Research article

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Selective surface-enhanced Raman scattering in a bulk nanoplasmonic Bi₂O₃-Ag eutectic composite

<https://doi.org/10.1515/nanoph-2020-0281>

Received May 11, 2020; accepted June 12, 2020; published online July 8, 2020

Abstract: A recent surge of interest in surface-enhanced Raman scattering (SERS) has stimulated the search for new systems that can be utilized to fabricate high-performance optical devices. However, the two-dimensional design of the vast majority of SERS-based assemblies has significantly hindered their real-life applicability, motivating the development of three-dimensional volumetric materials. Here, we report selective SERS observed in a volumetric Bi₂O₃-Ag eutectic composite obtained by the micro-pulling-down method utilizing directional solidification of eutectics. The enhancement of the Raman signal originates from the localized surface plasmon resonance, LSPR, resulting from silver nanoparticles embedded in the composite. The plasmonic origin of the enhancement is confirmed by characteristic features, such as (i) an enhancement magnitude $>10^3$, (ii) the correspondence between the Raman bands' intensity upon excitation by different wavelengths and the localized surface plasmon resonance (LSPR) intensity, and (iii) the occurrence of overtones, which are absent in the as-grown material that does not exhibit LSPR. The examined Bi₂O₃-Ag eutectic-based

composite is obtained by directional solidification using a simple crystal growth technique. It is the first case of a bulk SERS-active material fabricated by crystal growth techniques, which opens new perspectives towards scalable three-dimensional optical elements with tunable properties based on Raman scattering.

Keywords: 3D SERS substrates; eutectic composites; high-order Raman spectra; plasmonic composites; silver nanoparticles; surface-enhanced Raman scattering.

1 Introduction

Surface-enhanced Raman scattering (SERS) manifests as a gigantic amplification of the Raman signal of structural units, in close vicinity to plasmonic nanostructures, resulting from locally enhanced electromagnetic field. Field amplification is a consequence of localized surface plasmon resonance (LSPR): interaction of surface plasmons – collective electron oscillations at metal–dielectric interface of nano-objects – with photons of characteristic frequencies. Since its discovery [1], SERS has generated considerable interest as a sensitive detection method with signal enhancement reaching 10^{13} [2–7]. At the same time, the ability to amplify and tune the system response by exploiting the plasmonic origin of SERS makes it a promising technique in other fields where conventional Raman scattering has been successfully employed, e.g. in optical amplifiers and Raman lasers [8, 9]. Most of the developed SERS substrates are based on carefully designed assemblies of nanoparticles (NPs) stabilized by chemical bonds and assays generated on solid surfaces [10, 11], which are, however, challenging to incorporate into optical instruments. Even the reported 3D SERS platforms are not genuine volumetric systems but networks of NPs embedded on various surfaces or on other nano-/microparticles [12–14]. However, recent advances in manufacturing bulk nanoplasmonic composites via methods such as directional solidification of eutectics (DSE), nanoparticle direct doping (NPDD) and block co-polymer based techniques [15–19] have opened new paths for creating

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three-dimensional materials potentially suitable for SERS. It provides the necessary toolkit to develop novel bulk SERS-active materials.

Here, we achieve this goal by exploiting nanoplasmonic effects in eutectic composites, a class of solids that recently received much attention as new optical materials. Eutectics are two-phase, crystalline, self-organized composites where both phases grow simultaneously at a melting temperature which is lower than its component phases. Eutectic materials can be formed from various materials combinations, and exhibit a plethora of micro/nanostructures with geometrical motifs [20] which can provide interesting optical effects, among others. The two phases are separated with sharp interfaces which are often atomically smooth, and the size of the geometrical motifs (the micro/nanostructure refinement) can be controlled by technological parameters.

The research on utilizing eutectic composites as optical materials led to results in the areas of metamaterials [21, 22], eutectic photonic crystals [23, 24] and eutectic-based polaritonic materials operating in a wide wavelength regime, including visible, infrared and terahertz range [24–27]. Here, we demonstrate the SERS effect in a bulk material with a potential for application in optical devices. The effect is observed in a nanoplasmonic, volumetric Bi₂O₃-Ag eutectic composite exhibiting LSPR at approximately 595 nm [16], and the enhancement originates from the presence of Ag NPs in the volume of the material.

