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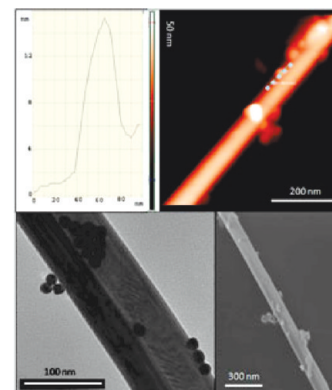
Gold Nanoparticles as Surface Defect Probes for WS₂ Nanostructures

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ABSTRACT WS₂ inorganic nanotubes (INT) and inorganic fullerene-like nanoparticles (IF) are well-known for their high mechanical strength and as superior solid lubricants. The outermost WS₂ layer is considered to be fully bonded; thus, it was suggested that the interactions of these WS₂ nanostructures with their surroundings are governed by purely van der Waals (vdW) interactions. However, in the case of IF-WS₂ nanoparticles, the faceted surface may contain sites with nonsaturated coordination, which, in turn, react with the surrounding media. Gold nanoparticles (GNP) were used as probes for the IF-WS₂ surface defects, mapped by both scanning and transmission electron microscopy. The interaction between the GNP and the reactive surface was investigated using INT-WS₂ as a model and was characterized by atomic force microscopy (AFM).

SECTION Nanoparticles and Nanostructures



Inorganic closed-cage nanostructures of WS₂ and MoS₂, such as nanotubes and fullerene-like nanoparticles (INT and IF), were shown to be the stable forms of layered (2-D) compounds in the nanoregime.¹ These nanoparticles consist, in general, of nested (closed-cage multilayer) structures where each molecular sheet consists of six-fold-bonded transition-metal atoms sandwiched between two three-fold-bonded chalcogenide atoms. The MX₂ (M = metal; X = chalcogenide) layers are stacked together by weak van der Waals forces. The closed cage IF-WS₂ were found to exhibit, among other unique features, superior tribological behavior, offering numerous applications.^{2,3} The IF-WS₂ structure requires that their surfaces be terminated by fully bonded sulfur atoms, suggesting that the effective interaction between the IF-WS₂ is of a purely van der Waals nature.⁴ However, crystal defects and elastic strain induced by surface curvature may lead to a much more complex and stronger adhesion between the IF-WS₂ within the agglomerate.⁵ Decoration of carbon^{6–10} and inorganic^{11–15} nanotubes as well as carbon fullerenes^{14,15} has been studied extensively. A recent study of the surface functionalization of the IF-WS₂, using alkylsilane molecules, showed a great improvement of the dispersion of the IF-WS₂ in oil-based suspensions. Moreover, a significant reduction in agglomeration tendency of these nanoparticles was reported.¹⁶ These results were ascribed to a propensity of the silane coating to bind to the IF-WS₂ edges and surface defects, which contain a higher concentration of adsorbed water molecules.⁵ It was further suggested that the alkylsilane coating passivated the reactive sites on the IF-WS₂ surface, thereby reducing their tendency to agglomerate. In the present work, the IF-WS₂ surfaces were decorated by gold nanoparticles (GNP). These GNP served as reactive site probes for scanning (SEM) and transmission electron microscopy

(TEM). In order to gain insight on the interaction between the GNP and the IF-WS₂, INT-WS₂ were used as a model substrate. INT-WS₂ are known for their large tensile strength coupled with high flexibility,¹⁷ reaching values expected for a defect-free tubule.¹⁸ The low defect concentration allows mechanical characterization of GNP interactions with INT-WS₂. The suitability of GNP as specific markers for point defects on IF-WS₂ and INT-WS₂ is demonstrated.

