

Research Article

Nonlinear Mechanooptical Transmittance Controlled by a Rotating TiO₂ Thin Solid Film with Embedded Bimetallic Au-Pt Nanoparticles

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The modification in the third-order nonlinear optical behavior exhibited by a titanium dioxide thin solid film with embedded Gold-Platinum nanoparticles was induced by nanosecond optical pulses. A Nd:YAG laser system was employed for the experiments explored by a vectorial two-wave mixing method with the sample in rotation. The nanostructures were prepared by a sol-gel technique. Transmission Electron Microscopy studies and ultraviolet-optical spectroscopy measurements were undertaken. The evolution of the optical transmittance exhibited by the sample in rotation controlled by a servomechanism was observed. Potential applications for developing mechanooptical functions based on third-order optical nonlinearities were contemplated.

1. Introduction

In regard to the hallmark of nanoscience for ultrafast applications, tremendous efforts to propose all-optical functions performed by advanced materials have been conducted by different research groups in all around the world. Many of the most fascinating optical properties exhibited by metallic nanostructures are mainly due to their Surface Plasmon Resonance (SPR) [1]. The SPR in NPs is a result of electronic charge oscillations in a collective form that emerge from light-metal interactions [2]. Gold and Silver NPs have been widely studied regarding their sharp selective response in the optical spectrum [3], together with biocompatibility [4], sensitivity for instrumentation of signals [5], or nanomedical actions [6]. Alternatively, Platinum NPs present a peak of their SPR band in the ultraviolet electromagnetic region, with potential applications for developing single-photon devices [7] or low-dimensional materials for processing quantum operations with high energy photons [8]. Other important

advantages of Platinum NPs are their powerful photoluminescence [9] and superlative photocatalytic behavior [10]. Hybrid nanostructured materials based on Platinum NPs seem to be attractive for proposing photoconductive [11] and ultrafast switching systems dependent on size or hierarchical architectures [12]. The incorporation of Platinum NPs in dielectric substrates with high refractive index pointed out the possibility of employing nanocomposites for designing plasmonic schemes [13]. Nevertheless, third-order nonlinear optical properties exhibited by metallic NPs seem to be strongly modulated by different parameters that depend on resonance and irradiation conditions such as pulse duration and wavelength [14]. In this direction, it has been reported that bimetallic NPs may be able to distinctively enhance the nonlinear optical response of nanosystems [15]. Particularly, it has been noted that energy transfer mechanism and nonlinear optical characteristics in bimetallic NPs implicate a plural and vectorial response [16]. With this motivation, an attempt to further explain exceptional nonlinear optical

behaviors exhibited by metallic nanocomposites is reported in this work. Bimetallic Au-Pt NPs were prepared by a sol-gel method. In order to investigate the nonlinear optical transmittance of the nanostructures, third-order nonlinear optical measurements were carried out by using nanosecond pulses. The explorations correspond to the change in the irradiation condition for studying random distributions of NPs dealing with controlled angular velocity of rotation. Attractive advantages related to potential quantum functions derived from the control of 2D regions of interaction in bimetallic NPs can be considered.

2. Experimental

2.1. Sample Synthesis. Thin solid films were prepared from a sol-gel solution containing TiO_2 particles and Au and Pt NPs that were synthesized in situ by direct irradiation, with an UV lamp source, of the TiO_2 solution containing Au^{+3} and Pt^{+3} ions [17].

