MoS2-Doped Polymeric Microstructures Fabricated by Two-Photon Polymerization

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Growing interest in integrated photonics is driving demand for efficient, versatile, and scalable materials. Twophoton polymerization (2PP) is a promising method for fabricating high-resolution, low-cost microstructures by embedding functional components in a polymer matrix. In this study, MoS_2 nanoparticles were incorporated into a commercial resin and used for 2 PP via direct laser writing. A range of characterization techniques - including SEM, DLS, EDX, AFM, and Raman spectroscopy - examined particle size, morphology, and MoS_2 integration. The characteristic $E_2 g^1$ and $A_1 g$ Raman modes confirmed successful integration, highlighting the potential of these hybrid composites for integrated photonic applications.

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Abstract - Growing interest in integrated photonics is driving demand for efficient, versatile, and scalable materials. Two-photon polymerization (2PP) is a promising method for fabricating high-resolution, low-cost microstructures by embedding functional components in a polymer matrix. In this study, MoS_2 nanoparticles were incorporated into a commercial resin and used for 2PP via direct laser writing. A range of characterization techniques - including SEM, DLS, EDX, AFM, and Raman spectroscopy - examined particle size, morphology, and MoS_2 integration. The characteristic E_2g^1 and A_1g Raman modes confirmed successful integration, highlighting the potential of these hybrid composites for integrated photonic applications.

Keywords – MoS_2, Hybrid materials, Photopolymerization

I. Introduction

Photonics, as a field of physics dedicated to the generation, control and detection of light and its direct interface between fundamental research and applications, justifies both its rapid rise and its promising nature in the production of new technologies [1]. In particular, the fabrication and integration of optoelectronic components into photonic platforms have enabled the creation of devices with applications ranging from ultrafast data communication to high-precision sensing systems [2,3]. From the perspective of technological integration, it is essential to consider the cost-effectiveness and scalability of both the materials and the fabrication techniques. In this context, two-photon polymerization (2PP) emerges as a key enabling technology, offering high resolution, thanks to its multiphoton absorption mechanism, alongside compatibility with commercial polymeric resins. The use of such materials ensures ease of handling, low cost, and the potential for incorporating new functional components, thereby opening opportunities for developing hybrid composites that combine the conventional properties of polymers with the specific functionalities of their added constituents [4].

In recent years, numerous studies have focused on formulating such hybrid systems for applications in photonic devices via two-photon polymerization (2PP). These investigations have explored the fabrication of microstructures doped with nanodiamonds [5], electroluminescent polymers [6], and microresonators using hybrid matrices of graphene oxide and rhodamine-6G [7,8]. A particularly promising candidate for hybrid integration is transition metal dichalcogenides (TMDs), a class of materials that has garnered considerable interest due to their unique mechanical, optical, and electrical properties. In particular, molybdenum disulfide (MoS_2) has characteristics such as high electron mobility (~200 $cm^2.V^{-1}.s^{-1}$), Young's modulus of approximately 33 TPa, tensile strength in the order of 23 GPa and a melting temperature of over 1000 ºC, as well as exhibiting nonlinear emissive effects due to the inversion symmetry breaking in the monolayer configuration [9-11].

The present work investigates the preparation and characterization of a suspension of MoS_2 nanoparticles and their integration into polymeric microstructures fabricated via two-photon polymerization (2PP). The primary objective is to evaluate the practical effectiveness of producing MoS_2–polymer hybrid materials and to pave the way for creating more complex optical devices, such as microresonators.

II. Experimental section

A. Materials

We investigated the production of hybrid materials composed of the commercial Anycubic standard resin and molybdenum disulfide (MoS_2) nanoparticles. Initially, two stock solutions were prepared, first, a suspension of MoS_2 nanoparticles in distilled water at a concentration of $(3.66 \pm 0.19)\times10^{-3}$ $mol.L^{-1}$, used for optical and morphological characterization of the nanoparticles. The second solution was obtained by mixing 2.5mL of the Anycubic resin with 0.5mL of the previously prepared suspension. After water evaporation, this resulted in a MoS_2-doped resin solution with a final concentration of $(7.32 \pm 0.04)\times10^{-4}$ $mol.L^{-1}$, which was used in the two-photon polymerization experiments.

