Synthesis of core–shell single-layer MoS₂ sheathing gold nanoparticles, AuNP@1L-MoS₂

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2017 Nanotechnology 28 24LT03
(http://iopscience.iop.org/0957-4484/28/24/24LT03)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 132.66.11.211
This content was downloaded on 17/08/2017 at 23:02

Please note that terms and conditions apply.

You may also be interested in:

Photonics and optoelectronics of two-dimensional materials beyond graphene
Joice Sophia Ponraj, Zai-Quan Xu, Sathish Chander Dhanabalan et al.

Light–matter interaction in transition metal dichalcogenides and their heterostructures
Ursula Wurstbauer, Bastian Miller, Eric Parzinger et al.

2D Materials Advances: From Large Scale Synthesis and Controlled Heterostructures to Improved Characterization Techniques, Defects and Applications
Zhong Lin, Amber McCreary, Natalie Briggs et al.

Two-dimensional hexagonal semiconductors beyond graphene
Bich Ha Nguyen and Van Hieu Nguyen

Defect engineering of two-dimensional transition metal dichalcogenides
Zhong Lin, Bruno R Carvalho, Ethan Kahn et al.

Second Harmonic Generation in WSe₂
J Ribeiro-Soares, C Janisch, Z Liu et al.

Surface plasmon resonance in gold nanoparticles: a review
Vincenzo Amendola, Roberto Pilot, Marco Frasconi et al.
Letter

Synthesis of core–shell single-layer MoS$_2$ sheathing gold nanoparticles, AuNP@1L-MoS$_2$

Anna Lavie$^1$, Lena Yadgarov$^{1,2,3}$, Lothar Houben$^4$, Ronit Popovitz-Biro$^4$, Tal-El Shaul$^1$, Achiya Nagler$^2$, Haim Suchowski$^2$ and Reshef Tenne$^1$

$^1$Materials and Interfaces Department, Weizmann Institute of Science, Rehovot 76100, Israel
$^2$The Raymond and Beverly Sackler Faculty of Exact Sciences School of Physics and Astronomy, Tel Aviv University, Israel
$^3$School of Chemistry, Tel Aviv University, Israel
$^4$Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel

E-mail: reshef.tenne@weizmann.ac.il

Received 7 March 2017, revised 30 April 2017
Accepted for publication 5 May 2017
Published 25 May 2017

Abstract

Nanoparticles, and more specifically gold nanoparticles (AuNPs), have attracted much scientific and technological interest in the last few decades. Their popularity is attributed to their unique optical, catalytic, electrical and magnetic properties when compared with the bulk. However, one of the main problems with AuNPs is their long-term stability. Two-dimensional materials like MoS$_2$ (WS$_2$) are semiconductors that exhibit a combination of properties which make them suitable for electronic, optical and (photo)catalytic devices. Few-layer MoS$_2$ (WS$_2$) nanoparticles (NPs), and in particular single-layer ones, show intriguing optical and electrical properties which are very different from those of the bulk compounds. Here we demonstrate the synthesis of AuNPs sheathed by a single layer of MoS$_2$ (WS$_2$), i.e. a core–shell nanostructure (AuNP@1L-MoS$_2$). The hybrid NPs exhibit optical properties that are different from those of either constituent and are amenable for modulation via their chemistry, offering a myriad of applications.

Supplementary material for this article is available online

Keywords: metal–semiconductor interactions, nanoparticles, nanoparticle synthesis, nanocomposites, 2D materials

(Some figures may appear in colour only in the online journal)

Introduction

In the last two decades zero-dimensional (0D) nanostructures, like gold nanoparticles (AuNPs), quantum dots and C$_{60}$, have been studied intensively due to their interesting optical [1, 2], electronic [3, 4] and magnetic [5] properties which cannot be seen in the bulk material [1]. Their unique properties arise, among other factors, from the high surface-to-volume ratio of the small NPs. The small (and confined) dimensions of the NPs produce increased quantum effects and also the dominance of surface atoms of the NPs over those in the interior [2, 6].

Noble metal NPs, and more specifically AuNPs, have been known for millennia [7]. AuNPs have unique catalytic properties [8–10], exhibit a red hue and show optical properties, known as localized surface plasmon resonance (LSPR) [11], significantly different from the bulk due to their nanosized dimensions [1]. LSPR produces an intense color, which
depends on the shape, size and dielectric constants of the metal and surrounding material [1, 11]. Due to their large surface-to-volume ratio they tend to agglomerate or react with the ambient. An important consequence is increased toxicity with their shrinking size. However, if AuNPs are covered with thiol moieties they become one of the most stable nanostructures [12], at least in chemically accommodating environments.

