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Thermophysical properties of thin fibers via photothermal quantum dot fluorescence spectral shape-based thermometry

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ABSTRACT

To improve predictions of composite behavior under thermal loads, there is a need to measure the axial thermophysical properties of thin fibers. Current methods to accomplish this have prohibitively long lead times due to extensive sample preparation. This work details the use of quantum dots thermomarkers to measure the surface temperature of thin fibers in a non-contact manner and determine the fibers' thermal diffusivity. Neural networks are trained on extracting the temperature of a sample from fluorescence spectra in calibrated, steady-state conditions, based on different spectral features such as peak intensity and peak wavelength. The trained neural networks are then used to reconstruct the evolution of the surface temperature in transient heating experiments. In order to determine the thermal properties of a thin fiber, modulated laser heating is applied and an FFT-based method is used to extract the phase and amplitude response of the temperature field at the modulation frequency. The spatiotemporal dependence of the fluorescence signal, obtained by scanning the distance between the excitation and detection laser spots and varying the frequency response due to an axial scan and a frequency scan, is then curve-fit to the resulting decay curves by a photothermal model in order to determine the thermal diffusivity of the fiber. The measured thermal diffusivity ($3.3 \pm 0.8 \times 10^{-7}\ m^2\ s^{-1}$) of a synthetic spider silk fiber by the current method has similar properties to other synthetic silk fibers, and demonstrates the ability of the current method to more rapidly measure thermophysical properties of thin fibers.

1. Introduction

Quantum dots with significantly temperature-dependent fluorescence properties have been considered for use as nano-sized temperature probes [1], because of their increased stability over organic dyes [2]. It should be mentioned that their fluorescence intensity can still be decreased when in contact with oxygen [3]. However, the use of quantum dots for temperature sensing remains attractive despite these and other limitations due to their small size [4], and their applicability in a variety of applications [5]. Quantum dots are nanometer-sized semiconducting crystals, whose emission spectrum in general and fluorescence peak wavelength in particular are a function of their size. CdSe/ZnS quantum dots represent one class of multiple probes that have been considered for nanothermometry at the cellular level [6], where improved temperature resolution is required [7,8,4]. They (and other fluorophores) have been used for thermal characterization of the solution they are suspended in [9,10], for spectroscopic investigation of materials via the thermal lens and optical absorption methods [9], and as contrast agents in photoacoustic and photothermal microscopy [11]. Their contribution to the effective thermal diffusivity of the system of interest is negligible [9], which is necessary for thermal characterization of materials. However, the temperature resolution with state-of-the-art quantum dots is on the order of 1 K [4] and methods to improve this accuracy are desired. Previous work [10,12] has demonstrated the potential for neural networks to improve this accuracy.

The accuracy of quantum dot thermometry can also benefit from the use of frequency domain-based methods. Many fluorescence spectroscopy measurements in the frequency domain have been focused on lifetime-based measurements [13], with the emphasis being on understanding the decay kinetics of chemical systems. These frequency domain lifetime measurement were coupled with a fast fourier transform (FFT) and intensity-modulated light source to induce fluorescence in a fiber optic-based temperature sensor [14], thereby improving the detected signal and aiding

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in fitting the lifetime decay as a function of temperature. However, for frequency domain modulated heating experiments (such as lock-in IR thermometry [15] or modulated optical reflectance [16]), the probe beam is usually continuously illuminating and the pump beam is modulated. The current study seeks to use quantum dot fluorescence thermometry as a method to probe the modulated surface temperature of fibers. Photoluminescence intensities in the time domain via spectrometer rather than lifetime measurements are investigated. This also motivates the investigation of fluorescent probes, rather than phosphorescent ones, because the lifetimes of typical phosphorescent probes are longer than desirable for typical frequencies used in photothermal methods [17].

There is the possibility to improve the signal-to-noise ratio of the FFT signal by improving the accuracy of the reconstructed temperature. Neural networks have successfully been used to reconstruct the surface signal for photothermal radiometric experiments [18]. They have the potential to improve the temperature accuracy of the quantum-dot shape-based thermometry. The current study seeks to expand shape-based, neural network reconstructed, time-domain fluorescence thermometry [10,12] with quantum dots. The reconstructed temperature evolution is then mapped into the frequency domain to determine the decay and phase delay of the thermal wave along a thin fiber caused by intensity-modulated laser heating for the purpose of determining thermal diffusivity.

Accurate measurements of the thermal properties of fibers are of interest, because of large uncertainties in the measured property for spider silk [19–21] and polyethylene nanofibers [22], which are induced by thermal contact resistance [23], modeling biases [24], and spatial resolution [25]. Additionally, axial heat conduction (and to a lesser extent, thermal diffusivity $\alpha = k/\rho c_p$) and Youngs modulus are properties of interest because they are the most sensitive characteristics to measure chain extension and continuity in polymers [26]. Hence, a non-contact thermometry based method is investigated for measuring the thermal diffusivity of a thin fiber.