B. Pre-characterization of the samples

The absorptive and emissive properties of the MoS_2 suspension in distilled water, as well as the commercial Anycubic resin were analyzed using a Shimadzu UV-1800 spectrometer and a Hitachi F-7000 fluorimeter. In addition, morphological analysis was performed using Scanning Electron Microscopy (SEM, JSM 7200F), particle size distribution was assessed by Dynamic Light Scattering (DLS, Zetasizer Nano ZS) and the Zeta potential of the nanoparticles was determined before the microfabrication process of the hybrid structures.

C. Femtosecond Laser-induced Two-photon Polymerization

Polymeric microstructures were produced using 2PP, following the experimental setup illustrated in **Fig. 1**. The

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system consisted of the components presented as: 1 - an erbium-doped fiber laser (1550 nm, > 250 mW, 80-110 Mhz and < 100 fs) coupled to a FYS-SHG second harmonic generation stage capable of producing beams at 775 nm, pulse time of < 200 fs and powers close to 60 mW; 2 - a shutter, for fabrication control; 3 - a polarizer for power adjustment; 4 - telescopic stage, for increasing focal resolution; 5 - a set of mirrors; 6 - a beam splitter; 7 - a CCD camera mounted above the focusing stage for real-time monitoring of the fabrication process; 8 - a focusing stage consisting of a microscope objective (NA = 0.8); 9 and 10 - translational XYZ stage which could be operated manually or through a custom-developed control interface.

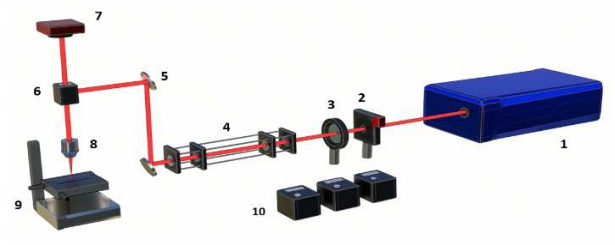

Figure 1 - Illustration identifying the experimental setup used in the femtosecond laser-induced 2PP.

D. Post-characterization of samples

Prior to characterization, the polymerized samples were deposited on glass slides cleaned by immersing in isopropyl alcohol heated to 75°C. These structures were analyzed using scanning electron microscopy (SEM, Hitachi TM3000), Energy Dispersive X-ray Spectroscopy (EDX) using a Quantax EDX-Bruker system integrated with a TM3000-Hitachi SEM, Atomic Force Microscopy (AFM - Nanosurf easyScan 2®) and Raman spectroscopy using a LabRAM HR Evolution micro-Raman system (532 nm and 0.90 NA).

III. Results and Discussions

SEM images of MoS_2 deposited on glass, presented in **Fig. 2A**, revealed a lamellar morphology, with average lateral dimensions below 1000 nm. Using the DLS technique, three main particle size distributions were identified, centered at approximately 100 nm, 400 nm and 5500 nm. The first two peaks are attributed to isolated particles, while the third corresponds to aggregates (**Fig. 2B**). Despite the presence of distinct populations, a triplicate analysis represented by green, red and blue lines indicated considerable homogeneity in the distribution, with an average particle size of (420 ± 10) nm, which is slightly higher than values previously reported in the literature [12,13]. The stability of the MoS_2 suspension was evaluated by determining the Zeta potential, which showed an average value of (-18 ± 2) mV, indicating moderate to low stability, and suggesting that the nanoparticles are susceptible to aggregation [13,14].