An aqueous suspension of native 12 nm diameter GNP has a bright red color. Upon agitating the colloidal solution with pristine IF-WS₂, the bright red color vanished, and the suspension became completely transparent (Figure 1a). The black IF-WS₂ sank to the bottom of the vial. Figure 1b is a SEM image showing the GNP adsorbed onto the agglomerated IF-WS₂. A thorough electron microscopy investigation using both SEM and TEM revealed that the GNP are preferentially adsorbed onto the IF-WS₂ at edges and corners, as seen in Figure 1c–e. However, since the GNP concentration is lower than that of the IF-WS₂, only some of the corners and edges are decorated. This may indicate a difference in the relative reactivity of the sites.

This remarkable phenomenon can be ascribed to the higher reactivity of the IF-WS₂ edges and corners in comparison to the planar surfaces. To test this theory, silane-coated IF-WS₂¹⁶ were mixed with a GNP suspension, using the same conditions as those for the pristine material. As mentioned, the silane coating passivates the reactive corners and edges on the IF-WS₂ surface. In this case, the red colloidal solution

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did not lose its color (Figure 1a). This result validates the role of the silane coating as a passivating agent, which reduces the reactivity of the IF-WS₂ toward their surroundings.

Further study of the nature of the GNP adsorption to the IF-WS₂ was carried out using INT-WS₂ as a substrate. INT-WS₂ are characterized by a lower density of reactive sites in general and defects in particular, as a result of their tubular structure as opposed to the quasi-spherical one of the IF-WS₂. This allows for characterization of isolated incidences of INT-WS₂/GNP interaction. Significant GNP adsorption was verified using the color change phenomenon as described above.

A detailed TEM investigation of the solution and the precipitate showed that most of the GNP were indeed ad-

sorbed on the INT-WS₂ surface. The GNP were frequently observed as large aggregates tethered to the INT-WS₂, although significant numbers of individual GNP were also scattered at various locations along the INT-WS₂. This suggests that the GNP are indeed adsorbed to reactive sites as can be observed in Figure 2a and b. Additionally, in several instances, GNP inside of a INT-WS₂ core were observed (Figure 2c–e). Here, three GNP are seen decorating the nanotube stem. Two of the GNP (marked with red circles) are adsorbed on the INT-WS₂ exterior. They can be observed rotating while the nanotube is tilted $\pm 30^\circ$ along the axial direction while the third (yellow circle) does not. The inner surface has a higher stress concentration and consequently a more reactive nature as compared to the outer one. This might explain the locations of the adsorbed GNP and concurs with the previous adsorption sites.

As in the EM measurements, AFM verified good dispersion of the GNP on the INT-WS₂, and both clusters and individual particles were seen. Whereas AFM images were obtained in semicontact mode, it was observed that reasonable images could be obtained also in a contact mode. This was intriguing since our experience is that nanoparticles dispersed on a surface with nonspecific bonding are unavoidably swept aside by the AFM tip and as a result stick to the tip itself or form into mounds at the borders of the scan region. This effect scales with size as the vdW interaction with the surface is larger for larger particles. In any event, the 12 nm diameter GNP employed here are not expected to remain immobile under typical contact mode scanning conditions using a cantilever with a spring constant of 40 N/m as employed here.

In order to further test the affinity of the GNP to the INT-WS₂, the AFM tip was used to push them with varying forces. The pushing experiments are described in Figure 3. First, the GNP were pushed at successively higher normal forces until substantial movement along the INT-WS₂ axis was observed. Up to a normal force of 30 nN, no movement of the GNP was observed. Figure 3a shows the starting position of the GNP.

