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Novel low-cost, compact and fast signal processing sensor for ratiometric luminescent nanothermometry

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ABSTRACT

We developed a new compact, low-cost and non-invasive temperature sensor based on a ratiometric luminescence technique. The setup included a commercial digital color sensor, which collects simultaneously signals in the blue, green and red regions of the electromagnetic spectrum, usually used to assess the quality of computer screens and used for the first time here as a sensor for luminescent thermometry, coupled to an optical system that focuses an excitation laser beam onto luminescent nanoparticles emitting at least in two of these electromagnetic regions, which simplifies considerably the design, alignment and measurement procedures of setups used up to now for the same purpose. The same optical system collects the emission arising from the luminescent nanoparticles and directs it towards the digital color sensor through a dichroic mirror. We probed the potentiality of this setup for luminescence thermometry in the biological range of temperatures using Er,Yb:NaYF$_4$, and up to 673 K for microelectronic applications using Tm,Yb:GdVO$_4$ up-converting nanoparticles. The thermal sensitivity obtained in both cases is similar to that previously reported for the same kinds of nanoparticles using conventional systems. This validates our setup for temperature measurements. Also, we developed new flexible and transparent polymer composites, in which we embedded upconversion luminescent nanoparticles of Er,Yb:NaYF$_4$ in PDMS, a standard polymer for microfluidic devices used for biomedical studies, which allow fabricating thermometric microfluidic chips in which temperature can be determined using our setup. The thermal sensitivity for these composites is slightly smaller than that of the bare nanoparticles, bur still allowing for precise and fast temperature measurements.

1. Introduction

There are many areas of industry, where temperature measurements are essential, such as metallurgical industries, glass manufacturing, material modeling or dairy products, among others. There are other fields like biomedical sciences, where temperature provides basic diagnostic criteria [1,2] and its control is essential during hyperthermia treatments [3,4], for instance. Despite modern temperature measurement instruments at the nanoscale are in general complex in nature and at the same time fascinating in operation [5], there are situations–because of hostile environments, presence of vibrations, electrical noise, strong electromagnetic fields, or other factors- where temperature measurements are difficult or even impossible with this kind of instruments. To overcome these difficulties and achieve temperature sensing in hardly accessible locations, optical non-contact thermometry methods have been developed since they provide electromagnetic immunity and possibilities for remote measurements [6,7]. Most of the optical non-contact temperature sensors are based on reflection, absorption, scattering, fluorescence or interference phenomena of light [8,9]. Among these optical non-contact thermometry methods, fluorescence thermometry is among the most versatile methods. It is based on fluorescence intensity, band-shift or lifetime changes produced by temperature [10]. Among these three techniques, it is difficult to select the optimal one, as each of them shows special features of interest. The lifetime-based technique allows performing measurements in objects in movement and at high temperature, for instance, avoiding the blackbody radiation effect [10,11]. However, this technique requires costly instrumentation, such as pulsed lasers for excitation of the luminescent probe, and monochromators to isolate the particular wavelength to be analyzed, and in some cases lock-in amplifiers to be able to measure

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small intensity signals. From another side, the band-shift technique can be very sensitive to temperature changes, but it can be only applied to a relatively narrow range of temperatures. Furthermore, since this technique has mainly used quantum dots a luminescent nanoparticles, it suffers from their signal bleaching. By using ratiometric measurements these problems can be avoided [6,7]. Ratiometric measurements are based on systems with different luminescence emission bands whose relative intensities strongly depend on temperature. This thermal dependency is caused by a thermally induced electronic population re-distribution among the corresponding emitting energy levels of the optical center. An additional advantage is that the relative intensity of the luminescence bands depends only on temperature but not on the local concentration of the emitting center. Also, effects derived from fluctuations in the excitation source are avoided since the different luminescence lines will be affected in an equal manner.

In these techniques, the choice of a particular luminescent material determines the temperature range, thermal sensitivity and stability of the nanothermometer. The most used materials for luminescent nanothermometry are quantum dots [12–14], organic dyes [15–17] and lanthanide-doped materials [18–21]. Although, organic dyes and quantum dots show a high thermal sensitivity, their main disadvantage is that they need to be excited using ultraviolet (UV) or visible light (although recently quantum dots have been developed that can be excited in the near-infrared that can overcome this problem, see for instance [22]). This may lead to the degradation of the fluorescent material. Furthermore, when used in biological applications, the excitation with UV or visible light might induce the appearance of background fluorescence, and even the damage of biological tissues. From another side, the use of lanthanide-doped up-converting nanoparticles (Ln-UCNPs), which absorb photons sequentially in the near-infrared (NIR) and emit radiation in the visible, has several advantages, such as the negligible photodamage to living organisms, a weak autofluorescence background, and a deeper penetration in biological tissues for biomedical thermometry purposes. Moreover, NIR excitation can be achieved with high power, and low cost laser sources. Finally, it is also important to note that Ln-UCNPs are more optically stable and have lower toxicity than quantum dots, for instance.

