Tungsten disulfide nanoparticles produced by femtosecond laser ablation in water for nanophotonic applications

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Abstract. We demonstrate nearly spherical nanoparticles of tungsten disulfide (WS₂) produced by femtosecond pulsed laser ablation of bulk target in deionized water. Structural and optical analysis reveals that produced nanospheres preserve the crystalline structure, high refractive index and support strong excitons and Mie resonances in the spectral range 400-700 nm, resulting in enhanced photothermal response probed by Raman spectroscopy.

1. Introduction

An emerging field of all-dielectric nanophotonics implies the utilization of dielectric nanoparticles with a high refractive index exhibiting a resonant optical response due to Mie resonances [1]. Currently, traditional semiconductor materials such as silicon [2], germanium [3] and others are mainly used for the implementation of optical devices based on nanostructures with Mie resonances. However, a fixed value of the dielectric constant of these materials imposes fundamental restrictions on the development of optical devices operating at a strict selectivity of resonant frequencies. One of the ways to improve the properties of modern photonic devices is to use materials with anisotropic dielectric properties. Recent results on the optical properties of nanoparticles synthesized from transition metal dichalcogenides (TMDC) [4] demonstrate their unique applied potential associated with their internal layered structure [5]. An important feature of these materials is their strong dielectric anisotropy and high refractive index [6]. Therefore, the high index TMDC materials are increasingly considered as a promising platform with rich excitonic physics and numerous nanophotonic applications. Thus, nanodisks made of TMDC were shown to provide significantly enhanced light-matter interaction due to excitation of so-called “anapole” states and its strong coupling to exciton resonances [4], resulting in a strong enhancement of second and third harmonic generation in such nanostructures [7]. However, despite the remarkable progress in nanopatterning of TMDC, the development of spherical nanoantennas from TMDC still poses a significant challenge.

In this work we demonstrate spherical nanoparticles of tungsten disulfide (WS₂) with variable size produced by femtosecond pulsed laser ablation of bulk target in deionized water followed by size separation step. Structural and optical investigations have shown that the produced nanoparticles are crystalline, have a narrow size distribution with an average diameter in the range from 5 to 150 nm, and support size-dependent Mie-resonant modes in extinction spectra along with exciton resonances in the spectral range 400-700 nm.
2. Results and discussion
First, for the production of WS\(_2\) nanoparticles (NPs), we adapted methods of ultra-short pulsed laser ablation and fragmentation in liquid ambiance, which were earlier used for the preparation of bare Si and Au nanoparticles [8, 9]. We observed a red-brownish coloration of solution within a few minutes of the ablation process, indicating the formation of WS\(_2\) NPs. The concentration of NPs increased linearly at the beginning of the process and then came to a saturation. In particular, for 100 μJ pulse energy and 10 kHz repetition rate, saturation time was 30 min, and the saturation concentration was about 100 μg mL\(^{-1}\). Once the ablation was completed, the colloidal aqueous solutions of WS\(_2\) were subjected to subsequent steps of centrifugation at increasing rotation speed 250-8000 min\(^{-1}\) (rpm) (45-2000g) to separate produced nanoparticles by size. Fig. 1a shows SEM image of the biggest nanoparticles separated at 250 rpm. It is seen that WS\(_2\) NPs have nearly spherical shape and an average size of 100 nm. The TEM image of the smallest WS\(_2\) NPs selected from the solution at 8000 rpm is shown at Fig. 1b. Insets show HR-TEM image of the selected area and size distribution. It is seen that the smallest WS\(_2\) with an average size of 5 nm are crystalline. The interlayer distance is about 0.67 nm, which corresponds to the d-spacing of WS\(_2\) (002).