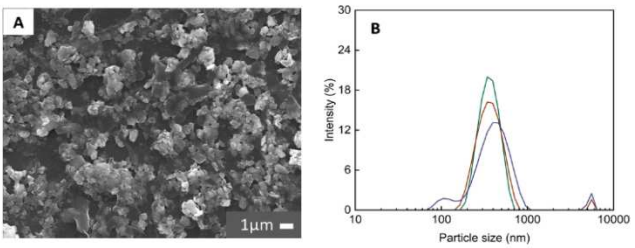

Figure 2 - A - SEM of the MoS_2 sample. B - Particle size distribution carried out in triplicate (green, red, and blue lines) using the DLS.

UV-Vis spectroscopy results, as shown in **Fig. 3A**, revealed the presence of three main absorption bands centered at 502 nm, 629 nm, and 688 nm. These bands are attributed to a direct electronic transition from deeper valence band states to the conduction band and the excitonic transitions B and A, respectively. Additionally, a significant contribution from Mie scattering was observed, consistent with previous reports [13,14]. **Figure 3B** shows the absorption spectrum of commercial Anycubic resin prior MoS_2 incorporation, showing characteristic absorption features in the ultraviolet region and a slight scattering background at wavelengths above 500 nm. These optical properties enable the efficient use of 2PP at the laser operation wavelength of 775 nm.

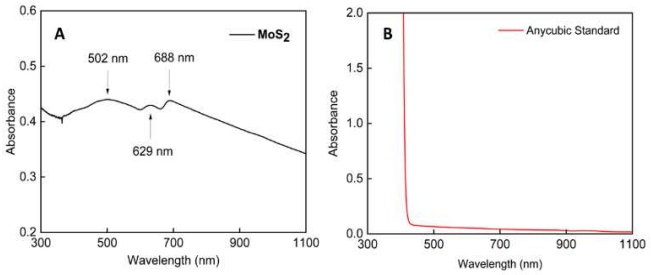

Figure 3 - UV-Vis absorption spectra for A - the suspension of MoS_2 in water, and B - for Anycubic standard commercial resin.

Fluorescence measurements of the MoS_2 suspension revealed no appreciable emissive signal under excitation in the A and B excitonic bands, which is consistent with the large particle size and its consequent association with the bulk form, drastically attenuating the photoluminescence [14]. In contrast, measurements performed on the Anycubic resin showed an emission centered around 440 nm, attributed to the TPO-L photoinitiator present in its composition [15].

Following the characterization of the precursor materials, the hybrid system was processed using the femtosecond laser-induced photopolymerization technique via two-photon absorption (2PA). **Figure. 4A** exhibits a SEM image of a group of four microstructures measuring 20 µm × 20 µm × 10 µm (width × depth × height), fabricated under 38 mW of average laser power, a scanning speed of 60 µm/s, with line spacing of 0.2 µm and interlayer spacing of 0.5 µm. MoS_2 agglomerates were observed both on the glass substrate, retained after the washing procedure, and within certain photopolymerized regions. These aggregates were analyzed via EDX technique, which confirmed the presence of MoS_2 through the detection of characteristic Lα and Kα lines, corresponding to Molybdenum (Mo) and Sulfur (S) - as shown in **Fig. 4B**

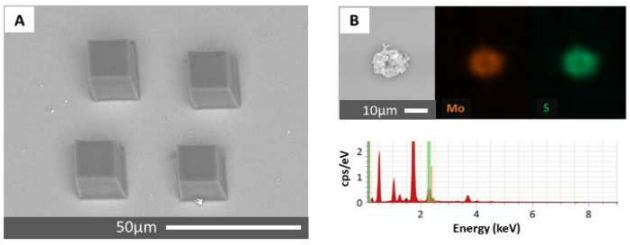

Figure 4 - A - SEM of the structures made from the hybrid material of resin and MoS_2. B - EDX analyses of one of the particles retained on the glass slide, elemental mapping corresponding to Molybdenum (Mo) and Sulfur (S).

