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Study of nonlinear optical phenomena in silicone films encapsulated with SiO_2 and Si/SiO_2 spherical particles

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Study of nonlinear optical phenomena in silicone films encapsulated with SiO_2 and Si/SiO_2 spherical particles

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Abstract. Infrared converters to visible range are in demand for creation of optoelectronic devices, infrared visualizers and other non-linear optical devices. In this work we study nonlinear optical properties of monodisperse SiO_2 and Si/SiO_2 spheres encapsulated into silicone films. The fabricated silicone films containing SiO_2 spheres demonstrated a bright third harmonic generation signal, and films with Si/SiO_2 spheres demonstrated a significant second harmonic generation signal in the whole visible range. The developed materials and methods provide a platform for future infrared to visible converters based on silicon.

1. Introduction

Infrared (IR) converters to visible range are in demand for creation of optoelectronic devices [1], IR visualizers [2] and other non-linear optics devices [3]. Commercial IR visualizers based on ceramics with a high sensitivity are available [4]. However, ceramic visualizers have a limited transparency and flexibility, and feature luminescence at a fixed wavelength not allowing visual distinguishing of wavelengths of the incident IR radiation. New solutions were presented for the visualization of IR radiation based on the second harmonic generation (SHG) in GaP nanowire (NW) arrays transferred into transparent silicone membranes [2]. The developed GaP NW / silicone membranes double the energy (half the wavelength) of incident radiation, allowing visualization of the IR radiation in the range of 800-1400 nm, but require an expensive molecular beam epitaxy.

An alternative material for IR-to-Vis converters are mesoporous silica ($mSiO_2$) nanoparticles, occupying a particular place among the materials promising for theranostics [5]. These nanoparticles

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possess unique structural characteristics: large specific surface area (750 m^2/g) and pore volume (1 cm^3/g), variable average pore diameter (2–10 nm), chemically stable mesostructure, two functional surfaces (exterior surface of particles and interior surface of pores), and controllable particle shape and size. Owing to the unique mesoporous structure and large specific surface area, particles have a high capacity for accumulation of various molecules and can be used as containers. The ordered structure of pores with variable size and configuration enables a homogenous incorporation of guest molecules with different sizes and properties. Mesoporous SiO_2 particles can protect pharmaceutical cargoes, such as drugs, imaging agents, enzymes, and oligonucleotides, from premature release and undesirable degradation in harsh media before reaching the target. In this work we profited from $mSiO_2$ spherical particles by introducing Si guest atoms inside them to create Si/SiO_2 spheres in order to achieve a strong third harmonic generation (THG) and SHG signals. Colloidal Si/SiO_2 spheres can be encapsulated into silicone films for inexpensive large scale IR-to-Vis converters.

2. Methods

In this paper, samples of silicone films with encapsulated spheres were studied: monodisperse SiO_2 spheres, and mesoporous Si/SiO_2 spheres. Monodisperse SiO_2 spheres of ~500 nm in diameter were obtained by slow hydrolysis of $Si(OC_2H_5)_4$ in an alcohol-water-ammonia medium [6-9]. Mesoporous SiO_2 particles were formed using organic surfactant as a pore-forming agent. The $mSiO_2$ spheres with pores of several nanometers in diameter were filled with amorphous silicon, the Si: SiO_2 ratio was close to 1: 1. The mean diameter of $mSiO_2/Si$ spheres was ~400 nm. For sphere/silicone films fabrication we used the suspensions of spheres in isopropyl alcohol with 5% mass concentration.

3. Experimental

The SEM images of spheres are presented in Figure 1. The diameter of SiO_2 spheres was found to be 530 nm (Figure 1 left), the diameter of $mSiO_2/Si$ spheres was 300-450 nm (Figure 1 right).