![Figure 1](image)

**Figure 1.** (a) SEM image of laser-ablated WS\(_2\) NPs selected from a colloidal solution at 250 rpm. Inset shows the corresponding size distribution of WS\(_2\) NPs. (b) TEM image of WS\(_2\) NPs selected at 8000 rpm. Insets show HR-TEM image of selected area and size distribution. (c) Extinction spectra of WS\(_2\) NPs selected at different rotation speed. (d) Raman scattering spectra of WS\(_2\) NPs selected at different rotation speed.
The extinction spectra of colloidal solutions of WS$_2$ NPs with different sizes selected at a different rotation speed of centrifuge were experimentally measured using standard UV-VIS technique calculated numerically using extended Mie theory. It is seen from Fig. 1c that the spectra are composed of several peaks in a broad spectral range from 400 to 700 nm (the excitonic transitions A, B and C are indicated on the graph). It was found that its spectral behavior can be well explained by taking into account the excitonic properties of WS$_2$ and Mie-scattering of light by high-refractive-index NPs with the size defined be SEM-measurements. The peak centered at 620-700 nm corresponds to magnetic-dipole (MD) resonances while the broad peak at 500 nm corresponds to electric-dipole resonance (ED). The position of these peaks shifts towards longer wavelengths with increasing the size of NPs in agreement with Mie-theory. Raman scattering spectra of WS$_2$ NPs with variable size (selected at different rotating speed) excited at 532 nm are presented in Fig. 1d. The spectra are in good agreement with previously reported data for bulk WS$_2$ and WS$_2$ flakes [10]. In particular, peaks at 420 and 356 cm$^{-1}$ are attributed to A$_{1g}(\Gamma)$ and E$_{12g}(\Gamma)$ modes correspondingly. The most intense peak of Raman spectra centered at 561 cm$^{-1}$ corresponds to scattering process involving two longitudinal acoustic phonons from the edge of the Brillouin zone 2LA(M).

Fig. 2 Raman spectra of WS$_2$ NPs with an average size of 65nm on glass substrate recorded under different laser excitation power and at two laser wavelengths: (a) 532 nm and b 633 nm correspondingly. (b) Shift of the frequencies corresponding to A$_{1g}$ and E$_{12g}$ Raman scattering modes. (d) Dependence of WS$_2$ NPs local temperature on the power of exciting radiation for $\lambda_{\text{exc}} = 532$ nm and $\lambda_{\text{exc}} = 633$ nm.
One of the most promising therapeutic applications of biocompatible resonant dielectric nanoparticles is photothermal therapy (PTT) of cancer cells that implies heating induced destruction of cells under optical or ultrasonic excitation [11]. To test the photothermal response of studied resonant WS\textsubscript{2} NPs, we investigated the power-dependent Raman scattering spectra of laser-ablated WS\textsubscript{2} NPs selected by the centrifugation at 1000 rpm and having the average diameter of 65 nm assuming the linear dependence of the frequencies of both A\textsubscript{1g} and E\textsubscript{12g} modes from the temperature \(\omega(T) = \omega_0 + \chi_1 \Delta T\), where \(\omega_0\) is the peak position of vibration A\textsubscript{1g} or E\textsubscript{12g} modes at room temperature and \(\chi_1\) is the first-order temperature coefficient of the A\textsubscript{1g} or E\textsubscript{12g} modes which was recently demonstrated for thin WS\textsubscript{2} on different substrates as well as for suspended layers of WS\textsubscript{2} [10]. Knowing the values of (A\textsubscript{1g}) and (E\textsubscript{12g}), we were able to recalculate the thermal shift of WS\textsubscript{2} Raman modes during the power-dependent Raman measurements into the local temperature of deposited on glass substrate WS\textsubscript{2} NPs. It should be noted that for the same values of the excitation power resonant WS\textsubscript{2} NPs demonstrate nearly 1.5 times higher local temperature rise when being excited at 532 nm then at 633 nm. It was explained by higher values of local electro-magnetic fields under the simultaneous excitation of ED and excitonic resonances under 532 nm excitation. This high photothermal response of WS\textsubscript{2} NPs opens the way to use them as new biocompatible agents for theranostics, providing high optical contrast and photothermal response.

3. Conclusions
We demonstrated spherical high-refractive nanoparticles made from bulk crystalline WS\textsubscript{2} by versatile laser-assisted technique. Structural and optical analysis reveals that produced nanospheres preserve the crystalline structure, high refractive index and support strong excitons and Mie resonances in the spectral range 400-700 nm, resulting in enhanced photothermal response probed by Raman spectroscopy.

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5. References
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