

Optical properties of multilayer films of nanocomposites based on WS₂ nanotubes decorated with gold nanoparticles

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Abstract. Multilayer films of WS₂ nanotubes decorated with gold nanoparticles are prepared for the first time using nanocomposite assemblage on the water-heptane interface and film transition onto optically transparent or semiconducting surfaces. The film morphology resembles a mosaic structure of 10-25 square micron areas with in-plane textured nanotubes. Optical properties demonstrate several features around 490, 545, and 675 nm connected either with excitonic transitions or scattering guided by high anisotropy of the nanotubes and their texturing peculiarities in the films.

1. Introduction

Nowadays, noble metal nanoparticles are widely studied due to their unique morphology-related optical properties such as surface plasmon resonance (SPR) becoming quickly of great importance in various devices. Gold nanoparticles (AuNPs) are proposed as promising optical antennas and scattering centers in metal-semiconductor composites implemented for Raman scattering and fluorescence enhancement, water-splitting hydrogen production, and light harvesting [1, 2]. Special attention is paid to AuNP-decorated carbon nanotubes (CNT) and TiO₂, SrTiO₃/TiO₂, sodium titanate tubular nanostructures employed in surface enhanced Raman scattering (SERS) detection of organic dyes, pollutants and explosives [3-9], SERS-based pH sensor for living cells [10], phototherapy [11], optical limiters [12-14], solar cells with improved efficiency [1, 15, 16], as well as photocatalytic systems [17-21]. A number of these applications require the development of thin films based on AuNP-nanotube composites.

After the discovery in 1992 [22], inorganic WS₂ nanotubes (INT-WS₂), found to be similar to multi-walled carbon nanotubes, have demonstrated their high effectiveness in applications either previously known for CNT, like visible light photocatalysis [23], field-effect transistors [24], or also special technologies such as heterogeneous catalysis in fuel hydrodesulfurization [25]. INT-WS₂ are synthesized readily on a large scale from WO₃ -like precursors using reduction by a H₂S + H₂/N₂ mixture in a fluidized-bed reactor [26, 27] resulting in nested S-W-S “sandwich” layers with a hexagonal graphene-like structure [28].

In the previous work [29], we developed a facile technique for decoration of INT-WS₂ with AuNPs involving a heterogeneous reaction of the disulfide with boiling HAuCl₄ solutions. Gold nanoparticles of tunable sizes formed near the surface defects of the nanotubes and seemed to be intimately



connected to the outer sulfur atomic layer of WS₂ via Au-S bond formation. Recently, gold-decorated MoS₂ (the closest analogue of WS₂) monolayers and flake crystals were reported to show enhanced photoluminescent properties [30-32], SERS activity [32], and high-performance in solar cells [33] or photoelectrochemical cells for water splitting [34]. Inspired with these works and known applications of WS₂ films in Schottky-barrier solar cells [35] and photosensors [36], we studied optical properties of gold-decorated INT-WS₂ in the form of suspensions and films, which are useful from both the fundamental point of view and for potential applications in light harvesting, optical sensing, optical limiting, and photocatalytic technologies.

2. Experimental

WS₂ nanotubes were provided by NanoMaterials Ltd. (Israel) and had rather broad size distribution (30-100 nm in diameter and 1-20 μ m in length). The HAuCl₄*3H₂O reagent was purchased from Sigma-Aldrich (G4022-1G product, ACS reagent, $\geq$ 49.0 Au basis). All other reactants were of an analytical grade. All aqueous solutions and suspensions were prepared using purified water (Milli-Q RG, Millipore). Glassware and magnetic stirring bars utilized for AuNP deposition were washed by aqua regia (1:3 v/v HNO₃:HCl mixture).