The solution of TiO_2 was prepared with 0.03 mol of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ precursor that was first dissolved in 200 mL of absolute ethanol and mixed later with a mixture of water-ethanol 30% v/v, whose pH was adjusted at 1.25 with hydrochloric acid. This sol was stored one week before the UV-light irradiation experiments. The volume fraction between Au and Pt employed for the preparation of the samples was 1 : 1. Standard solutions of Au and Pt precursors were employed in equivalent volume of 0.7 ml of metal solutions with concentrations of 1000 mg/L each. The processing route involves a 0.76% molar ratio exhibited by a (Au + Pt)/ $\text{Ti}(\text{OC}_3\text{H}_7)_4$ mixture contained in 11.5 mL. An ultraviolet irradiance of approximately $700 \mu\text{W}/\text{cm}^2$, with 320 nm to 390 nm emission wavelengths, promoted the photocatalytic reduction of Au^{+3} and Pt^{+3} ions. Thin solid films of TiO_2 with Au-Pt NPs and thickness of about 200 nm were fabricated by a spin coating method. Spectrophotometric measurements were undertaken by a Perkin Elmer UV-VIS XLS system. Transmission Electron Microscopy and High-Resolution Transmission Electron Microscopy (TEM and HRTEM; JEM-ARM200CF&Gatan-Ultrascan 1000XP system) evaluations were carried out with 80–200 kV accelerating voltages. The bimetallic characteristics of the NPs were analyzed by energy-dispersive X-ray spectroscopy (EDX; JEOL JSM-7800F) in Scanning Transmission Electron Microscopy (STEM) mode.

In Figure 1 is schematized the experimental setup employed for measuring the third-order nonlinear optical response exhibited by the sample in mechanical rotation [18]. We used the second harmonic of a Nd:YAG system (Continuum Model SL II) with linear polarization as an optical source to carry out vectorial two-wave mixing explorations. The maximum pulse energy employed at the output of the laser system was 60 mJ with a pulse repetition rate of 10 Hz, 532 nm wavelength, 4 ns pulse duration, and 6 mm of beam waist. In the scheme, the mirrors are represented as M1-4, the beam splitter is BS, and PD1-2 are PIN photodetectors. A1 is an analyzer with transmission axis orthogonal to the initial polarization of the probe beam. R/2 represents a half-wave plate employed for changing the polarization of the

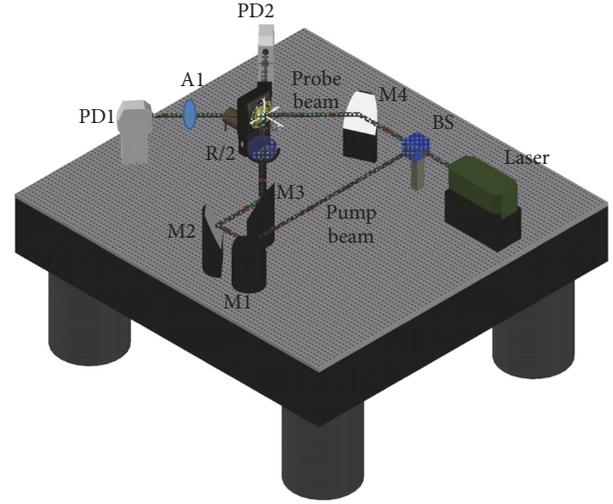


FIGURE 1: Experimental setup for the nonlinear mechano-optical modulation controlled by frequency rotation of the sample.

pump beam during the measurements. The optical irradiance relation between probe and pump beam was fixed to be about 1 : 1. The geometrical angle that separates the interacting optical rays was close to 30° . The beam waist in the film was about 6 mm.

The propagation of the optical beams in the vectorial two-wave mixing configuration was approximated by using the finite-differences method. The mathematical description of the transmitted beams can be numerically solved by using the wave equation [19]:

$$\nabla^2 E_{\pm} = -\frac{n_{\pm}^2 \omega^2}{c^2} E_{\pm}, \quad (1)$$

where the right and left circular components of the electric field are E_+ and E_- , respectively. The optical frequency is ω and the refractive index was approximated [19]:

$$n_{\pm}^2 = n_0^2 + 4\pi \left(A |E_{\pm}|^2 + (A + B) |E_{\mp}|^2 \right), \quad (2)$$

where $A = \chi_{1122}^{(3)}$ and $B = \chi_{1212}^{(3)}$ are the components of the third-order susceptibility tensor and n_0 is the weak-field refractive index.