Earlier studies have identified this material to be made up of two separate phases. The structure consists of a matrix of α -Bi₂O₃ grains separated by an amorphous phase of precipitates containing Ag, Bi and O [28]. Post-growth heat treatment transforms this non-crystalline phase to a phase containing Ag and Bi NPs, as well as γ -Bi₂O₃ nanocrystals. The Ag NPs (5–13 nm in diameter) in the annealed material are responsible for the observed LSPR [16, 29]. The polymorphs of Bi₂O₃ present in the material have significantly different properties. The monoclinic alpha polymorph is the most common form of the Bi₂O₃ at room temperature. It belongs to the *P21/c* (*C52h*) space group, with four structural units per spectroscopic cell (*Z* = 4) [30, 31], and in principle it exhibits 30 Raman-active vibrational modes active in Raman spectra assigned to phonons of the lattice and oscillations of molecular units, i.e. BiO_x [30]. At the same time, the γ -Bi₂O₃ polymorph has a body-centred cubic structure and is a metastable phase that can exist at room temperature only under specific conditions [31]. The γ -Bi₂O₃ polymorph crystallizes in the *I23* (*T3*) space group, with a unit cell consisting of two spectroscopic cells (*Z* = 2), and has 40 Raman-active vibrational modes [31]. The distinctive tetrahedral BiO₄ units in the structure of the crystal give rise to the characteristic Raman bands of this phase.

In the present study, the following experiments were performed to characterize and explain the described effect: (i) Raman spectroscopy of Bi₂O₃-Ag composite and γ -Bi₂O₃ single crystal – to determine the influence of the plasmonic NPs on the composite's Raman signal; (ii) Raman mapping of the composite – to monitor spatial distribution of the effect; (iii) wavelength-dependent Raman measurements and search for overtones to confirm the SERS effect by showing the resonance nature of the effect.

2 Experimental section

2.1 Synthesis

The Bi₂O₃-Ag composite was grown from pure starting materials of bismuth oxide powder (Alfa Aesar, 99.99% purity) and Ag (Alfa Aesar, 99.95% purity). The materials were mixed with isopropanol in an alumina mortar to a composition of 84.6 mol% Bi₂O₃ and 15.4 mol% Ag. This composition was calculated to give a 7.8 vol% volume fraction of Ag in the eutectic-based composite [16]. The Bi₂O₃-Ag material was grown at the Institute of Electronic Materials Technology (ITME) by the micro-pulling-down method [32] in a N₂ atmosphere. After growth, some of the as-grown samples were annealed in ambient air at 600 °C for 10 h.

To obtain a Bi₂O₃ crystal, Bi₂O₃ powder was directly melted in a ceramic crucible (Al₂O₃) at 870 °C in ambient air using a resistance furnace.

2.2 Raman measurements

The Raman spectra were collected at room temperature on a LabRAM HR Evolution spectrometer (Horiba Jobin Yvon) equipped with an Olympus BFXM-ILHS confocal microscope working in backscattering geometry. Measurements were performed over the spectral range 50–4000 cm⁻¹, the scattered signal was acquired with a 100× objective (NA = 0.9), the diameter of the confocal hole was 200 μm, and the diffraction grating was 1800 lines/mm. In the mapping mode, spectra of the Bi₂O₃-Ag eutectic were acquired with an accumulation time of 3 s, and three measurements were averaged. For γ -Bi₂O₃, single-crystal spectra were collected with a laser power of approximately 1 mW and 10 s of accumulation, and two measurements were averaged. Investigations were performed with three excitation laser sources: 473 nm (solid-state Cobolt Blues 25), 532 nm (Nd:YAG laser, Torus Laser, Laser Quantum, U.K.) and 633 nm (He-Ne laser), with beam powers of 370, 546 and 502 μW, respectively. Given the

differences in the laser output powers, spectra collected with the 473 and 633 nm lasers were normalized to the intensity of spectra obtained from the 532 nm laser by multiplying them by a power factor, defined as the ratio of the green 532 nm laser power to the power of the exciting laser (473 nm or 633 nm). This factor equalled 1.48 for the blue and 1.09 for the red laser. The collected Raman spectra were processed by subtracting the baseline, performing a Lorentzian-type fit and calculating the integral intensities. Excitation-dependent Raman scattering was measured at one spot with the three available laser sources.

2.3 Extinction coefficient measurements

LSPR was detected by extinction measurements using CRAIC 20/20 PV UV–VIS–NIR microspectrophotometer in a transmission mode. Measurements were performed using a xenon light source at room temperature in the spectral range from 200 to 1000 nm on a $21.1 \times 21.1 \mu\text{m}$ sampling area and collected 5–7 times for every sample and averaged.