INT-WS₂ were decorated with gold nanoparticles according to the previously developed and reported procedure [29]. Briefly, INT-WS₂ aqueous suspension was injected into boiling HAuCl₄ solutions under vigorous stirring. Boiling was continued for 3 min; then the reaction mixture was cooled down to room temperature. Typical HAuCl₄/MoS₂ molar ratios were of 1:56 – 1:5 resulted in 4-10 nm (in diameter) AuNPs, respectively. In order to obtain dry samples, the resulted Au-INT-WS₂ suspensions were rapidly frozen by immersion into liquid nitrogen and then dried in Labconco FreeZone freeze dry system (-50 °C, 0.03 mBar pressure).

For Au-INT-WS₂ film preparation, the composite aqueous suspension was mixed with 1/2 volume of heptane and sonicated in ultrasonic bath for 10 minutes. Within 30 min after sonication, the liquid phase segregates and Au-INT-WS₂ film forms on the liquid-liquid water-heptane interface. Such-prepared films were easily transferred onto different substrates like quartz slides and silicon wafers. Pristine INT-WS₂ films were synthesized as the reference samples using the same technique.

The films microstructure was studied by scanning electron microscopy (SEM) and optical microscopy. For SEM imaging, the films on silicon wafers were used. Micrographs were taken at 15 kV using Carl Zeiss NVision 40 microscope. For optical microscopy study, the films were deposited on quartz slides. Images were taken in a reflectance configuration using Nikon Eclipse E600 POL microscope in polarized light.

Optical properties of the Au-INT-WS₂ nanocomposites were studied by means of ultraviolet – visible – near infrared (UV-Vis-NIR) extinction spectroscopy and angle resolved reflectance spectroscopy in polarized light (for the films only). The film samples were deposited on fused quartz slides and aqueous suspensions were placed in quartz cuvettes; brief (20-30 s) sonication of suspensions before the measurement was used. UV-Vis-NIR extinction spectra were registered in a common transmission configuration using Perkin-Elmer Lambda 950 spectrophotometer (200-900 nm wavelength range, 1° step). For angle resolved reflectance spectroscopy, an original laboratory set-up was used. Reflectance spectra were registered using p-polarized light in the 400-800 nm wavelength range. The angular resolution was about 5° in 5-70° (relative to normal) angle range. Pristine INT-WS₂ films and suspensions were used as reference samples.

3. Results and Discussion

The assembly of nanoparticles on the liquid-liquid interface is widely used to produce nanocrystalline thin films of metals (especially, gold [37-41] and silver [42-46]), semiconducting chalcogenides and oxides [47, 48]. This technique is also highly effective for designing the films based on graphene sheets [49], carbon nanotubes [50-53], and their composites with plasmonic metal nanoparticles [54, 55]. Here, the assembly of pristine and gold-modified INT-WS₂ on water-heptane

liquid-liquid interface was shown for the first time to result in dense composite films easily transferable onto different substrates; in particular, up to 2 cm² films were deposited on quartz (figure 1) and silicon.

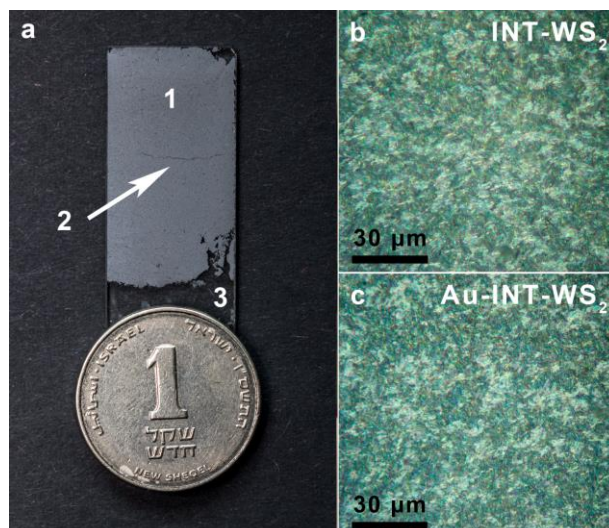


Figure 1. A general view (a) and optical images (b, c) in polarized light of WS₂ nanotubes and their composite with AuNPs. The shekel coin size in the picture (a) is 18.0 mm in diameter; 1 – textured film, 2 – a crack appeared upon film transfer from the liquid-liquid interface, 3 – quartz substrate.

