Local temperature determination based on Titanium dioxide anti-Stokes/Stokes micro-Raman thermometry

V. Zani (1,2)*, D. Pedron (1), R. Pilot (1,2) and R. Signorini (1,2)**
(1) University of Padua, Department of Chemical Science, Via Marzolo 1, Padua, Italy; (2) Consorzio INSTM, Italy; **Correspondence to: raffaella.signorini@unipd.it; *Poster presenter, veronica.zani@studenti.unipd.it

Overview

The measurement of temperature with sub-micrometric spatial resolution is assuming an increasing importance from a basic science point of view as well as for application in nanomedicine, where heat treatment of tumoral cells aggregates has been demonstrated to be fundamental for medical therapy. Optical nanothermometry has the great advantage of a contactless measurement. The aim of this work is the investigation of Raman thermometry of nanostructured samples based on **titanium dioxide** (TiO_2), which is particularly interesting for its high temperature sensitivity and, thanks to its high biocompatibility, could be appropriate for biological applications. In particular the ratio of Stokes and anti-Stokes peak areas (aS/S) is the parameter that is derived from experimental Raman spectra and can be used for efficient local temperature determination.

Raman Spectroscopy: set-up and sample preparation

Raman spectroscopy is the inelastic scattering of light. When the incident laser beam illuminates the sample, Stokes and anti-Stokes events occurs, depending if the starting level is the ground state or the first excited vibrational state of the molecule.

Raman measurements have been performed using the excitation lines of the CW Ar+/Kr+ ion laser, at 488.0, 514.5, 568.2 and 647.1 nm. The laser beam is focalized through a microscope on the sample, kept at defined temperature using a temperature controlled-stage. The scattered light is collected by the microscope, analyzed through a triple monochromator and detected by a liquid nitrogen-cooled CCD camera.

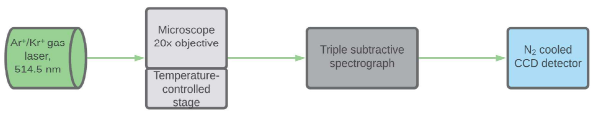

Fig. 1: Micro-Raman Set-up scheme

For Raman spectroscopy measurements the powder was pressed on KBr pellet sample, with a thickness of few hundreds μm. The homogeneity of the samples is tested by mapping the intensity of Raman peak at 143 cm^{-1}.

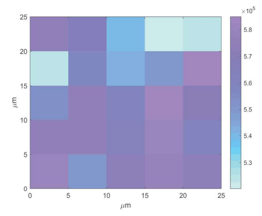

Fig. 2: Map of Raman Intensity for TiO_2

Raman Spectra of Titanium Dioxide

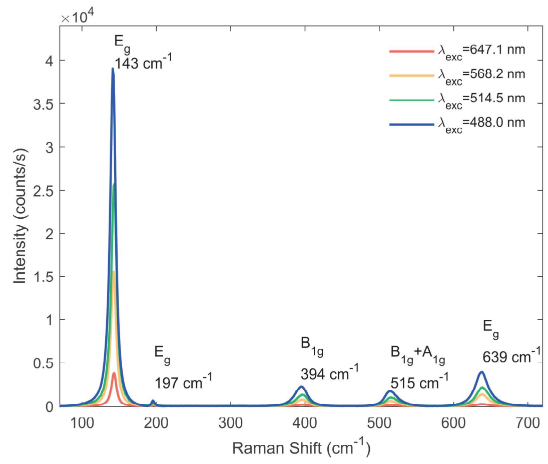

Fig. 3: Raman spectrum of TiO_2 recorded at different excitation wavelengths.

All the principal anatase Raman peaks are identified, the most intense E_g mode at 143 cm^{-1}, the B_{1g} mode at 400 cm^{-1}, the $B_{1g} + A_{1g}$ mode at 515 cm^{-1} and the E_g mode at 640 cm^{-1}.

The Raman peak position and width depend on the size of nanoparticles. Commercial TiO_2 nanoparticles used in this work have a dimension of approximately 220 nm, confirmed by XRD measurements, in agreement with a relatively low peak frequency (the smaller the crystallite size, the higher the shift of the Raman peak towards higher frequencies).

The method

The experimental values of anti-Stokes/Stokes ratio are obtained by fitting the Stokes and anti-Stokes Raman peaks with a Lorentzian curve in Matlab.

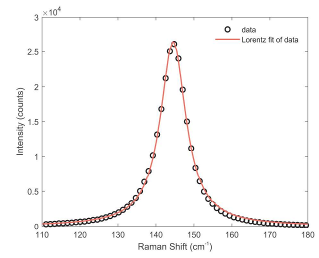

Fig. 4: Example of Lorentz fitting to experimental Raman spectrum.

The ratio of anti-Stokes and Stokes areas derived by the fit is related to temperature through the following equation

$$aS/S = \frac{(v_0 + v)^3}{(v_0 - v)^3} exp\Big(-\frac{hv}{kT}\Big) \quad (1)$$

where v_0 is the excitation frequency, v the frequency of the Raman mode, h the Planck's constant, k the Boltzmann constant and T the temperature.