2.4 Scanning electron microscopy (SEM)

SEM measurements were performed on an AURIGA™ CrossBeam® Workstation (Carl Zeiss). SEM images were collected with a back-scattered electron detector. An electron accelerating bias of 30 kV was applied.

2.5 Evaluation of the phase content

Concentration of γ -Bi₂O₃ nanocrystals in the precipitates was assessed based on high-resolution transmission electron microscopy (HRTEM) dark field images [28]. The area showing the precipitates was selected and the number of bright pixels representing γ -Bi₂O₃ crystals was divided by the total number of pixels. The procedure of evaluating the concentration of γ -Bi₂O₃ is described in Supplementary material.

3 Results and discussion

3.1 Raman micro-properties of the component

In order to characterize structural properties of the studied eutectic material, Raman spectra and maps were acquired

from the Bi₂O₃-Ag composite with embedded Ag NPs (Figure 1a and b). The maps revealed significantly different features between the Bi₂O₃ matrix and the Ag-containing precipitates (SEM image of the composite microstructure with marked regions of the matrix and precipitates is presented in Figure 1c). The spectra collected from the matrix (Figure 1a, red spectrum) exhibited 13 Raman bands between 50 and 450 cm⁻¹ that can be directly assigned to α -Bi₂O₃ [33]. Lower-wavenumber bands (from 50 to ca. 250 cm⁻¹) are assigned to translations of heavy bismuth cations and vibrational modes of bismuth and oxygen in the Bi–O crystal lattice [34]. Bands above 250 cm⁻¹ are associated with stretching modes of BiO₅ and BiO₆ units [33]. On the other hand, spectra collected from the Ag-containing precipitates in the annealed material (Figure 1b) showed additional Raman bands, the main one being at 826 cm⁻¹, which were not observed in the α -Bi₂O₃ matrix, nor in the spectra collected from analogous areas in the non-annealed, as-grown composite (Figure S1). These new features could result from another polymorph of Bi₂O₃. This is in agreement with the transmission electron microscopy (TEM) measurements [28] which demonstrated another polymorph: γ -Bi₂O₃ nanocrystals in the areas containing Ag precipitates. The spectroscopic distinction between the alpha and gamma polymorphs is ambiguous, given the overlapping of their bands up to 550 cm⁻¹; however, at larger wavenumbers, characteristic bands of γ -Bi₂O₃ are apparent, assigned to stretching vibrations in tetrahedral BiO₄ units. At the same time, band at 826 cm⁻¹ had an unexpectedly high intensity, when compared with the literature reports [33]. Furthermore, scattering intensity from the Ag-containing precipitates was weaker than from the matrix phase (Figure 1a, blue spectrum). This may result from the presence of Raman-inactive Bi and Ag NPs next to Bi₂O₃, thus Bi₂O₃ giving rise to the Raman signal does not compose the entire volume of the precipitates [16, 28].

3.2 SERS in the volumetric nanoplasmonic composite

To verify the unusually high intensity of the 826 cm⁻¹ band in the composite, we compared it with the Raman spectrum of the γ -Bi₂O₃ single crystal, grown for this study (Figure 1d). The intensity ratio of the Raman bands varies significantly between the spectra collected from the precipitates in the investigated composite and those from the pure γ -Bi₂O₃ microcrystal (Figure 1e). The Raman spectrum of the microcrystal exhibited a low-intensity 826 cm⁻¹ band assigned to the asymmetric stretching mode of Bi–O bonds in BiO₄ tetrahedral units in the pure gamma phase [30, 31].

Figure 1: Microstructure and selective SERS observed in the volumetric eutectic-based Bi₂O₃-Ag composite exhibiting LSPR at visible wavelengths. Raman spectra (a) and map (b) presenting the contrast between areas containing silver precipitates and the matrix of the composite. Red colour (spectrum and map) is assigned to the α -Bi₂O₃ phase (the 450 cm⁻¹ peak intensity); blue represents the γ -Bi₂O₃ phase (illustrating the intensity of the 826 cm⁻¹ peak characteristic of this phase). (c) SEM image of the micro-/nanostructure of the composite: light grey – Bi₂O₃ matrix, dark grey – Ag-containing precipitates. (d) The optical image of the γ -Bi₂O₃ single crystal. (e) Strong enhancement specifically of the γ -Bi₂O₃ phase band at 826 cm⁻¹ for the Bi₂O₃-Ag eutectic composite in Ag-containing precipitates (blue line) in comparison with the γ -Bi₂O₃ single crystal (green line), $\lambda_{\text{exc}} = 532$ nm.

