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Incorporation of $BaTiO_3$:Er/Yb Nanoparticles into Polymeric Resins for Two-Photon Polymerization

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***Abstract*—** Barium titanate ($BaTiO_3$) perovskites exhibit notable optical properties, which are further enhanced by Er/Yb ions doping, making them promising for advanced photonic applications. Embedding $BaTiO_3$: Er/Yb (BTEY) in polymeric resins can boost optical nonlinearities and enable the creation of functional 3D microstructures. This study presents the fabrication and characterization of BTEY-embedded microstructures via two-photon polymerization (2PP), including analysis of powder and resin properties. The resulting structures exhibit a smooth surface (RMS ~27 nm) and uniform nanoparticle incorporation, with morphological and structural characteristics that are suitable for integrated photonic device applications.

Keywords*— *two-photon polymerization, barium titanate, microstructure fabrication

I. Introduction

Barium titanate ($BaTiO_3$), a perovskite-structured oxide, exhibits a broad spectrum of functional properties, including strong photovoltaic response, photoluminescence, and pronounced nonlinear optical behavior [1,2]. These characteristics make it an attractive material for advanced photonic applications. When doped with rare-earth ions such as erbium (Er^{3+}) and ytterbium (Yb^{3+}), $BaTiO_3$ gains enhanced optical functionalities due to efficient up- and down-conversion mechanisms enabled by energy transfer processes between the dopant ions [3]. The incorporation of $BaTiO_3$:Er/Yb (BTEY) nanoparticles into polymer matrices offers a promising route to developing functional composite materials with enhanced optical nonlinearities, especially for use in three-dimensional (3D) photonic structures [4,5].

Despite the promising properties of $BaTiO_3$-based materials, laser-based fabrication techniques have traditionally relied on subtractive approaches, limiting the complexity and resolution of the resulting structures. Two-photon polymerization (2PP) emerges as a powerful additive manufacturing technique that enables the fabrication of highly precise 3D microstructures through localized photopolymerization, driven by the nonlinear absorption of femtosecond laser pulses. This method enables the spatial confinement of polymerization to the laser's focal volume, offering sub-micrometer resolution and compatibility with functional nanoparticle-loaded resins.

In this study, the fabrication of microstructures composed of a photopolymerizable resin doped with $Ba(Ti_{0.94}Er_{0.03}Yb_{0.03})O_3$ nanoparticles is explored using the 2PP technique. To enable photopolymerization, the BTEY particles were dispersed within a resin composed of monomeric compounds and a suitable photoinitiator. These matrices provide a chemically stable and protective environment for the perovskite particles. Upon laser irradiation, the photoinitiator is activated through two-photon absorption, initiating localized polymerization within the focal volume. Coupled with a precise 3D scanning system, this process allows the direct writing of complex microstructures with high spatial resolution and functional integration of BTEY-based materials.

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II. Experimental

A. Sample preparation

The perovskite powders were synthesized via the conventional solid-state reaction method (SSRM) by combining barium carbonate (99.98%) and titanium dioxide ($\geqslant$99%) in a 1:1 molar ratio. To control particle size, the precursors were ball milled in 2-propanol with zirconium oxide media for durations of 2, 12, and 24 hours at 40 rpm. The resultant mixtures were calcined at 1200 °C. For the microfabrication experiments, powders milled for 2 h were used. BTEY powders were prepared in different concentrations depending on the characterization technique. For particle size analysis via dynamic light scattering (DLS), the powders were dispersed in ultra-pure water (UPW) at a concentration of 8.84×10^8 particles/mL. For UV–Vis spectroscopy, a higher concentration of 4.42×10^9 particles/mL in UPW was used to ensure sufficient optical absorption for spectral analysis.

For microfabrication, the powders were first dispersed in isopropanol at a concentration of 4.42×10^9 particles/mL to promote uniform distribution, then combined with a commercial photopolymerizable resin (Anycubic® High Clear) in a 1:1 volume ratio, forming a homogeneous composite suitable for two-photon polymerization.

B. Microfabrication

Microfabrication was carried out using a frequency-doubled femtosecond Erbium-doped fiber laser operating at 775 nm, delivering pulses of <200 fs duration at a repetition rate of 80 MHz. The laser beam was focused onto the sample using an objective lens with a numerical aperture (NA) of 0.8, confining polymerization to the focal volume through nonlinear two-photon absorption, as illustrated in Figure 1.

To optimize the 2PP process, different fabrication parameters were evaluated, including (i) laser power, (ii) scanning speed, (iii) interlayer spacing, and (iv) interline distance. These parameters critically affect the polymerization process: (i–ii) determine whether the material is effectively crosslinked, and (iii–iv) influence the structural integrity between adjacent layers and lines. Proper tuning of these conditions is crucial for achieving mechanically stable and high-resolution 3D microstructures.