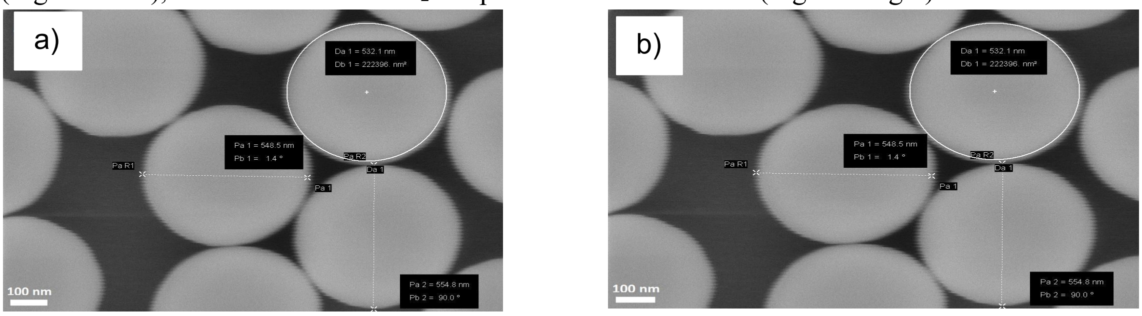

Figure 1. SEM images of a) monodisperse SiO_2 spheres and b) spherical mesoporous Si / SiO_2 composite particles**.**

The fabrication of the silicon spheres starts with a droplet of SiO_2 or $mSiO_2/Si$ colloid was applied to a treated piece of Si (100) wafer, then the solvent was evaporated during several minutes. When the isopropyl alcohol was almost completely evaporated, the rest of it was blown away with a compressed air pistol, so monolayers of spheres on the Si wafer were obtained. The monolayers of spheres were encapsulated into polydimethylsiloxane (PDMS), and after PDMS baking the fabricated films were unsticked from Si wafers and transferred onto glass. The optical microscopy images of monolayers of spheres and fabricated PDMS films with encapsulated spheres are presented in Figure 2.

