Investigation of nonlinear optical effects of hybrid thermosensitive platforms modified with plasmonic and dielectric nanoparticles

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ABSTRACT

Various scientific areas, including imaging, portable sensors, and smart devices, are extremely interested in mechanically switchable optical systems that are responsive to external stimuli. Due to their capacity to modify the phase or frequency of the optical field, which results in mechanical changes in their structure, micro- and nanoscaled optomechanical systems offer a lot of potential. As a result, optical response may be changed in real time based on surface pattern and design.

This work presents a thermally-sensitive mechanically driven platform based on poly(N-isopropylacrylamide) (pNIPAM) microspheres modified with high refractive index dielectric (silicon, Si) and plasmonic (gold, Au) nanoparticles for second harmonic generation tuning. The platform enhances second harmonic generation depending on the applied temperature, amplifications of its signal more than 7 times for pNIPAM@Si and 32 times for pNIPAM@Si@Au. The tunability of these platforms makes them potential for robotic controllers. The enhancement of second harmonic generation after phase transition exceeds 7 times, and both platforms are reversible and reproducible.

Keywords: thermosensitive polymer, pNIPAM, gold nanoparticles, silicon nanoparticles, second harmonic generation, electrical-field-induced second harmonic

In recent years, there has been a significant research interest in tunable platforms and their properties. These platforms, often referred to as "smart" surfaces, have the ability to switch their physical properties such as absorption and transmission in response to external stimuli like temperature, pH, electric or magnetic fields. Among the various materials being explored for these applications, the thermosensitive polymer poly(N-isopropylacrylamide) (pNIPAM) stands out due to its several advantages over traditional materials. These features include: versatility (pNIPAM-based smart surfaces can be designed to respond to a wide range of stimuli, making them suitable for a variety of applications); reversibility (the changes in properties of pNIPAM-based smart surfaces are reversible, which means they can return to their original state once the stimulus is removed); tunability (the response of pNIPAM-based smart surfaces can be tuned by adjusting the concentration of the material or the nature of the stimulus); biocompatibility (pNIPAM-based smart surfaces are biocompatible, making them suitable for use in biomedical applications such as drug delivery and tissue engineering); low cost t(he synthesis of pNIPAM-based smart surfaces is relatively simple and inexpensive compared to other responsive materials). The focus of this work is on creating two different configurations of a thermosensitive platform using pNIPAM particles. The first configuration involves coating the pNIPAM particles with silicon nanoparticles, resulting in Si@pNIPAM. The second configuration involves coating the pNIPAM particles with both silicon and gold nanoparticles, forming Si-Au@pNIPAM. One of the key properties of pNIPAM is its ability to transition from a hydrophilic state to a hydrophobic state when the temperature exceeds 32 °C. This transition causes around 90% of the fluid contained within the material to be displaced[1]. Importantly, this alteration is reversible, allowing for repeated switching between the two states. By modifying the pNIPAM polymer with nanoparticles, the optical properties and reaction of the resulting structure can be altered[2]. This opens up possibilities for utilizing these thermosensitive materials in various applications such as sensors, indicators, and interfaces in interdisciplinary fields including biology and medicine. Overall, the study of tunable structures and their properties, particularly those involving thermosensitive polymers like pNIPAM, holds great potential for advancements in various fields where responsive materials are needed.

The first approach in this study involves utilizing silicon nanoparticles coated with pNIPAM to generate a signal from the second harmonic (SHG) when irradiated with laser power. The polycrystalline structure of the particles, created through laser ablation under a liquid layer, enables this reaction to occur. The large number of crystallites within the nanoparticles

near the interface eliminates the inverse symmetry of the crystal lattice locally, resulting in SHG. The surface area of the polymer particle changes as its volume changes, leading to a modification in the signal. Additionally, the local amplification of the electric field at the pump frequency (Mi resonances)[3] contributes to the amplification effect. In the second configuration, gold nanoparticles are also coated onto the pNIPAM particles, forming Si-Au@pNIPAM. This system not only increases the second harmonic signal but also excites localized plasmon resonance and local amplification of the field between the gold nanoparticles[4]. These findings highlight the potential of utilizing tunable structures and their properties, particularly those involving thermosensitive polymers like pNIPAM, in various applications such as sensors, indicators, and interfaces in interdisciplinary fields including biology and medicine. The ability to manipulate the optical properties and reaction of these materials through nanoparticle modification opens up new possibilities for advancements in responsive materials.