3. Results and Discussions

Bimetallic Au-Pt NPs were observed in our experiments by HRTEM studies in bright field mode. In Figure 2, it can be clearly noticed the dark regions that represent the NPs incorporated in the sample. We carried out statistical nanoscopic measurements through different regions of the films to determine the approximated shape and size of the NPs. The estimated NPs size in the films can be geometrically described by spheres with an average size close to 12 nm. Our EDX analysis in the NPs corroborated the simultaneous elemental content of Gold and Platinum in the NP with

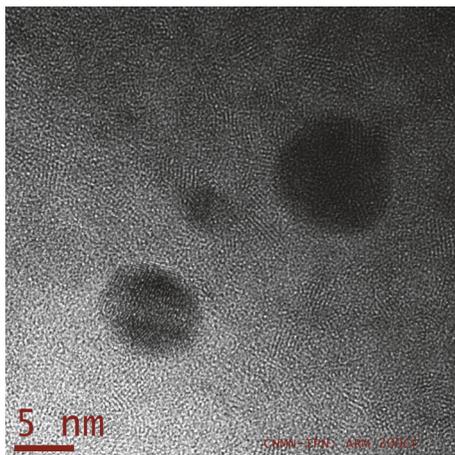


FIGURE 2: Typical TEM image of the Au-Pt NPs.

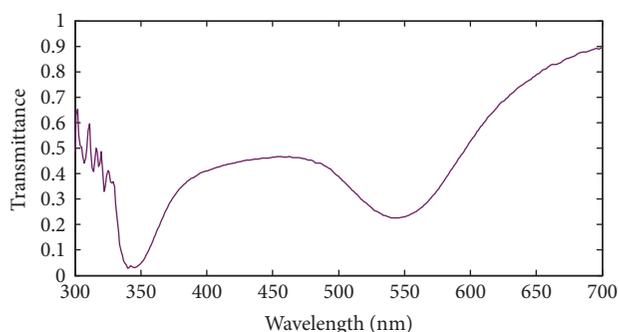


FIGURE 3: Transmittance spectrum of the Au-Pt NPs in an ethanol solution.

a resultant nanoparticle composition of Au and Pt that was approximately 10 : 1.

For simplicity, the UV-VIS spectrum associated with the Au-Pt NPs was evaluated when the NPs were suspended in ethanol in order to guarantee evidences of the plasmonic response of the NPs. In Figure 3 was plotted the transmittance that corresponds to the two distinct SPR bands associated with the Au and Pt metals in the NPs, with valleys close to 550 nm and 340 nm, respectively.

Figure 4 illustrates the influence of the mechano-optical action on the optical transmittance of the rotating sample. The frequency of rotation of the sample is defined by the angular velocity of a servomotor. From the plot, a proportional decrease in the transmittance can be clearly distinguished as a function of the angular velocity of the sample.

Nanosecond two-wave mixing results are shown in Figure 5 with the best fitting achieved by (1)-(2). The symmetric vectorial behavior exhibited by the sample seems to reveal the homogeneous nanosecond third-order nonlinear optical response. Each point in the plot is related to the average of 20 laser shots. The third-order nonlinear optical response exhibited by metallic NPs is closely related to the SPR effects. By using a near-resonance wavelength of excitation, it is possible to observe an enhancement in the

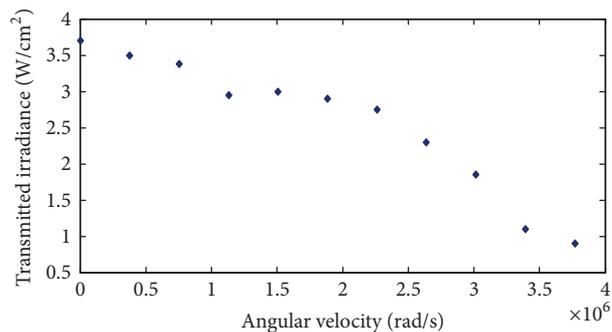


FIGURE 4: Single-beam transmittance versus frequency of rotation of the thin film.