According to SEM micrographs, the obtained films generally contain 1-2 layers of INT-WS₂ or gold-decorated INT-WS₂ aligned horizontally (figure 2). Only a minor fraction of larger aggregates of randomly oriented nanotubes was found. Although the complete in-plane alignment of INT-WS₂ and gold-decorated INT-WS₂ along any specific direction has not yet been observed, the films were found to contain small domains (up to 25 μm²) in which the nanotubes are textured in one direction with respect to each other. Micrographs of the composite film (figure 2d) also confirm the presence of gold nanoparticles on the INT-WS₂ surface, like reported previously [29].

Optical microscopy in a near-crossed analyzer configuration confirms the appearance of up to 5*5 μm² domains in which the films change the reflected light polarization identically (figure 1b, c). Since this feature was found for both INT-WS₂ and Au-INT-WS₂ films, it was ascribed to the strong light polarizing properties of INT-WS₂ observed also in [56]. It was suggested that the polarizing domains on OM images correspond to the domains with the same nanotube orientation as shown by SEM.

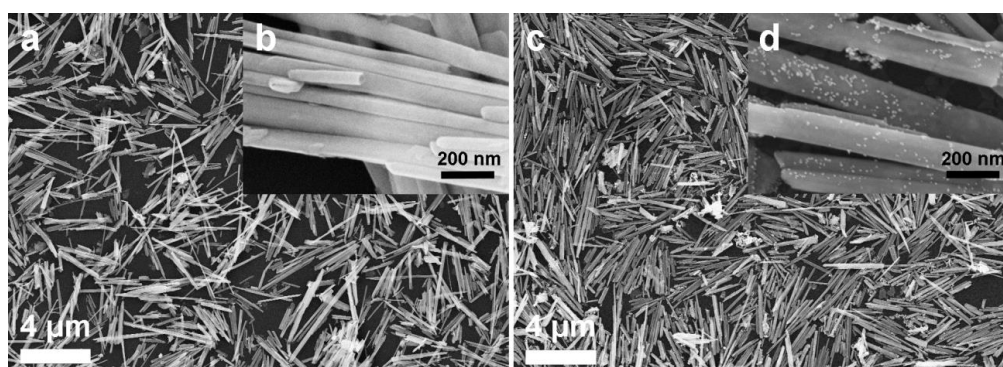


Figure 2. SEM micrographs of WS₂-based nanocomposites. (a) pure WS₂ nanotubes aligned onto silicon (b - a magnified view), c - Au-INT-WS₂ nanocomposite (d - its magnified view).

UV-Vis-NIR extinction spectra of INT-WS₂ and Au-INT-WS₂ films and suspensions are shown in figure 3. Pristine INT-WS₂ suspension spectrum contains three characteristic peaks at ca. 505, 575,

and 675 nm. The last two features were previously attributed to B and A excitonic transitions, respectively [23]. However, as mentioned in [29], the extinction spectrum of INT-WS₂ suspension seems to contain a strong scattering impact. Interestingly, the same features were found in the extinction spectrum of INT-WS₂ film, however, their positions were red-shifted (ca. 490, 545, and 675 nm, respectively) while relative intensities are changed drastically (figure 3). Assuming the (partial) scattering origin of these features, the intensity changes can be explained by the alignment of nanotubes within the film and the red shift can be attributed to the changes of the medium refractive index (water, $n=1.33$, for the suspensions and air, $n=1.00$, for the films). However, this phenomenon needs a further study involving identification of scattered signals.