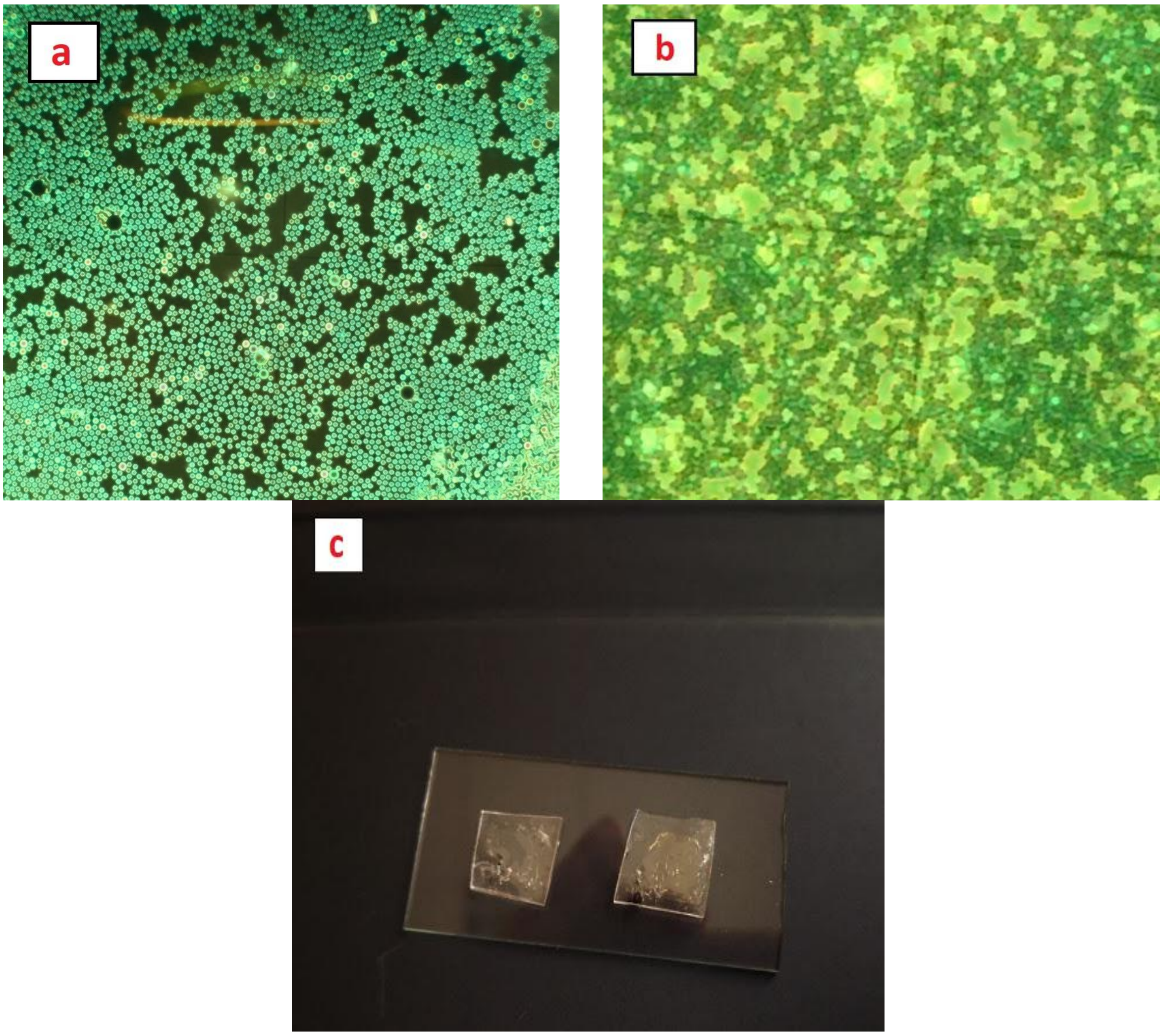

Figure 2. Optical microscopy images of a) monodisperse SiO_2 spheres and b) spherical mesoporous composite Si / SiO_2 particles on Si substrate, c) photo of PDMS films encapsulating (left) SiO_2 spheres and (right) $mSiO_2$/Si spherical particles.

Measurements of the SHG and third harmonic generation (THG) signal were performed in a setup of IR femtosecond laser and visible range spectrometer, the IR radiation power was 0.2 mW on the studied samples. Measurement results can be seen in Figure 3. Silicone film samples with $mSiO_2$/Si spherical particles demonstrated a strong THG visible with a naked eye, and a significant SHG signal. We associate the SHG signal with the surface of amorphous Si, since neither Si located deep in the particle nor SiO_2 container can generate the second harmonic. Surprisingly monodisperse SiO_2 spheres demonstrated even higher THG signal in comparison to $mSiO_2$/Si spherical particles (1.5 times higher) (Figure 4), while having a minor but distinguishable SHG signal. We speculate that the SHG signal of monodisperse SiO_2

spheres was produced by the sphere surface, however, we do not know the light conversion mechanism. The THG signal had a slope of 2.97 for $mSiO_2/Si$ spherical particles and 3.03 for SiO_2 spheres.

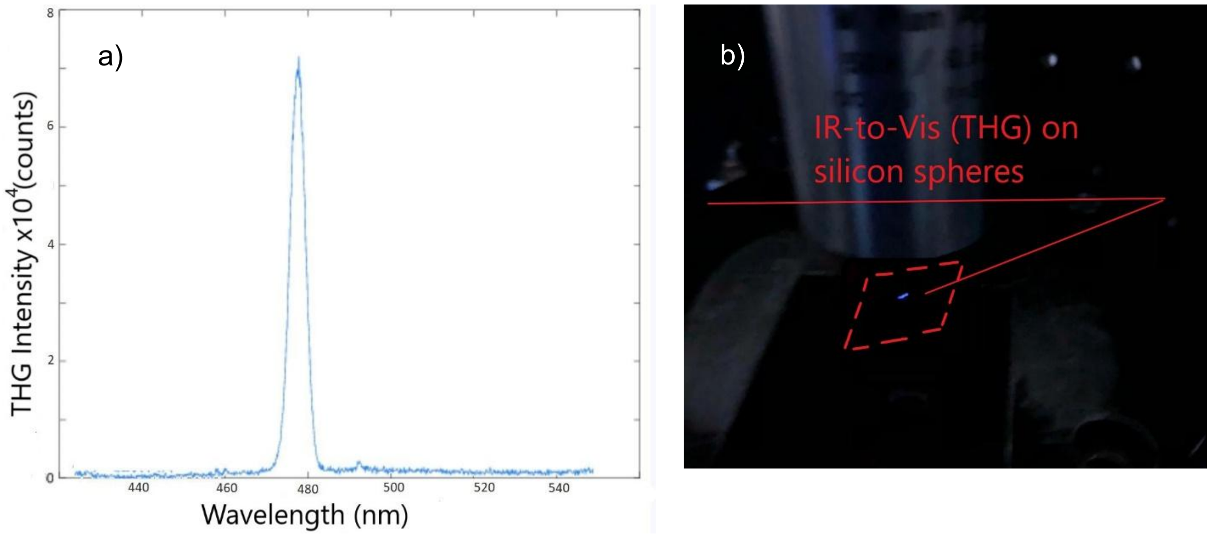

Figure 3. Representative spectrum and photo of visible THG signal of $mSiO_2/Si$ spherical particles in a silicone film (left); photo of THG by a PDMS film encapsulating $mSiO_2/Si$ spheres.