However, the setups used up to now to determine changes in luminescence intensity with temperature in these ratiometric techniques require bulky and relatively costly equipment, such as monochromators, luminescence detectors (photomultiplier tubes, CCD cameras, etc.), lock-in amplifiers, oscilloscopes, sophisticated aligning mechanical systems, etc. The size of these devices also limits the practical applications of these thermometric techniques and their transfer to real industrial or medical environments, where the measurement conditions change continuously. Furthermore, recording an emission spectrum with these devices requires some seconds, or even minutes, a timeframe during which the temperature of the sample might change, which represents an additional disadvantage of this technology.

Here, we report a new low-cost, compact, fast signal processing, and non-invasive temperature sensor using a ratiometric fluorescence thermometry technique that simplifies substantially the design, alignment and measurement procedures of setups used previously for the same purpose. Our setup uses a commercial digital color sensor, usually used to assess the quality of computer screens and used here for the first time to undertake luminescence thermometric measurements, coupled to an optical system that allows simultaneously the excitation of the Ln-UCNPs and the collection of their emission, simplifying the alignment of the optical components (excitation sources, lenses, mirrors and detectors) of the measurement setup. The emission from the Ln-UCNPs is separated from the excitation radiation, and diverted towards the detector. The detector is build in a mosaic structure, and containing different filters that allows it detecting simultaneously signals in the red, green and blue channels. With a microprocessor we calculated the fluorescence intensity ratio corresponding to the signals of two of these channels, and after comparing it to a previously determined calibration curve, temperature is visualized in a LCD display [23]. This reduces substantially the measurement procedures, times and processing of the luminescent signals used to determine the temperature. We used different Ln-UCNPs to demonstrate the potentiality of this thermometer to operate in different temperature ranges. We also reported, for the first time, the fabrication of transparent polydimethylsiloxane (PDMS)/luminescent Ln-UCNPs composites, from which microfluidic microchips can be fabricated since PDMS is one of most used polymers for this purpose [24,25]. These composites would allow to determine temperature directly in the internal walls of the microchips, taking into account that the fluid should be pumped to the wall of the microchannel so that as being in contact the fluid and the composite, the temperature determined might be representative of the temperature of the fluid, avoiding in this way that the fluid had to carry the luminescent thermometric material. This would simplify the fabrication and performance of similar systems reported previously involving the use of surface plasmons [26].

2. Experimental section

2.1. Temperature measurements setup

The setup we propose for temperature measurements comprises a diode laser that can be adapted to emitting at a wavelength that can be absorbed by the Ln-UCNPs, a focusing system (a microscope objective in the particular applications we are showing here, but that can be substituted easily by an optical lens) to focus the laser beam onto the sample and, that at the same time, collects the light emitted by the nanoparticles, a dichroic mirror that deviates the visible light generated by the nanoparticles towards the digital color sensor and at the same time filters the excitation radiation, and a S9706 Hamamatsu digital color sensor. A schematic representation of this setup is shown in Fig. 1(a). The S9706 Hamamatsu digital color sensor consists on 9 × 9 arrayed photodiode elements arranged in a mosaic pattern integrated on a chip (see Fig. 1(b)) with a photosensitive area of 1.2 × 1.2 mm. Each element has an on-chip filter that is sensitive to a particular range of wavelengths corresponding to different colors: red (590–720 nm), green (480–600 nm) and blue (400–540 nm), as shown in Fig. 1(c). This sensor allows the RGB components of the incident light to be simultaneously measured with high accuracy. This digital color sensor is connected to a microchip that converts and amplifies the light signals into 12-bit digital signals, with independent reading for the blue, green and red channels, which allows us to analyze the intensity ratios between these signals, and to compare these data with a previous calibration curve to determine the temperature of a particular measurement. The integration time of this kind of sensor depends on the illuminance conditions, ranging from 100 s for low illuminance conditions to 10 μs for high illuminance conditions [27].

To establish the calibration curve, the Ln-UCNPs were introduced in a Linkam THMS 600 heating stage, taking measurements every 5 °C when we analyzed the biological range of temperatures (25–60 °C) and every 50 °C for higher temperature applications. An Apollo Instruments Inc. diode laser with emission at 980 nm and 100 mW was used as the excitation source. The laser beam was focused on the sample using a 40× microscope objective and a N.A. of 0.6, producing a laser spot ~10 μm on the sample. The emission was collected by the same microscope objective, and after passing