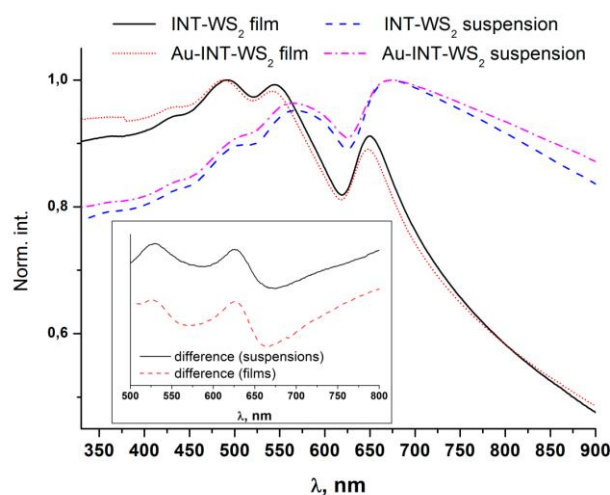


Figure 3. UV-Vis-NIR extinction spectra of INT-WS₂ and Au-INT-WS₂ films and suspensions; inset – the difference graphs between the spectra of gold-modified and pristine nanotube samples

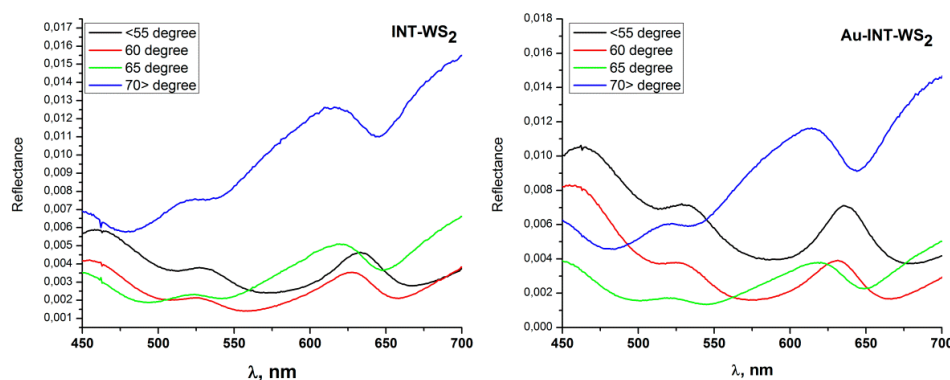


Figure 4. Reflectance spectra of INT-WS₂ and Au-INT-WS₂ films measured at different angles of incidence (relative to normal) using p-polarized light.

Similarly to the results, reported previously [29], decoration with gold nanoparticles did not result in appearance of any additional peaks in both suspension and film spectra of the nanocomposites relative to the ones of pristine nanotubes. However, subtraction of INT-WS₂ spectra from those of Au-INT-WS₂ helped to identify a weak impact of plasmonic gold nanoparticles: the difference graphs (figure 3) for suspension and film spectra contain distinct peaks at ca. 530 and 525 nm, which have to be attributed to the surface plasmon resonances of gold nanoislands (truncated spheres) grown on the disulfide surface.

Reflectance spectra of the INT-WS₂ and Au-INT-WS₂ films measured using a p-polarized beam are shown in figure 4. In the 5–55° range (relative to normal incidence), the spectra were almost unchanged. However at high angles (55–70°), the spectra change drastically. Most probably, the

changes are due to the difference of excitonic and scattering contributions at low and high incidence angles due to INT-WS₂ horizontal ordering within the films; a shift of the features with angle is evidently observed. The further work on preparation of biaxially textured INT-WS₂ and Au-INT-WS₂ films is in progress.

4. Conclusions

Assembly of INT-WS₂ and their composites with AuNPs on a water-heptane interface were shown to be an effective technique for preparation of thin films based on these materials. Almost all nanotubes were found to be aligned horizontally within the 1-2 layered films. Additionally, the films contained domains, in which neighbouring nanotubes were aligned in one direction with respect to each other. Such an alignment resulted in unusual changes in extinction spectra of the films relative to the ones of the same material suspensions. For the first time, an angular dependence of INT-WS₂ film reflectance spectra in p-polarized light was shown evidencing for the possibility of new optical applications of WS₂-based materials in the future.

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