The comparison clearly demonstrates that the strikingly high intensity of this band in the Bi₂O₃-Ag composite cannot have its origin exclusively in the pure γ -Bi₂O₃ phase.

The 826 cm⁻¹ band in the Raman spectrum of the composite precipitates is approximately two hundred times more intense than that in the spectrum of a pure γ -Bi₂O₃ crystal. This value will increase when we take into account the volume fraction of the Bi₂O₃ phase. Estimation based on previous studies indicates that γ -Bi₂O₃ nanocrystals make up approximately 4% of the precipitate volume in the Bi₂O₃-Ag composite. That is why the

enhancement factor (EF) increases by a factor of 25 to EF = 5000.

We hypothesised that the observed approximately 5000-fold enhancement of the 826 cm⁻¹ Raman band intensity can be explained by SERS resulting from LSPR of Ag NPs present in-between the γ -Bi₂O₃ nanocrystals in the Ag-containing precipitates. In the case of the plasmonic origin of the effect, dependence of the enhanced Raman band intensity on the excitation wavelength is expected to reflect the LSPR peak in the extinction spectrum [35]. Thus, to verify this hypothesis, we collected Raman

spectra with different excitation wavelengths in the range of the LSPR peak in Bi₂O₃-Ag composite (Figure 2a). In Figure 2b, the integral intensities of the 826 cm⁻¹ band characteristic of the γ -Bi₂O₃ phase for three excitation wavelengths: 473, 532 and 633 nm, are compared with the LSPR represented by the band corresponding to the extinction coefficient of Bi₂O₃-Ag [16]. The intensity of the enhanced band follows the same trend as the intensity of the LSPR peak at each particular wavelength. The highest signal occurs for the 532 nm excitation, which is closest to the LSPR maximum among the applied excitation wavelengths. On the other hand, the described effect is weakest for the shoulder of the LSPR band in the spectrum collected upon illumination of the Bi₂O₃-Ag material with the 633 nm laser. The systematic shift of the points towards lower wavelengths with respect to the LSPR curve in the studied system has been also observed for other SERS systems [35]. It stems from the fact that both the incident and scattered beams undergo electromagnetic enhancement in SERS [36]. As a result, maximum of the excitation profile does not fall exactly at the LSPR maximum wavelength. The direct correspondence of the wavelength-dependent Raman signal intensity with the LSPR peak proves the resonant (plasmonic) origin of the strong enhancement of the 826 cm⁻¹ band.

As we observed in the plasmonic Bi₂O₃-Ag eutectic composite, SERS enhancement occurs only for Raman

bands assigned to vibrational modes of the BiO₄ groups. This fact can be explained on the basis of the internal/external vibration model for crystals [37]. In many solids, specific molecular groups of tightly bound atoms, loosely connected to the rest of the lattice, can be identified. Their vibrational modes (internal vibrations) are expected to exhibit higher frequencies than the lattice vibrational modes (external vibrations) [37]. In the same way, the structure of the γ -Bi₂O₃ crystal can be described as a combination of the bismuth-oxygen lattice surrounding isolated tetrahedral BiO₄ groups, behaving like free molecules [38]. Evidently, isolated BiO₄ groups behave like chemical molecules exposed to the amplified electromagnetic field: for those located in the direct vicinity of the metallic nanostructures, an increase in the Raman scattering intensity is observed. This results in the selective SERS enhancement of bands assigned to the vibrations of these specific molecular groups; the effect is observed for 826 cm⁻¹ band in the Bi₂O₃ composite.

3.3 Overtones observed due to the SERS effect

To further confirm the resonant origin of the observed enhancement, we inspected Raman spectra at higher wavenumbers in search for overtones, which are hard to

Figure 2: LSPR as the origin of the Raman enhancement in the Bi₂O₃-Ag composite. (a) Raman spectra from the precipitates containing Ag and γ -Bi₂O₃ nanocrystals, collected with three excitation wavelengths, 473, 532 and 633 nm. (b) Excitation profile: integral intensities of the 826 cm⁻¹ Raman bands (triangles) obtained with different excitation wavelengths, compared with the LSPR peak in the extinction spectrum (solid black line). The grey dashed line presents the Gaussian fit to the excitation profile. The relationship between the intensities of the LSPR and the investigated Raman band is consistent with the plasmonic resonant origin of the Raman band enhancement.