Surface roughness analyses were performed on a microstructure with dimensions of 30 µm × 30 µm × 10 µm,

fabricated under the same laser power and line/layer spacing conditions as previously described (see SEM image in the **Fig. 5A**), using atomic force microscopy (AFM). The two-dimensional AFM image presented in **Fig. 5C**, along with its three-dimensional reconstruction in **Fig. 5D**, reveals an sinusoidal surface morphology. When compared to the SEM image in **Fig. 5B**, this pattern suggests that the high scanning speed applied during fabrication resulted in pulse discretization along the polymerized lines. In addition, valley-like regions were observed on the surface, likely caused by the combined effect of the high focal resolution and the ~0.2 µm line spacing employed during the photopolymerization process. Despite these features, the topographic analysis indicated a root mean square (RMS) roughness of approximately 42.38 nm, which is considered low for 2PP-fabricated composites with lateral dimensions on the order of tens of micrometers [8].

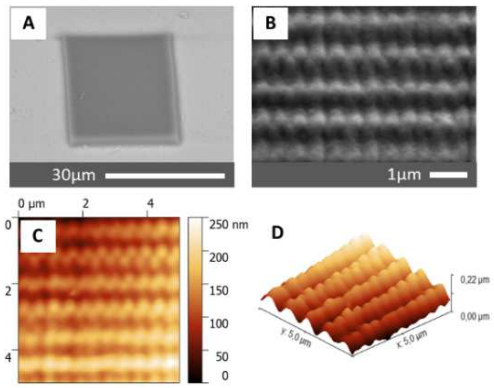

Figure 5 – A-SEM image of the fabricated microstructure. B-SEM image showing a magnified view of the top surface of the structure in A. C- 2D AFM color map of the surface topography for the structure in (A). D- 3D AFM surface map.

Finally, the incorporation of MoS_2 into the fabricated structures was assessed through Raman spectroscopy performed on selected regions. **Figure 6** displays the Raman spectra obtained under two conditions: one for a structure fabricated only from standard Anycub resin (black line), and the other for the hybrid system formed by the resin and molybdenum disulfide (blue line), corresponding to the microstructure in **Fig. 5A**.

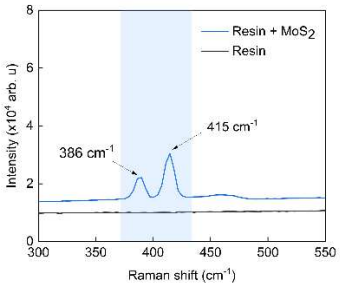

Figure 6 - Raman spectra obtained from two microstructures: one composed solely of the standard Anycubic resin (black line) and the other formed by the hybrid system of resin and MoS_2 nanoparticles (blue line).

The hybrid sample exhibits two distinct Raman peaks centered at 386 cm^{-1} and 415 cm^{-1}, corresponding to the E_2g^1 and A_1g vibrational modes of MoS_2, respectively [14]. These modes are absent in the spectrum of the structure composed only of the commercial resin, thus confirming the successful incorporation of MoS_2 nanoparticles into the polymer matrix. These results validate the fabrication of a TMD–polymer hybrid interface and support the feasibility of using such systems in the development of more complex structures for integrated photonic applications.

IV. Conclusion

This study demonstrated the feasibility of incorporating MoS_2 nanoparticles into Anycubic commercial resin. Initially, the MoS_2 suspension was characterized, showing the characteristic absorptive excitonic peaks, an average particle size of 420 nm with lamellar morphology, and low to moderate stability of the suspension. Cubic microstructures were produced via two-photon polymerization (2PP) using the polymer/MoS_2 hybrid material. EDX analysis confirmed the presence of nanoparticles agglomerates retained in the non-polymerized regions, while AFM analyses revealed low surface roughness in the fabricated structure. The successful incorporation of MoS_2 was further confirmed through Raman spectroscopy, which showed the characteristic E_{2g}^1 and A_{1g} vibrational modes of MoS_2 in the hybrid sample, absent in structures fabricated solely from the resin. These findings lay the groundwork for developing integrated photonic devices based on TMD–polymer hybrids, paving the way for the production of polymer photonic microdevices, such as microresonators, that leverage the unique properties arising from the polymer–MoS_2 association.

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