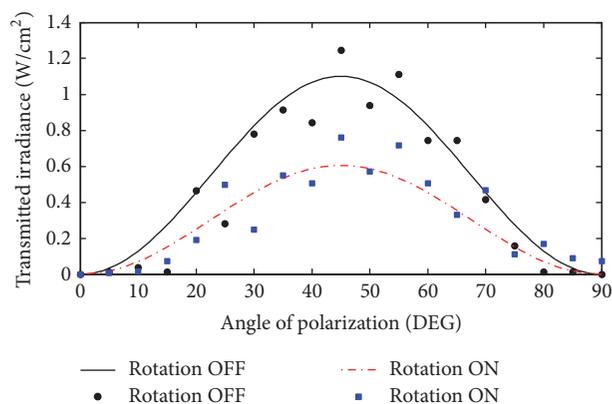


FIGURE 5: Nonlinear optical transmittance versus angle of polarization.

optical nonlinearities related to metallic NPs. The influence of different metals in a metallic nanoparticle contributes to the participation of additional resonances. These distinct resonances of bimetallic NPs can be located in the visible or in the ultraviolet spectrum, as it is the case of Au and Pt, respectively. Metal concentration in the TiO_2 film can promote particle interaction to enlarge the nonlinear optical response. The optimization of the nanoparticle density in a thin solid film depends on the application, since the evolution of optical absorption coefficient and index of refraction dependent on irradiance in nanocomposites usually presents a nonlinear behavior.

Through systematic changes in the experimental conditions for the rotation of the sample in the two-wave mixing experiment, we were able to notice important variations in the $|\chi^{(3)}|$ value estimated to decrease from 10^{-8} esu to 10^{-9} esu by the effect of the rotation of the sample. We take into account a random participation of Au or Pt in the rotating bimetallic NPs, as it has been previously demonstrated for the gyroscopic behavior of free-rotating bimetallic samples [19]. Since the laser wavelength employed for the experiments corresponds to a near-resonance wavelength for Au, in contrast to a far-resonance wavelength for Pt, these results can be explained as a consequence of a modification in the contributions associated with the different nonlinear optical phenomena involved in the light-matter interactions.

There has been an important growth in nanotechnologies capable of detecting small forces and motion related to low-dimensional systems [20]. Furthermore, attractive applications to facilitate nanomechanical spectroscopy also have originated a great interest for fabrication and characterization of nanomaterials [21]. Optomechanics for improving engineering science are also a counterpart in current research [22]. In this work, we highlighted advantages of mechanooptics which can be useful for future research in energy transference mechanisms based on nonlinear optics and instrumentation of ultra-low level signals.

4. Conclusions

The collective third-order nonlinear optical response exhibited by bimetallic Au-Pt NPs incorporated in a rotating TiO₂ thin solid film was analyzed by using nanosecond pulses.

The mechanooptical transmittance of the sample was controlled by the frequency of rotation of the system and the modification of the optical nonlinearities by an ablation process. Within this work is highlighted the possibility of controlling the optical absorption in a quantic fashion by mechanical functions in nanostructured systems with strong third-order optical nonlinearities.

Conflicts of Interest

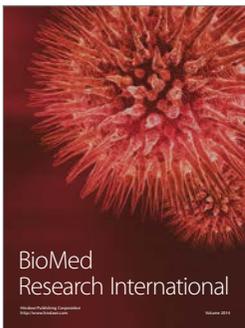
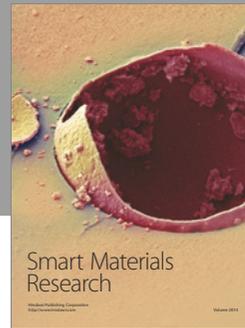
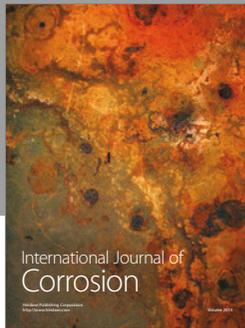
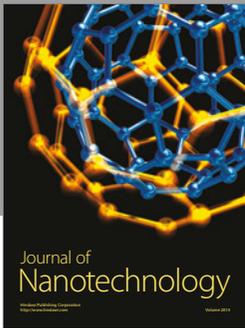
The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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