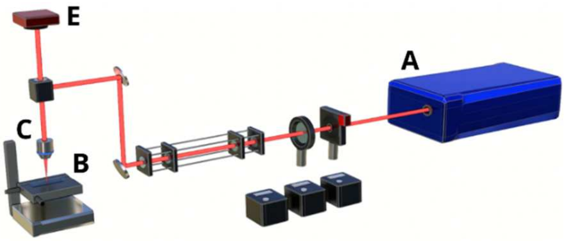

Fig. 1. Schematic of the 3D microfabrication setup. The femtosecond laser (A) is focused onto the sample (B) via an objective lens (C) mounted over a motorized x/y/z stage (D). A live camera (E) provides real-time visualization of the fabrication process.

For structural characterization, a reference cubic microstructure was fabricated using optimized parameters: 30 mW laser power and a scanning speed of 50 µm/s. The resulting BTEY-embedded microstructures were analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM), and confocal Raman spectroscopy using a 532 nm excitation laser.

III. Results and Discussions

A. Physical and optical properties

The synthesized BTEY powders were first characterized by X-ray diffraction (XRD) combined with Rietveld refinement, confirming a tetragonal perovskite phase with space group P4/mm [6].

The DLS results (Figure 2) revealed a broad hydrodynamic particle size distribution, with a peak centered at 735 nm and a full width at half maximum (FWHM) of 165 nm. The polydispersity index (PDI) of 0.7 ± 0.2 indicates moderate heterogeneity. The zeta potential of −28.0 ± 0.7 mV suggests incipient colloidal instability and the presence of some particle agglomeration. Even so, 2PP yielded microstructures with smooth surfaces and homogeneous nanoparticle distribution, indicating adequate dispersion for this study, though further stabilization methods could be explored.

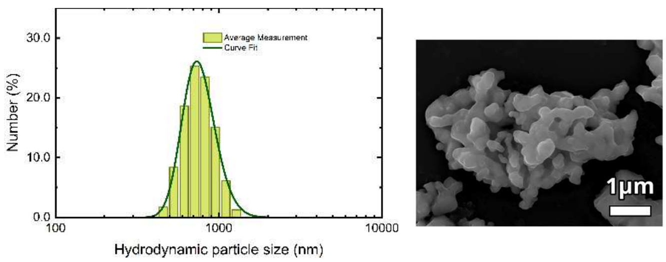

Fig. 2. DLS measurement of BTEY particles dispersed in ultra-pure water (left). SEM image of a BTEY nanoparticle agglomerate (right).

The optical absorption properties of the particles were evaluated by UV–Vis spectroscopy. The resulting spectrum (Figure 3, blue curve) exhibited a primary absorption peak at 265 nm and a broadband absorption extending into the visible region, attributed to Mie scattering from sub-micron particles.

To assess the optical response of the final composite, a 200µm-thick layer of BTEY-embedded resin was polymerized under UV irradiation and also characterized by UV–Vis spectroscopy (Figure 3, green curve). The polymerized composite exhibited absorption peaks at 360, 380, and 400 nm, with absorption saturation below 285 nm, a spectral feature characteristic of the resin.

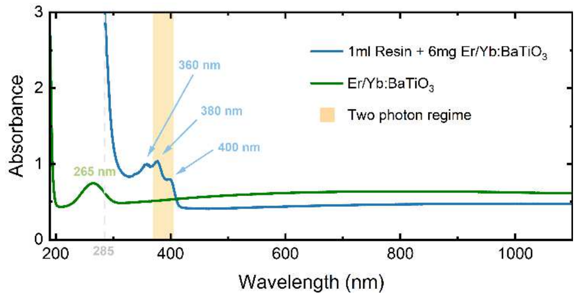

Fig. 3. UV–Vis spectra of Er/Yb:$BaTiO_3$ dispersed in UPW (green) and of the polymerized composite resin (blue). The yellow-shaded region highlights the two-photon absorption regime.

B. Microfabrication

Figure 4 presents SEM and AFM images of a BTEY-embedded 3D microstructure. The structure exhibits well-defined geometrical features with preserved structural integrity, demonstrating that the two-photon polymerization (2PP) process effectively maintained the desired shape and resolution. The surface of the printed structure displays discrete bright spots, which can be attributed to embedded BTEY particles, indicating successful nanoparticle incorporation.

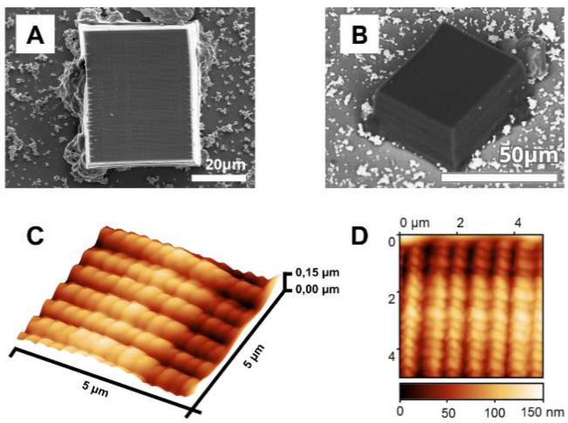

Fig. 4. SEM image showing (A) the top and (B) side view of a $BaTiO_3$:Er/Yb-embedded 3D microstructure. AFM image of the microstructure top surface (C), and the corresponding 3D surface topography (D), revealing a uniform and homogeneous surface morphology at microscale.