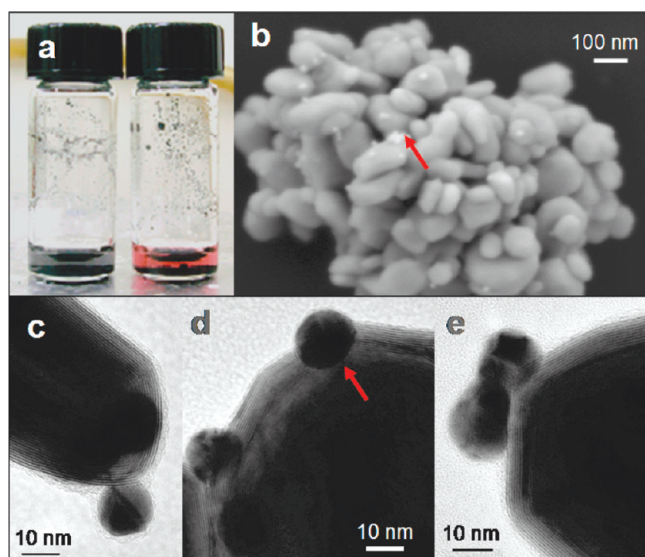


Figure 1. (a) Uncoated and silane-coated IF-WS₂ after mixing with gold colloidal solution; (b) SEM image of GNP adsorbed to IF-WS₂; (c–e) TEM images of GNP adsorbed preferably onto IF-WS₂ nanoparticle corners and edges.

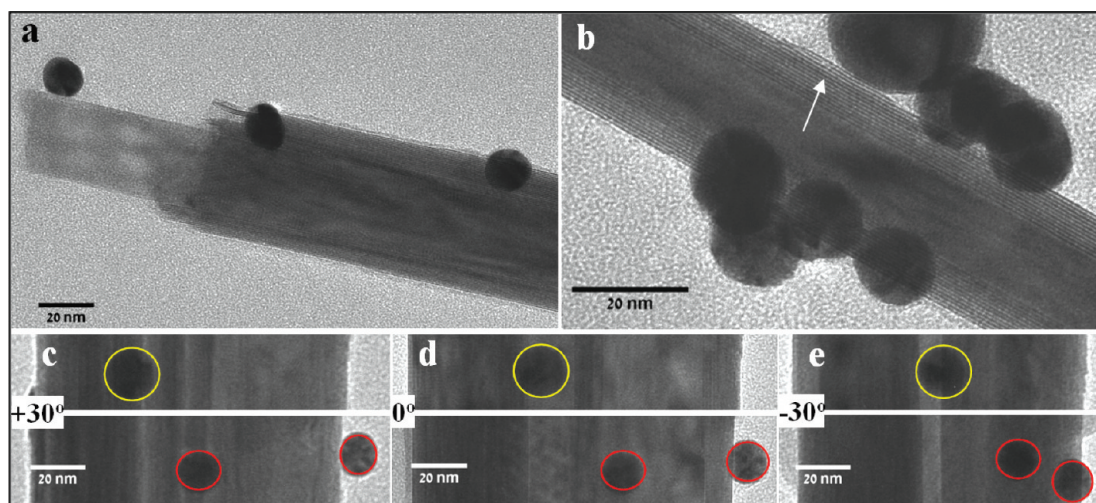


Figure 2. TEM images of GNP on INT-WS₂. (a) GNP next to INT-WS₂ defects (termination); (b) GNP clustered around a partial-layer defect (white arrow); (c–e) cross sections of an INT-WS₂ at different tilt angles suggest two GNP (red circles) on the INT-WS₂ surface and an additional GNP (yellow circles) in the INT-WS₂ core.