Following the discovery of graphene [13, 14] analogs of graphene in other two-dimensional (2D) materials, such as layered transition metal dichalcogenides (TMD), have attracted much interest. The lattice of the layered TMD, like MoS₂, consists of a 2D X–M–X sandwich structure, M being the transition metal atom which bonds to the chalcogen (X = S, Se or Te) atoms via strong covalent bonds. The MX₂ layers are stacked together by weak van der Waals forces [1, 11]. Due to their large surface-to-volume ratio they tend to agglomerate or react with the ambient. An important consequence is increased toxicity with their shrinking size. However, if AuNPs are covered with thiol moieties they become one of the most stable nanostructures [12], at least in chemically accommodating environments.

Most notably, the properties of 2D TMD semiconductors can be engineered through mechanical or structural changes. For instance, due to coupling between their mechanical and electrical properties [18], the electronic structures can be altered by introducing curvature to the 2D topology [19–21]. The light–matter interaction of 2D TMDs can be tailored by integrating them with photonic crystal cavities [22–26], optical microcavities [27] and plasmonic nanostructures [22, 28–31] and by application as optical limiters for pulsed laser technology [32]. For example, attaching gold nanorods to single-layer MoS₂ resulted in enhanced luminescence of the MoS₂ monolayer [15, 33]. In another report, plasmon-induced modulation of light–matter interaction was accomplished in 2D TMD layers (MoS₂, WS₂, MoSe₂ and WSe₂) hybridized with Ag NPs [34] and a VSe₂ monolayer [35]. The most intriguing feature in these unique hybrid metal–semiconductor systems is the exciton–plasmon interaction which occurs at room temperature, making them promising candidates for electro-optical modulation devices.

Despite the apparent benefits in a hybrid metal @ TMD NP, no attempt at complete sheathing of plasmonic NPs with a single TMD layer has been reported in the literature [36]. In most of the reports the metal NP was placed on the monolayer which was grown (placed) on a flat substrate: no firm attachment between the AuNPs and single-layer (1L) MoS₂ was accomplished.

Herein, we present a preliminary report on a new strategy for obtaining hybrid core–shell AuNP@1L-MoS₂ nanos-structures [37]. The AuNP core is sheathed conformably by one fully closed MoS₂ layer. Thus, the shell can be considered to have the structure of a curved (closed cage) monolayer of MoS₂ which surrounds the whole AuNP. The plasmon resonance of the AuNP was shifted to the near IR by the engulfing MoS₂ monolayer, demonstrating the versatile optical light modulation in such hybrid NPs. At the end of this report, further work and future prospects for this strategy are discussed in some detail.

**Methods section**

**Experiment/synthesis**

The AuNPs were synthesized using a known method [38] in which gold (III) chloride trihydrate (HAuCl₄·3H₂O) was reduced by sodium borohydride (NaBH₄) in an aqueous environment. Following the addition of NaBH₄, the gold yellow solution turned red. By inserting ammonium tetra-thiomolybdate ((NH₄)₂MoS₄) into the AuNP solution and stirring overnight, the AuNPs were coated by a conformal sheath of MoS₂⁻² anions (denoted as AuNP@MoS₄⁻²; figure 1(A)). Following these two steps, the precursor material (AuNP@MoS₄⁻²) was placed in evacuated (3 × 10⁻⁵ Torr) quartz ampoule (length ≈10 cm, diameter ≈9.5 mm). The edge with the precursor material in the sealed ampoule was heated at 516 °C while the other edge was kept at 428 °C, producing a gradient of 88 °C (figure 1(B)) for 30 min.
Methods

The AuNP@1L-MoS2 hybrid structures were characterized using a JEOL JEM-2100 transmission electron microscope (TEM) equipped with a LaB6 emitter operating at 200 kV and a high-resolution FEI Tecnai F30-UT FEGTEM operating at 300 kV, equipped with a Gatan imaging filter (GIF). This mode permitted a parallel electron energy loss spectroscopy (EELS) analysis. For atomic resolution analysis, a chromatic aberration-corrected FEI Titan 50–300 ‘PICO’ [39] and a FEI Titan 80–200 ChemiSTEM [40] were used, operating at 80 kV (Ernst-Ruska-Centre Juelich, Germany). Energy dispersive x-ray spectroscopy (EDS) elemental maps were recorded on the ChemiSTEM with a Super-X large solid angle EDS detector. A FEI Tecnai F20 Twin was used to record tilt series for STEM tomography, operating at 200 kV.