AFM surface characterization revealed the presence of nanoscale surface protrusions, likely formed by localized polymer expansion during pulse exposure in the scanning process. Despite these features, the surface exhibited a relatively low average roughness (RMS) of approximately 27 nm, indicating a smooth and homogeneous topography at the microscale. Additional analysis of the surface profile revealed a skewness (Rsk) of −0.1652 and a kurtosis (Rku) of −0.6111, suggesting a flatter surface with rounded peaks and predominant presence of valleys. This low roughness confirms the high fidelity of the fabrication process and suggests minimal disruption caused by the presence of nanoparticles. Surface uniformity is essential for optical applications, as surface irregularities can result in scattering losses or interference with guided light modes in photonic devices.

To evaluate the spatial distribution of BTEY particles within the structure, confocal Raman microscopy was employed. Figure 6 shows an optical sectioning of the microstructure and its corresponding Raman mapping. The mapping reveals a homogeneous distribution of nanoparticle agglomerates of varying sizes throughout the polymer matrix volume. This spatial uniformity confirms the effective incorporation of the particles during the resin formulation and two-photon polymerization process.

Three representative regions were selected from the Raman map to illustrate the spectral differences within the microstructure: region (R1) corresponds to the pure polymeric matrix; region (R2) exhibits spectral features associated with undoped $BaTiO_3$, such as the typical phonon modes of the tetragonal perovskite phase; and region (R3) shows additional Raman peaks that are attributed to the presence of $BaTiO_3$ doped with Er^{3+} and Yb^{3+} ions, confirming the successful incorporation of doped perovskite particles [7]. It should be noted that the coexistence of undoped and doped $BaTiO_3$ Raman modes does not imply phase segregation, but rather local variations in dopant incorporation, as Er^{3+}/Yb^{3+} partially substitute Ti^{4+} sites. Similar coexistence has also been reported for doped $BaTiO_3$ systems [8].

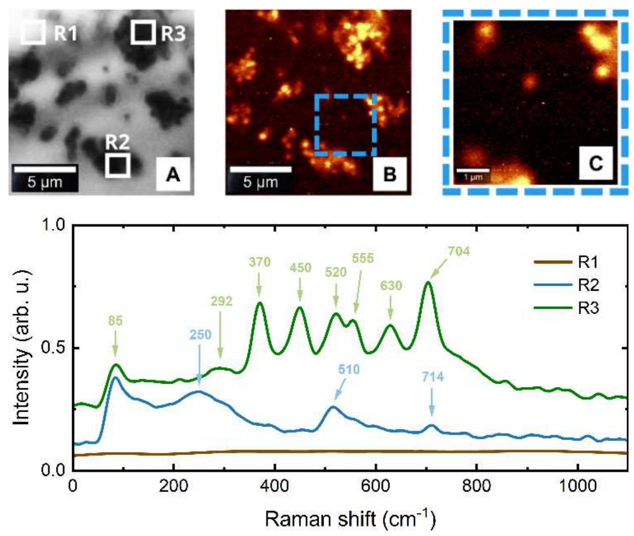

Fig. 5. Top: (A) Confocal Raman optical section and (B-C) Raman mapping of a $BaTiO_3$:Er/Yb-embedded microstructure in two different scales. Bottom: Raman spectra from three selected regions: (R1) polymer matrix, (R2) undoped $BaTiO_3$, and (R3) Er^{3+}/Yb^{3+}-doped $BaTiO_3$.

The detection of both doped and undoped $BaTiO_3$ in different regions of the structure indicates the expected compositional diversity. Yet, the overall Raman mapping confirms a uniform distribution of these particle types within the polymer matrix. The presence of agglomerates with consistent spatial dispersion suggests that the resin preparation process was effective in maintaining nanoparticle homogeneity despite variations in agglomerate size. The Raman mapping demonstrates that the particles are distributed throughout the internal volume of the structure, which is essential for enabling volumetric nonlinear optical or light-conversion effects in future photonic applications.

IV. Conclusion

The study demonstrated the fabrication of three-dimensional microstructures composed of a photopolymerizable resin embedded with Er^{3+}/Yb^{3+}-doped $BaTiO_3$ nanoparticles via 2PP. SEM analysis confirmed the formation of well-defined and structurally robust microstructures, validating the precision and resolution achievable through the 2PP process. Complementary AFM measurements revealed a homogeneous surface profile with an average roughness of approximately 27 nm, indicating a high-quality polymerization process with minimal surface irregularities. Confocal Raman microscopy provided insight into the internal structure of the microfabricated features, confirming not only the effective incorporation of BTEY nanoparticles within the polymer matrix but also their spatially homogeneous distribution throughout the volume. Raman spectral analysis across different regions identified the presence of both undoped and BTEY particles, organized into agglomerates of varying sizes, uniformly dispersed within the polymerized structure. These results demonstrate that the proposed approach enables the controlled fabrication of BTEY-based 3D microstructures with morphological and structural features suitable for integrated photonic device applications.

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