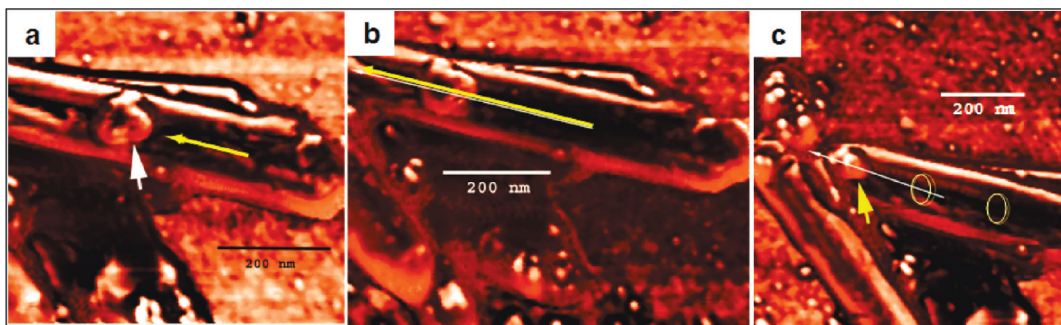


Figure 3. Pushing experiment. (a) Initial GNP position. The GNP are indicated by the white arrow, and the pushing direction is shown by the yellow arrow; (b) after pushing along the path indicated by the arrow at normal contact force of 30 nN; (c) resting position of GNP (yellow arrow) after pushing along the path indicated at a force of 60 nN. Initial and intermediate positions of GNP are indicated by yellow circles. Images are phase images, chosen for enhanced contrast and clarity.

Above a force of 30 nN, the GNP moved with the tip over a distance of 100 nm. At a force of 60 nN, the GNP were pushed to the end of the INT-WS₂, where they were stuck at the terminus of the INT-WS₂. After this, attempts were made to push the GNP completely off of the INT-WS₂ by pushing the particle in the direction perpendicular to the INT-WS₂ axis. In these preliminary experiments, it was not possible to remove the GNP from the INT-WS₂ for forces up to 100 nN. At such higher forces, rather than moving the GNP, the entire nanotube was displaced.

The results of this last experiment indicate that the binding of the GNP to the INT-WS₂ is significantly stronger than that of the INT-WS₂ to the Si substrate. If both interactions (GNP/INT-WS₂ and INT-WS₂/substrate) are governed by vdW interactions and the force required for sliding or slip on the surface can be equated to static friction, then the interaction giving rise to the friction should scale with the effective contact area. The contact area of the INT-WS₂ on the substrate is estimated to be 3 orders of magnitude larger than that of the GNP on the INT-WS₂ (see Supporting Information). This observation indicates that the latter interaction involves forces much stronger than the vdW forces between INT-WS₂ and Si substrate.

The calculations invoke standard vdW interactions for the ideal geometries and contact mechanics and therefore cannot account for such factors as surface roughness or debris and other nonidealities. However, it can be assumed that the force governing the GNP/INT-WS₂ interaction is minimally 1–2 orders of magnitude larger than a pure vdW force. AFM has been used to measure single bond forces in vertical pulloff experiments.¹⁹ The pushing experiments reported here do not represent a clean bond rupture; therefore, exact bond strengths cannot be determined. However, the range of forces estimated is within the range of a chemical bonding interaction. Two possibilities are (1) the thiol bond between GNP and sulfur dangling bonds or (2) interaction of the electron-rich citrate capping the GNP with an electron-deficient defect on the INT-WS₂.

Citrate-capped GNP colloidal solutions were kindly supplied by Prof. Israel Rubinstein's research group at the Weizmann Institute of Science. One milliliter of 12 nm GNP (diameter) in aqueous solution was mixed with 3 mL of deionized water and 30 mg of IF-WS₂ in a glass vial. The described dilution of the GNP solution was made in order to

prevent the agglomeration of the GNP on top of the IF-WS₂ surface. The vial was hand shaken for several seconds to improve the interaction between the GNP in the solution and the IF-WS₂ at the bottom of the vial.

Following the sedimentation of the IF-WS₂ to the bottom of the vial, the supernatant was removed and replaced by ethanol. The ethanol was used as part of a standard procedure for the preparation of a TEM grid sample; the vial containing ethanol and IF-WS₂ was sonicated for 10 min in a sonication bath, and the resulting suspension was used to prepare the TEM sample by applying 5–6 drops on the grid. A Philips CM120 TEM operating at 120 kV, equipped with EDS detector (EDAX-Phoenix Microanalyzer) was used. The grids were also examined by SEM (LEO model Supra 55vp) at an acceleration voltage of less than 5 kV and a working distance (WD) of 5–6 mm.