Further in-depth study of non-linear properties of mesoporous spheres will be published elsewhere. This study will be supported by fabrication of mesoporous Si spherical particles produced from $mSiO_2/Si$ particles by a selective wet etching of SiO_2 material. mSi spherical particles are expected to produce a predominant SHG signal.

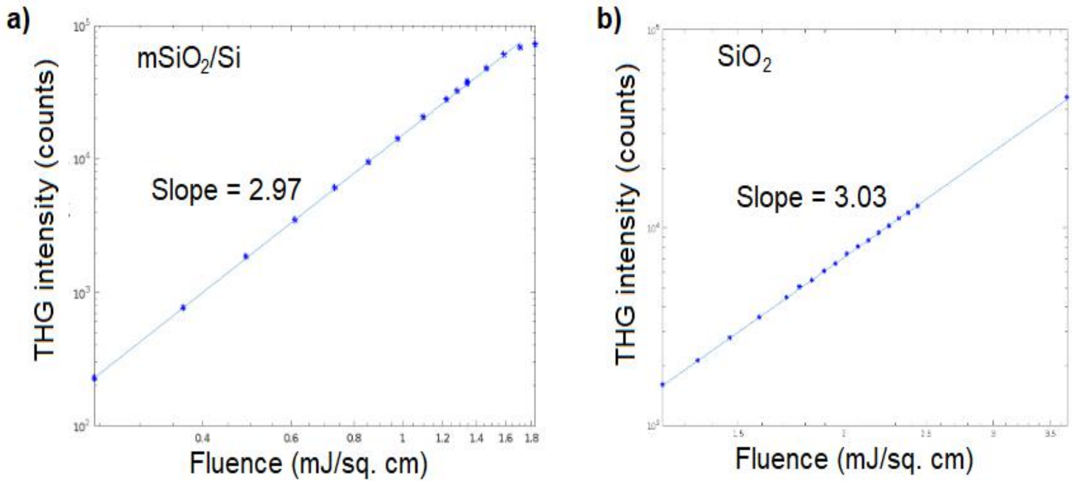

Figure 4. Representative slopes in log-log scale for THG in a) $mSiO_2/Si$ spherical particles and b) SiO_2 monodisperse spheres.

4. Summary

We demonstrated effective large scale IR-to-Vis converters based on silicone films containing monolayers of $mSiO_2/Si$ spherical particles. The measured spectra of both reference SiO_2 spheres and $mSiO_2/Si$ spherical particles demonstrated predominant THG signal visible to the naked eye. Films with $mSiO_2/Si$

spherical particles also demonstrated a significant SHG signal. Silicone encapsulation prevents crystalline silicon oxidation, while the refractive index of PDMS is close to the refractive index of silicon oxide, which allows for the passage of the flat wave of incident radiation through the medium with a suppressed internal scattering. The developed materials and methods provide a platform for future IR-to-Vis converters based on silicon materials.

Acknowledgments
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References

[1] Litvin A P & Gun'Ko Y K 2017 *Journal of Materials Chemistry* **5**(26) 13252-13275
[2] Fedorov V V & Mukhin I S 2020 *ACS Nano* **14**(8) 10624-10632
[3] Vecchi C & Pavesi L 2020 *Integrated Photonics Platforms: Fundamental Research, Manufacturing and Applications* **11364-**113640
[4] The company for the production of optoelectronic components [Electronic resource]. 2017. weblink:https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=296 (last accessed 16.02.2021)
[5] Eurov D A & Golubev V G 2015 *Journal of Nanoparticle Research* **17** (82) 1-10
[6] Igor I, Slowing B, Trewyn G, Giri S, Victor S, & Lin Y 2007 *Appl. Adv. Funct. Mater* **17** 1225-1236
[7] Ambrogio M W., Thomas C R, Zhao Y L, Zink J I, & Stoddart J F 2011 *Accounts of chemical research* **44**(10) 903-913
[8] Tang F, Li L, & Chen D 2012 *Advanced materials* **24**(12) 1504-1534
[9] Colilla M, González B, & Vallet-Regí M. 2013 *Biomaterials Science* **1**(2) 114-134.