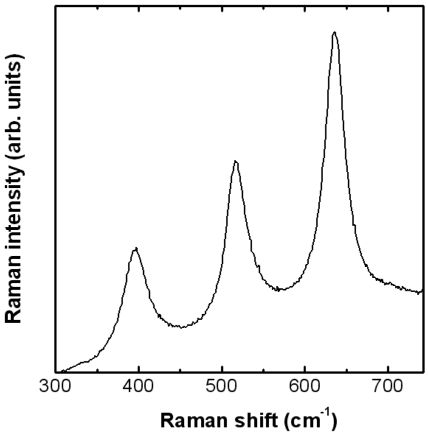

Fig. 3. Raman spectrum of TiO_2 NTs measured at room temperature.

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 [10]. 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 [11].

The data presented in Fig. 2 demonstrate that covering of TiO_2 NTs with Ag films with thickness of 5 to 20 nm leads to increased near-bandgap luminescence intensity. The thicker is the Ag film the stronger is luminescence. However, the increase of the film thickness beyond 20 nm results in a decrease of the luminescence intensity (not shown in this graph). We believe that this decrease is due to increased absorption in the metal film of both excitation and emission light. As concerns the increase of the luminescence intensity with Ag films up to 20 nm, it is suggested to be due to the enhancement of both the excitation field and the bandedge emission via surface plasmons in the Ag film, the second effect being stronger, since the excitation wavelength (351 nm) does not match very well the surface plasmon (SP) resonance. Fig. 4 shows the dispersion relations of surface plasmon polaritons (SPP) on Ag/TiO_2 and Au/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 [12]:

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

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.

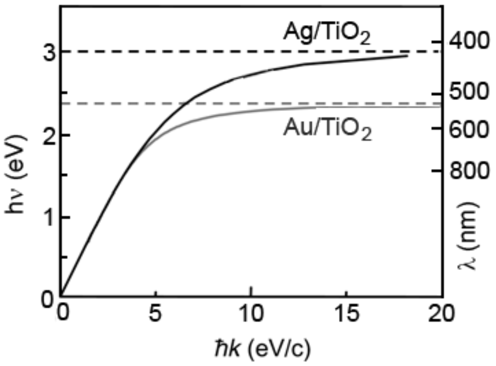

Fig. 4. Dispersion relations of the SPP at Ag/TiO_2, and Au/TiO_2 interfaces.

One can see from Fig. 2 that the emission around 380 nm is enhanced by a factor of 2 with Ag coating, while the emission around 400 – 440 nm is enhanced by an order of magnitude, since the energy of this emission corresponds to the resonance energy of the surface plasmons. At the same time, one should note that the emission intensity from samples coated with Au 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. 5). Absorption bands are observed around 420 nm and 630 nm in Ag and Au coated samples, respectively. One can expect that the luminescence intensity in the range of 600 nm would be increased by Au coating. However, our samples do not exhibit any emission at these wavelengths.

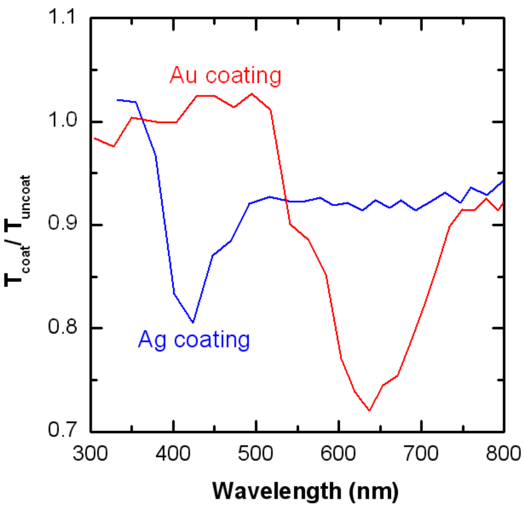

Fig. 5. Transmission curves of Ag (20 nm) and Au (20 nm) coated TiO_2 NTs. The transmission of coated samples (T_{coat}) is divided by the transmission of uncoated ones (T_{uncoat}).

IV. CONCLUSION

The results of this study demonstrate possibilities to enhance the luminescence from titania nanotubes via coating with metal films. The near-bandgap photoluminescence intensity from anatase titania nanotubes with average diameter of 250 nm and wall thickness of 70 nm is increased by an order of magnitude by coating with an Ag film with the thickness of 20 nm. The enhancement is due to the effect of surface plasmons in Ag coatings.

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