Figure 3: Occurrence of overtones due to the SERS effect in the Bi₂O₃-Ag eutectic composite and comparison with the spectrum of the γ -Bi₂O₃ single crystal. The eutectics' spectrum (blue spectrum) reveals overtones ($2\tilde{\nu}$) and ($3\tilde{\nu}$) of the 826 cm⁻¹ band, whereas the single crystal does not exhibit resonant effects (green spectrum), $\lambda_{\text{exc}} = 532$ nm.

find in standard Raman spectra. Due to the enhancement of a Raman band in SERS, overtones of this particular vibration are also affected, thus they can be detected more easily [39]. The higher-wavenumber region of the spectra disclosed well-resolved bands at 1650 cm⁻¹ ($2\tilde{\nu}$) and 2474 cm⁻¹ ($3\tilde{\nu}$), which so far have not been observed in the pure γ -Bi₂O₃ phase (Figure 3) nor in the as-grown eutectic material (Figure S1). Their positions and relatively low intensities indicate that they are second- and third-order modes of the enhanced band at 826 cm⁻¹. Observation of the overtones is consistent with the manifestation of the SERS effect in the studied plasmonic material. The presence of second- and third-order modes is possible due to the interaction of isolated BiO₄ tetrahedra with a plasmon-driven amplified electromagnetic field from Ag NPs in the composite.

4 Conclusions

In summary, we report the first case of a selective SERS effect in a genuine bulk nanoplasmonic material, supported by the presence of Ag NPs in the multiphase structure of the self-organized Bi₂O₃-Ag eutectic material.

When it comes to tunability of the presented effect, two aspects should be considered. First, tunability in a small range can be executed by using different excitation wavelengths within the width of LSPR – as shown in our studies of Bi₂O₃-Ag eutectic composite. However, even in this

material, the range of tunability can be widened by shifting the LSPR resonance: dependence of LSPR position on different post-growth annealing parameters: time, temperature and atmosphere has already been shown in this material [29]. Annealing in different conditions may influence the size and chemical composition of generated NPs as well as dielectric constant, resulting in the shift of the LSPR in the material.

Opportunities to tune the maximum amplification over a broad range of wavelengths can be accessed by manufacturing new composite materials with nanoparticles exhibiting plasmonic resonances at different wavelength ranges. Alternatively, combining various NPs in a single composite may result in a material tunable in a wide wavelength range. Novel fabrication methods, such as DSE [16], NPDD [15], block-copolymer-based techniques [19] or nanoparticles aligned in porous matrices [40] can enable manufacturing of such advanced materials.

Volumetric materials with such a control over the effect, as well as high intensity of the enhanced Raman scattering (SERS), are desirable in various optical devices. For example, in Raman lasers, which offer spectral flexibility, with the operating wavelength tuned by selecting a suitable pump wavelength, or Raman amplifiers, where the bulk crystal Raman-active medium amplifies the intensity of the input signal. Also, as a well-localized effect confined to small areas in a large platform, it may be relevant in space-resolved applications.

Finally, SERS has been mostly explored for chemical molecules adsorbed on an active surface. Mechanism of the effect in the solid state, where not only vibrations of isolated molecules but also oscillations of the whole lattice must be considered, has not been fully elucidated. Thus, our research is a first report on SERS in volumetric samples and opens discussion on the SERS phenomenon in bulk materials. Overall, we expect that our studies will inspire follow-up research on SERS in other ordered volumetric eutectic-based materials, both in terms of applications and mechanism of the phenomenon.

Acknowledgments: The authors thank the TEAM Project (TEAM/2016-3/29) of the Foundation for Polish Science, co-financed by the European Union under the European Regional Development Fund and the HARMONIA Project (2013/10/M/ST5/00650) from the National Science Centre for support of this work. The authors thank Prof. Marie-Helene Berger from MINES ParisTech for providing dark-field images of Bi₂O₃-Ag using high-resolution transmission electron microscopy.

Author contribution: K. Szlachetko and P. Piotrowski contributed equally to this work.

Research funding: The authors thank the TEAM Project (TEAM/2016-3/29) of the Foundation for Polish Science, co-financed by the European Union under the European Regional Development Fund and the HARMONIA Project (2013/10/M/ST5/00650) from the National Science Centre for support of this work.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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Supplementary Material: Supplementary material to this article can be found online at <https://doi.org/10.1515/nanoph-2020-0281>.