To examine the structure, we utilized a custom-made platform equipped with a Peltier element to heat the system within a temperature range of 25-40 °C. To simulate an aqueous environment, we investigated the dependency of the second harmonic signal intensity (SHG) in an agarose matrix. To irradiate the material, we employed a femtosecond laser LightConversion Pharos with a wavelength of 1030 nm. In the Si@pNIPAM configuration, the SHG signal was amplified by a factor of 7, while in the Si-Au@pNIPAM configuration, it was amplified by a factor of 32 (Fig. 1).

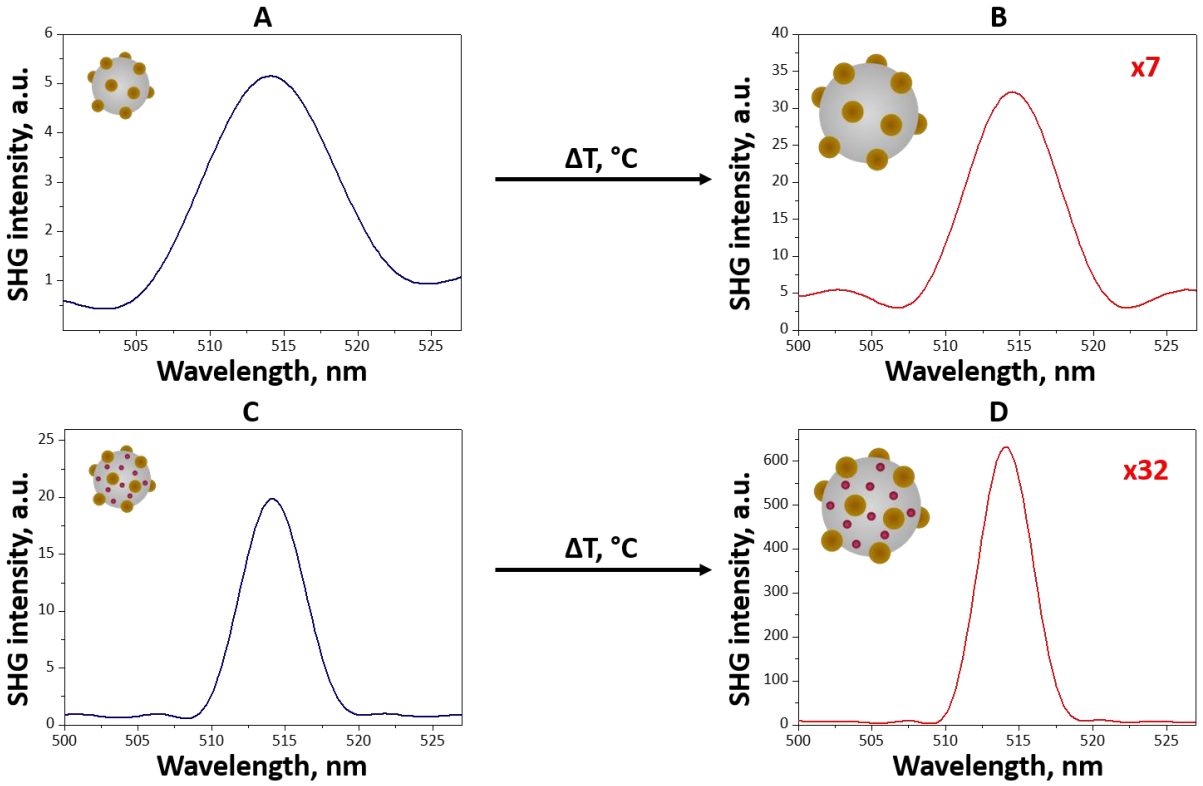

Figure 1. Intensity of the second harmonic at room temperature and at the temperature of the critical transition from: A, B – Si@pNIPAM configuration; C, D – Si-Au@pNIPAM configurations

