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Silver-Titania Nanocomposites as Raman Nanothermometer and Nanoheater for Photothermal Applications

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Extended Abstract.

For a wide variety of physical, chemical, and biological processes, temperature is a fundamental parameter, so it is not surprising that research in nanothermometry is increasing with regard to many applications. In the biomedical field, temperature monitoring is fundamental for diagnosis, but also for treatment of cancer. Photothermal therapy, that employs localized hyperthermia to induce a local overheating and selectively destroy cancer tissues, requires a precise temperature control to prevent damage to the surrounding healthy tissues [1-3]. Raman spectroscopy [4] is a very interesting and promising technique, as it offers a non-disruptive contactless measurement of temperature with high spatial resolution, down to a few µm.

This work is developed within the research area of photothermal therapy and nanothermometry to address interesting challenges. It consists in the realization of new optical nanothermometers based on multifunctional nanostructured systems operating from the visible to the near-IR range (within the biological window). Hybrid structures realized by combining active Raman materials with plasmonic systems are explored to enhance the Raman signal and realize a local heater.

The use of the Raman scattering technique for the determination of the local temperature is based on the acquisition of Stokes and anti-Stokes Raman spectra of the active material. The ratio of Stokes and anti-Stokes Raman intensities is temperature-dependent because of the population distribution of vibrational states in the electronic ground state. As a Raman thermometer, Titanium dioxide, in the Anatase phase, has already been tested in the visible [5] and near-IR [6] ranges: the ratio of its intense Raman signal ν_{E1g}, centred at ~145 cm^{-1}, has been clearly correlated with the local temperature of the sample.

In this work, new composite nanoparticles are designed to place the nanothermometer nanoparticles of Anatase in contact with the nanoheater silver nanoparticles (AgNPs). The synthesis follows a multi-step process and is adapted from Hong et al. [7]. Silver cores are prepared through a seed-mediated reaction, where $AgNO_3$ is reduced and stabilized to produce a seed suspension, with an average particle size of ~ 7 nm, with a subsequent growth step the nanoparticle size increases to ~ 46 nm. TiO_2 coverage is formed using a sol-gel method, starting from an ethanol solution of titanium tetrabutoxide (TTB) as the precursor. Crystallization of TiO_2 from the amorphous phase to the Anatase phase is obtained through a final hydrothermal treatment. Different hydrothermal experimental conditions, such as temperature, reaction time, and solvent choice, have been tested, to find the most efficient process.

The morphological and optical characterization of the new synthetized nanothermometers, has been performed using a wide range of optical techniques and clearly shows the structure of the synthesized nanocomposite, in which Ag cores are decorated by small TiO_2 NPs. In particular, Raman spectra, collected at 532 nm excitation wavelength and acquired at different laser irradiation powers, allow the determination of the local temperature and heat released. Particular attention is devoted to the evaluation of the sensitivity and the thermal resolution of nanothermometers. The other experimental parameter, which has been carefully evaluated, is the local temperature increase following irradiation with laser radiation.

This study demonstrates the feasibility of fabricating nanocomposite structures to obtain the double effect of a thermometric probe and a photothermal agent inside a single nanoparticle; they possess high potential for the local temperature control during photothermal applications, providing a foundation for further advancements in the field.

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