In the present work the perturbative method and some further adjustment were used to yield equation (1) [41]:

\[
\frac{\omega - \omega_0}{\omega} = -\frac{f}{2} \left( \varepsilon_{\text{MoS}_2}(\omega) - \varepsilon_{\text{H}_2\text{O}} \right) \varepsilon_{\text{H}_2\text{O}}.
\]

Here \(\omega\) is the resonance frequency of the shifted plasmon, \(\omega_0 = 514\ \text{nm} (5.83 \times 10^{14}\ \text{Hz})\) is the original resonance frequency of the plasmon, \(\varepsilon_{\text{H}_2\text{O}} = 1.33\) is the dielectric constant of water, \(\varepsilon_{\text{MoS}_2}(\omega)\) is the dielectric function of 1L-MoS2 [42] and \(f\) is the fraction of the volume of interaction (with light). Here \(f = V_1/V_2\), where \(V_1\) is the volume of 1L-MoS2 in the AuNP@1L-MoS2 \(\varepsilon_{\text{MoS}_2} = 0.62\ \text{nm} [15]\) and \(V_2\) is the total volume of interaction of the electromagnetic radiation with the NP. The fraction of the volume of interaction \(f\) was calculated assuming that the MoS2 shell is part of the fields which interact with the light. It was shown in [43] that the field penetrates to about 1.4 of the NP diameter. Thus the total radius for \(V_2\) was estimated as \(r_{\text{tot}} \approx 1.35r_{\text{AuNP}}\) and \(r_{\text{AuNP}}\) was considered to be about 5 nm. The intersection between the left and right parts of equation (1) produce the value of the resonance frequency of the shifted plasmon \(\omega\). Note that since the exact information about the exponential decay of the fields around the plasmonic NP is unknown, equation (1) just provides a qualitative approximation of the plasmonic shift.

Results and discussion

The hybrid AuNP@1L-MoS2 core–shell nanostructures were obtained via a three-step synthesis: (a) AuNP synthesis; (b) formation of the AuNP@1L-MoS2\(-2\) structure by adding MoS2\(-2\) (ammonium thiomolybdate) anions to AuNPs; and (c) crystallization of AuNP@1L-MoS2 NPs by heating and release of H2S and sulfur. Besides the first well-documented step, the other two steps depend on careful temperature control; the ratio between Au and MoS2\(-2\) precursors and the annealing time. A high-resolution transmission electron microscopy (HRTEM) micrograph of the yielded NPs is shown in figure 2. It is important to note that while many of the AuNPs (>90%) are indeed coated with a MoS2 monolayer, imperfect coatings are visible as well as multilayer MoS2 particles. Using EELS/HRTEM, the weak interparticle contrast in figure 2(A) was confirmed to be mostly carbonaceous in nature. Furthermore, whereas AuNP@1L-WS2 NPs were also obtained (figure 2(C)), their synthesis was not optimized and consequently the yield was rather low (5%). Here, the MoS2/WS2 monolayer is seen as a dark fringe on the contour of the NPs and the gold lattice is clearly observed in the center. The size distribution of the obtained AuNP@1L-MoS2 NPs is 9.9 ± 1.8 nm, as assessed by a statistical analysis of the TEM images (see the online supplementary information section SI3.1 available online at stacks.iop.org/NANO/28/24LT03/mmedia).

The formation of 1L-MoS2 on the AuNPs is achieved due to the attachment of the MoS2\(-2\) anions, promoted by the affinity of gold to sulfur, i.e. similar to the well-documented thiol–Au bond [38, 44]. Moreover, the ligation of the MoS2\(-2\) anions to AuNPs is self-limiting, forming a ‘passivating ligand layer’. The coating protects the AuNPs and prevents their aggregation, at least for the duration of the next steps in the synthesis. During the annealing (the final step), the MoS2\(-2\) sheath converts into a MoS2 layer by releasing H2S, S and NH3 and forming AuNP@1L-MoS2 NPs. To achieve sufficient energy needed to break the thiomolybdate bonds, the annealing was performed at a relatively high temperature (>500 °C). Another control parameter for the formation of single-layer MoS2 is the release rate of the gases, which was controlled by the temperature gradient in the ampoule. The rate of release of H2S and S is dependent on the pressure of H2S and S in the cold zone. When the pressure in the cold zone is too low (temperature gradient >88 °C), the driving force for the reaction is too large and the kinetics of the reaction (in the hot zone) is too fast. In this case the rate of growth of MoS2 could not be controlled and much of it segregated into the (Au) interparticle space. On the contrary, when the pressure in the cold zone was too high (temperature gradient <88 °C), the MoS2 crystallites did not grow as fast and the AuNPs were not completely coated. Therefore, the release of H2S and S from the thiomolybdate film should not be too quick nor too slow and the optimum conditions are achieved (for a fixed hot temperature of 516 °C) when the temperature gradient in the ampoule is 88 °C.