Dodecyltrichlorosilane (DTS)-coated IF nanoparticles were prepared using the procedure reported in the literature.¹⁶

Further study on the nature of the interaction between the IF-WS₂ and the GNP was carried out by using INT-WS₂ as a model substrate. While the IF-WS₂ phase is omni-pure, the nanotubes phase is only 80–90 % pure at this stage. The INT-WS₂ were coated with GNP using the same procedure as that described for the IF-WS₂. The grids were then examined at various tilt angles with a TEM. The same grids were examined by SEM.

AFM was used to further characterize the interaction. AFM characterization required a different substrate. A single-crystal Si wafer with native oxide patterned with an evaporated gold grid (mask) served as a substrate for the measurement. The INT-WS₂ decorated by GNP were dispersed on the substrate. A suitable location (within a well-dispersed and isolated nanotube region) was identified on the marked grid by SEM. These coordinates were then used in the AFM analysis.

AFM measurements were performed on an NTEGRA system using the SU005 head with 10 μ m *xy* scanner which incorporated an equivalent closed loop for precise positioning (NT-MDT, Zelenograd, Russia). FESPA silicon cantilever probes with a force constant of 40 N/m were used (Veeco, Santa Barbara, CA). These probes are designed for semicontact mode operation, but after obtaining high-quality topographic images, they were then used in contact mode for pushing experiments. The high forces led to some breakage and dulling

of the Si tip. The pushing experiments were performed by zooming in on the region of interest, then disabling the drive amplitude used for semicontact operation, and touching the tip to the surface with feedback control of the tip deflection (i.e., at predetermined force feedback). This transition was performed automatically and rapidly within a few milliseconds using a custom-script (Nova power Script, NT-MDT), and the tip was immediately translated in the path defined to push the nanoparticle in the desired direction and at fixed force. This procedure minimized drift and allowed accurate placement of the AFM tip. After the pushing experiment, a postscan was performed in semicontact mode to determine the effect of pushing.

In conclusion, the adsorption of GNP to the surface of WS₂ nanostructures was investigated. GNP adhere to WS₂ reactive sites, which occur in both INT and fullerene-like nanoparticles. The aforementioned adsorption to the IF-WS₂ surface was prevented by the prepassivation of the IF-WS₂ surface defects with an alkylsilane coating. The nature of the GNP/INT-WS₂ interaction was evaluated by AFM pushing experiments. This interaction was estimated to be approximately 2 orders of magnitude stronger than the vdW force, implicating a chemical bonding interaction.