To analyze the microgel particles, we employed dynamic light scattering (Photocor Compact, Photokor LLC, Russia) and scanning electron microscopy (Inspect SEM FEI, USA). The diameter of the PNIPAM particles in the hydrophilic state was found to be 465 ± 20 nm, while in the hydrophobic state, it was 266 ± 13 nm. In addition to analyzing the particle size, we also studied the variation in signal intensity over time when the thermosensitive platform was repeatedly heated and cooled. To do this, we varied the temperature every 4 minutes from 20 to 40 °C and measured the strength of the SHG (Fig. 2). The resulting systems showed slight alterations in intensity levels, making them suitable candidates for "on/off" type switches.

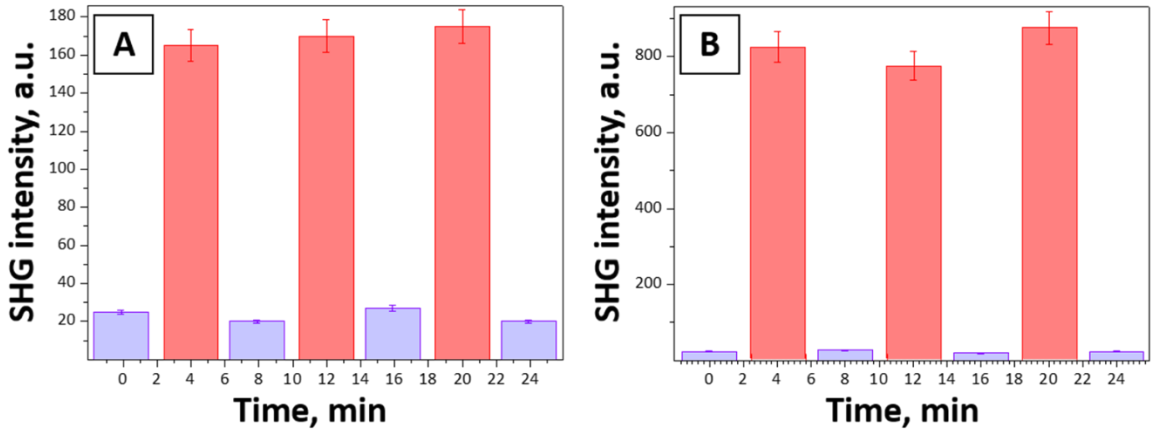

Figure 2. Variation of the SHG intensity during multiple repetitions of heating and cooling cycles with time. A – Si@pNIPAM configuration, B – Si-Au@pNIPAM configuration

The slow response of the pNIPAM microgel to temperature changes can be attributed to the formation of a surface structure that hinders the outward flow of water during the hydrogel's transition to a hydrophobic state. To enhance the system's responsiveness to external stimuli, pore-forming compounds can be introduced during synthesis. Additionally, the temperature of the polymerization process can be controlled by using high-molecular binding agents. However, it is important to note that these modifications do not impact the mechanical strength of the hydrogel. Therefore, for this study, the polymer was synthesized without any additional structural modifications.

The hybrid structures that have been obtained show great potential for use in nanooptomechanical devices. One of the most significant benefits of these structures is their ability to localize tuning on a nanoscale, which sets them apart from the majority of optomechanical devices that only allow for localization on sub- and micrometer scales. This breakthrough could lead to the development of more precise and efficient devices that are capable of operating at an even smaller scale than ever before.

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