Interestingly, hybrid AuNPs covered by multilayered MoS2 are also achievable using a similar synthetic path. Here, multiple layers can be formed by prolonging the high-temperature annealing process. The amount of added (NH4)2MoS4 could also probably influence the number of sheathing MoS2 layers, but not in a linear fashion (see the discussion in section SI3.4 in the online supplementary information). Note that full control over this process has not yet been accomplished.

The MoS2 layers were observed from the side in their two main lattice-symmetry projections using atomic resolution HRTEM analysis (figure 3(A)). EELS analysis of the NPs (figure 3(B)) confirmed that Mo, S and Au are indeed the sole elements of the AuNP@1L-MoS2 NPs. Additionally, complete coverage of the AuNPs by the MoS2 monolayer was confirmed using high-angle annular dark field (HAADF) analysis and elemental mapping with a large solid angle windowless EDS detector (figures 3(C), (D)). The EDS
Figure 2. HRTEM images of AuNP@1L-MoS$_2$ (WS$_2$). (A) Overview image of AuNP@1L-MoS$_2$ particles. (B) A single AuNP@1L-MoS$_2$ NP. (C) Single NP of AuNP@1L-WS$_2$. (Images taken on a LaB$_6$ JEOL 2100 TEM at 200 kV acceleration voltage.)

Figure 3. AuNP@1L-MoS$_2$ and elemental characterization. (A) Atomic resolution TEM image showing the single MoS$_2$ layer coverage of a AuNP. The triple atomic layer model of MoS$_2$ is presented on the right together with the matching magnified view in the image. (B) EELS data for an individual AuNP@1L-MoS$_2$ NP. (C) HAADF scanning TEM image of another NP. (D) EDS elemental map of the same NP as in (C) showing complete coverage with a double layer of MoS$_2$. 
elemental map (figure 3(D)) revealed that the MoS2 molecules indeed surround all the AuNPs. Further proof of the complete coating was accomplished by tomography of the NPs using scanning TEM (STEM) (see tomography-Au@MoS2.mp4 and technical details in section SI3.2 of the online supplementary information).

The presented electron microscopy analysis strongly indicates that, in contrast to common nucleation models, the MoS2 layer grows by nucleating on a single (or very few) site and propagates superficially with a single growth front on the AuNP substrate. Obviously, the MoS2 layer coating the NP conformationally, is not defect-free. Indeed, much more research is needed in order to elucidate the detailed structure of this conformal coating.

Raman measurements

Raman measurements of AuNP@1L-MoS2 are presented in the online supplementary information (section SI3.3). The Raman spectrum of MoS2 consisting of a few layers has been investigated by a number of authors [45–48]. The frequency of the shear mode $E_{2g}^2$ is reduced gradually from 32 to 30 cm$^{-1}$ when the number of layers shrinks from ten to four and then goes down abruptly to 23 cm$^{-1}$ for two layers. The Raman spectrum of the core–shell AuNP@1L-MoS2 are compared with bulk MoS2 and silicon in figure 4(a). The bulk 2H-MoS2 particle shows the expected $E_{2g}^2$ peak at 32 cm$^{-1}$. However, this peak is absent in the core–shell NPs, corroborating the notion that these NPs consist of a single layer of MoS2. The origin of the low-intensity peaks below 20 cm$^{-1}$ is not known and requires further study.

The Raman spectrum of the intralayer modes in the range 350–430 cm$^{-1}$ is compared with that of fullerene-like (IF) NPs and bulk (2H)-MoS2 (see online supplementary table S1 in SI3.3). The main conclusion from this Raman study is that the closed MoS2 monolayer in the core–shell NP resembles the IF-MoS2 and not the bulk phase. These results are consistent with the idea that the MoS2 single-layer shell accommodates an IF structure, i.e. a structure of seamless folded layers [45–47].