SUPPORTING INFORMATION AVAILABLE AFM force calculations of GNP attached to inorganic nanotubes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Seifert, G.; Terrones, H.; Terrones, M.; Jungnickel, G.; Frauenheim, T. Structure and Electronic Properties of MoS₂ Nanotubes. *Phys. Rev. Lett.* **2000**, *85*, 146.
- (2) Rapoport, L.; Bilik, Y.; Feldman, Y.; Homyonfer, M.; Cohen, S. R.; Tenne, R. Hollow Nanoparticles of WS₂ as Potential Solid-State Lubricants. *Nature* **1997**, *387*, 791.
- (3) Rapoport, L.; Fleischer, N.; Tenne, R. Applications of WS₂ (MoS₂) Inorganic Nanotubes and Fullerene-Like Nanoparticles for Solid Lubrication and for Structural Nanocomposites. *J. Mater. Chem.* **2005**, *15*, 1782.
- (4) Schwarz, U. S.; Komura, S.; Safran, S. A. Deformation and Tribology of Multi-Walled Hollow Nanoparticles. *Europhys. Lett.* **2000**, *50*, 762.
- (5) Späth, B.; Kopnov, F.; Cohen, H.; Zak, A.; Moshkovich, A.; Rapoport, L.; Jägermann, W.; Tenne, R. X-ray Photoelectron Spectroscopy and Tribology Studies of Annealed Fullerene-Like WS₂ Nanoparticles. *Phys. Status Solidi B* **2008**, *245*, 1779.
- (6) Satishkumar, B. C.; Vogl, E. M.; Govindaraj, A.; Rao, C. N. R. The Decoration of Carbon Nanotubes by Metal Nanoparticles. *J. Phys. D: Appl. Phys.* **1996**, *29*, 3173.
- (7) Raghuvver, M. S.; Agrawal, S.; Bishop, N.; Ramanath, G. Microwave-Assisted Single-Step Functionalization and in Situ Derivatization of Carbon Nanotubes with Gold Nanoparticles. *Chem. Mater.* **2006**, *18*, 1390.
- (8) Qu, L.; Dai, L. Substrate-Enhanced Electroless Deposition of Metal Nanoparticles on Carbon Nanotubes. *J. Am. Chem. Soc.* **2005**, *127*, 10806.
- (9) Jiang, K.; Eitan, A.; Schädler, L. S.; Ajayan, P. M.; Siegel, R. W.; Grobert, N.; Mayne, M.; Reyes-Reyes, M.; Terrones, H.; Terrones, M. Selective Attachment of Gold Nanoparticles to Nitrogen-Doped Carbon Nanotubes. *Nano Lett.* **2003**, *3*, 275.
- (10) Balasubramanian, K.; Burghard, M. Electrochemically Functionalized Carbon Nanotubes for Device Applications. *J. Mater. Chem.* **2008**, *18*, 3071.
- (11) Whitby, R. L. D.; Hsu, W. K.; Zhu, Y. Q.; Kroto, H. W.; Walton, D. R. M. Novel Nanoscale Architectures: Coated Nanotubes and Other Nanowires. *Philos. Trans. R. Soc. London, Ser. A* **2004**, *362*, 2127.
- (12) Tremel, W.; Yella, A.; Tahir, M. N.; Panthöfer, M.; Meuer, S.; Zentel, R. Synthetic Approaches to Functionalized Chalcogenide Nanotubes. In *Solid-State Chemistry of Inorganic Materials VII*; Woodward, P. M., Mitchell, J. F., Brock, S. L., Evans, J. S. O., Eds.; Materials Research Society Symposium Proceedings Volume 1148E, Warrendale, PA, 2009; 1148-PP07-01.
- (13) Bavykin, D. V.; Walsh, F. C.; *Titanate and Titania Nanotubes: Synthesis, Properties and Applications*; Royal Society of Chemistry: London, 2009.
- (14) Dmitruk, N. L.; Borkovskaya, O. Y. u.; Mamykin, S. V.; Naumenko, D. O.; Berezovska, N. I.; Dmitruk, I. M.; Meza-Laguna, V.; Alvarez-Zauco, E.; Basiuk, E. V. Fullerene C60Silver Nanoparticles Hybrid Structures: Optical and Photoelectric Characterization. *J. Nanosci. Nanotechnol.* **2008**, *8*, 5958.
- (15) Xiao, W.; Zhang, W. Synthesis and Characterization of Hybrid Materials Formed by C60 in Situ Decorating Copper Clusters. *Mater. Lett.* **2007**, *61*, 1064.
- (16) Shahar, C.; Zbaida, D.; Rapoport, L.; Cohen, H.; Bendikov, T.; Tannous, J.; Dassenoy, F.; Tenne, R. Surface Functionalization of WS₂ Fullerene-like Nanoparticles. *Langmuir* **2009**, doi: 10.1021/la903459t.
- (17) Kis, A.; Mihailovic, D.; Remskar, M.; Mrzel, A.; Jesih, A.; Piwonski, I.; Kulik, A. J.; Benoit, W.; Forro, L. Shear and Young's Moduli of MoS₂ Nanotube Ropes. *Adv. Mater.* **2003**, *15*, 733.
- (18) Kaplan-Ashiri, I.; Cohen, S. R.; Gartsman, K.; Ivanovskaya, V.; Heine, T.; Seifert, G.; Wiesel, I.; Wagner, H. D.; Tenne, R. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 523.
- (19) Grandbois, M.; Beyer, M.; Rief, M.; Clausen-Schaumann, H.; Gaub, H. E. How Strong Is a Covalent Bond?. *Science* **1999**, *283*, 1727.