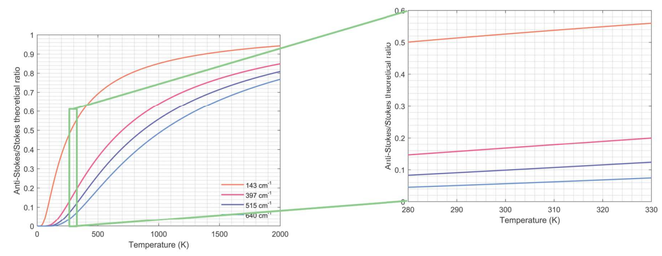

Fig. 5: Theoretical anti-Stokes/Stokes ratio as function of temperature in a wide range of temperatures and in the range of interest ($\lambda_{exc} = 514.5nm$).

Titanium dioxide in the anatase phase is a very promising material, as it possesses an intense Raman peak at low Raman shifts, near the Rayleigh line, implying a high temperature sensitivity of its anti-Stokes/Stokes ratio.

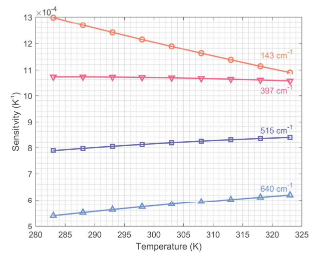

Fig. 6: Sensitivity of the anti-Stokes/Stokes ratio for all the four peaks of TiO_2 at 514.5 nm.

The problem of sample self-heating

The aS/S, calculated from the ratio of Stokes and anti-Stokes areas, is determined as function of incident laser power in order to test whether the sample experiences **self-heating**, thus suggesting the range in which temperature measurments can be conducted.

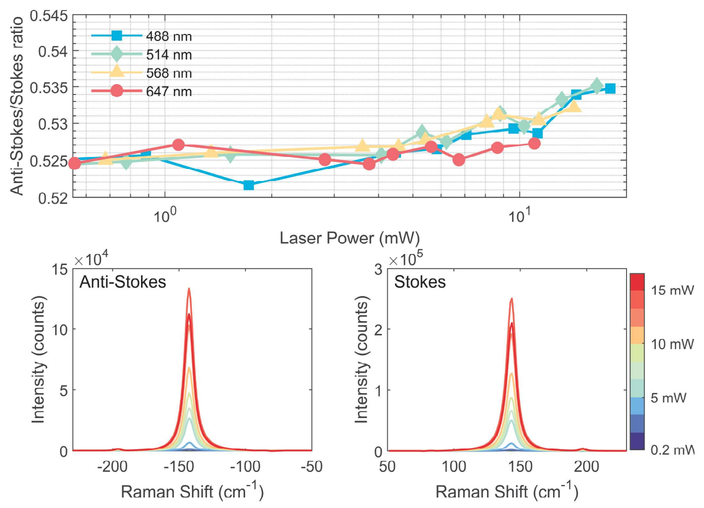

Fig. 7: Anti-Stokes/Stokes ratio at different excitation wavelengths as function of the input power.

Local temperature determination

Once the laser power has been set, the calibration of aS/S is investigated by changing the temperature of TiO_2 sample with steps of 5 K in the range 283 - 323 K by inserting the sample in the temperature-controlled stage; output values of aS/S are fitted using the Equation 1.

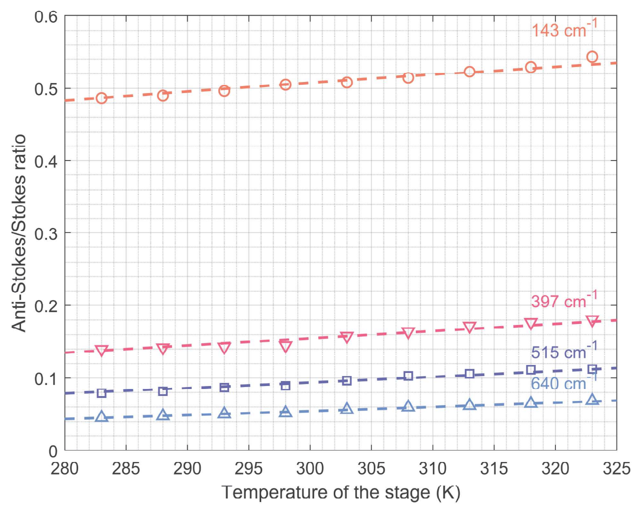

Fig. 8: Temperature calibration curves of the Anatase anti-Stokes/Stokes ratios for all the Raman modes at 514.5 nm.

Conclusions and future perspectives

The investigation of new materials for high resolution contactless thermometry is crucial for many applications. The Raman mode of Anatase at 143 cm^{-1} is chosen for Raman thermometry for its high thermal sensitivity. The behaviour of the aS/S as function of input power is useful to find a suitable range to avoid self-heating effects. The local temperature is determined for TiO_2 in the range 283 - 323 K. In conclusion, the material studied in this work is suitable for Raman thermometry in a wide range of excitation wavelengths, and the uncertainty of the temperature measurement could be extimated to be 2 K at λ_{exc}=514.5 nm, by performing repeated measurments. Future measurments will be conducted also in the infrared region, especially in the biological window, as many biological applications require that range of wavelengths.

This research was funded by Chemical Science Department of University of Padova, project P-DiSC#10BIRD2019-UNIPD.