In this work, a neural network approach is used for extracting temperature information from the fluorescence spectrum of inorganic fluorophores, both in time- and frequency-domain. An FFT-based method is elaborated upon in order to perform this frequency domain mapping operation and obtain the needed amplitude and phase at the modulation frequency. Laser heating experiments and simulations are investigated to determine the feasibility of this approach to measure the thermal diffusivity of thin fibers.

2. Experimental setup

The experimental setup consisted of a pump-probe laser system with the sample fiber mounted on a sample holder capable of measuring and controlling its temperature (Fig. 1). Quantum dots (Lumidot™ 640 nm peak wavelength, CdSe/ZnS from Sigma Aldrich) deposited on the surface of the fiber were illuminated with the probe beam (532 nm Coherent Compass CW laser) at a spot size of 30 μm. The resulting fluorescent emission was collected by an Olympus microscope objective (10X, 0.25 NA) into the fiber optic of an Ocean Optics USB4000 spectrometer, after having passed though band pass filters to remove the probe light. After passing through an optical chopper, the pump laser (a 1064 nm Coherent Vector) was focused onto the fiber with the top half of a bifurcated plano-convex lens mounted on a position scanning stage, with a resulting spot size of 90 μm. The laser beam contained some residual green light, which was filtered out prior to arriving at the sample, and the reflected light from the filter was focused onto the spectrometer to provide a reference for the

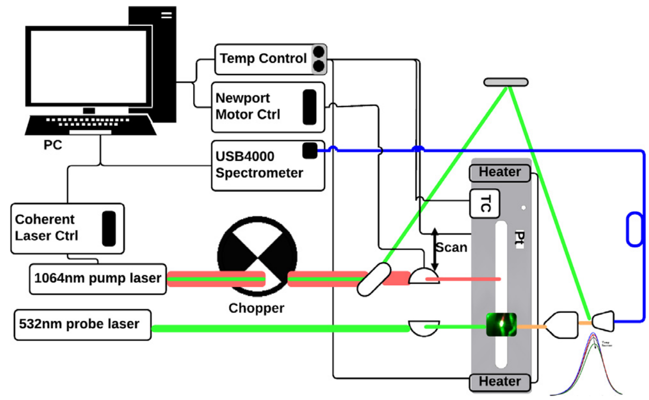

Fig. 1. Experimental setup for quantum dot fluorescence measurement.

intensity-modulation of the laser light for photothermally generated temperature variations.

The longer wavelength of the pump beam was selected to not induce fluorescence of the quantum dots. The absorption of the quantum dots at IR wavelengths is insignificant, so that the pump beam did not interfere with the emitted fluoescence spectra. Focusing of the lasers by half lenses allowed independent motion of the pump laser from the probe laser, as well as maintaining the same focal plane for both collimated laser beams.

The sample holder consisted of an aluminum plate with four heating resistors that provided control of the sample temperature from a Labview-controlled PID control routine. The fiber was placed in a slit on the plate to allow optical access for front and rear illumination. Temperature was measured by both an Omega F3141 PT1000 RTD (measured by an HP-34401 via GPIB control, with an uncertainty of 0.065 K) and an Omega type T thermocouple (welded in-house, measured by an HP-34970A via GPIB with an uncertainty of 0.1 K). Samples were placed inside a Janis cryostat to provide optical access and high vacuum (10^{-5} mTorr). The significantly decreased vacuum pressure insured the absence of convective contributions to the heat transfer around the fiber [27].

In order to relate the fluorescence spectra to the fiber surface temperature, a calibration is needed. The calibration process of the experiment began by stabilization of the fiber at ±0.015 °C for 15 min, after which 250 spectra were acquired, while recording the sample mount temperature using a PT1000 resistor. Temperature increments of 2 K (between 300 K and 312 K) resulted in 1750 total recorded calibration spectra to provide the training data for the neural network.

Upon a successful calibration and alignment of the pump and probe beams, the position of the pump laser with respect to the probe laser was scanned between +2000 and −2000 μm, with scanning steps of 50 μm. At each position, the laser was turned to full power (1 W) to provide enough modulated heating on the fiber to produce a sufficient photothermal signal. After a waiting period of 10 s (to allow the fiber to reach a stabilization of the gradual heat from the laser, resulting in mainly square wave modulated temperature oscillations), the spectrometer began measuring at a sampling rate of 50 ms. The experiment ran sufficiently long enough to collect 100 periods of the excitation laser modulation, resulting in an improved phase measurement during the FFT analysis.

3. Methods

The following sections focus on: the neural network training process for time domain temperature reconstruction, the FFT procedure to find the amplitude and phase of the complex temperature (compared to the FFT of commonly used spectral features),