The Raman spectrum of single to multilayer MoS2 is well established (see, for example, [47, 49]). When the number of MoS2 layers is reduced, the $A_{1g}$ mode softens from 412.0 to 410.3 cm$^{-1}$, while the in-plane $E_{2g}^1$ mode hardens from 387.8 to 391.7 cm$^{-1}$). Direct comparison with the present results is not possible, however, due to the effect of the underlying (electron-rich) Au substrate and the considerable strain on the MoS2 monolayer induced by the curvature. Moreover, the present results were obtained with a micro-Raman set-up. Here, the laser beam was focused on a group of NPs, and accidental excitation of MoS2 particles cannot be ruled out completely. Future studies will make use of advanced Raman techniques, analyzing individual AuNP@1L-MoS2 NPs at a time, which could be much more informative.

Optical properties

The optical properties of the hybrid NPs are not likely to be a simple linear combination of the two phases but rather a confluence of the two components. Extinction measurements were performed by dispersing the AuNP@1L-MoS2 NPs in an aqueous solution, and the results are presented in figure 4(B). Interestingly, the LSPR of the AuNPs (pink) is missing from the extinction spectrum of the dispersed AuNP@1L-MoS2 NPs (black) and multiple maxima superposed on a new broad feature appear in the visible range extending to the near IR. The quenching of the LSPR can be attributed to two main mechanisms: (1) coupling of the C exciton with the AuNP plasmon and (2) the effective medium phenomenon. It was shown previously that the plasmon oscillations on a AuNP might be strongly damped due to the mixing with MoS2 electronic states [50, 51]. The strong structural coupling in epitaxial metal–semiconductor nanocomposites promotes mixing of the electronic states at their domain interfaces, which then causes a significant suppression of both the plasmonic and excitonic features [51]. Indeed, the existence of small epitaxial domains between the AuNP and MoS2 domains can be observed in the HRTEM images at the AuNP@1L-MoS2 interface (figure 3(A)).

The C exciton of 1L-MoS2 (see figure 4(B), green line) is close to the resonance of the AuNP LSPR (see figure 4(B), purple line), which is ideal for strong coupling (figure 4(C)). Indeed, a large transparency deep in the vicinity of the Au LSPR is apparent in the extinction spectrum of AuNP@1L-MoS2 (figure 4, black line). Similar extinction features with a large transparency dip were previously observed in plasmonic nanostructures hybridized with molecules, and were attributed to Rabi splitting and the emergence of plexcitons [52–54]. Strictly speaking, strong plasmon–exciton coupling will manifest as well-separated response peaks in the extinction spectrum. Here, the coupling constant should be larger than both the plasmon and exciton linewidth ($\gamma_{\text{LSPR}} > \gamma_{\text{exc}}$). In this regime, the plasmon and the exciton modes are hybridized and thus form two new normal (orthogonal) modes with similar linewidths and different frequencies [52, 53, 55]. While at this stage strong evidence in support of mode splitting is not yet available, the clear transparency dips in the extinction spectrum reveal effective plexcitonic coupling in this system.

In addition, the absence of an LSPR peak in the AuNP extinction spectrum could possibly originate from the fact that both the MoS2 shell and water serve as an effective medium which redshifts the plasmonic resonance. A perturbation approach was used to consider the effect of the (1L-MoS2) thin layer and the water on the LSPR of the AuNPs. The approach is based on the variational principle and was used to calculate the effect of a small perturbation on the solution of the Maxwell equations. It further assumes a small difference between the thin layer and the medium (water) permittivities, which results in a shift of the resonance LSPR frequency [56]. This calculation revealed that the Au plasmon resonance peak shifts to a new position (957 nm) [57] (for further details see Methods). Indeed, the extinction spectra (figure 4(B)) exhibit
a quenching of the LSPR of the ‘bare’ AuNPs and the appearance of a maximum at \( \sim 960 \) nm.

In addition to the suppressed LSPR feature at 514 nm, the characteristic MoS\(_2\) maxima at 665 and 625 corresponding to the A and B excitons can be observed superimposed on a large extinction band (figure 4(b)). Notably, the excitonic features are substantially weaker than that for pure 1L-MoS\(_2\) (figure 4(B), green line) \cite{42} and they are somewhat red-shifted (see the supporting information for further details). The exciton shift and the corresponding change in spin–orbit splitting can be ascribed to the small NP diameter (9.9 \( \pm \) 1.8 nm), which induces lattice strain on the MoS\(_2\) layer \cite{58–60}.

Interestingly, an additional weak maximum at 715 nm can also be observed. The origin of this peak can be attributed to a trion (A\(^-\)), which is a free electron bound to the neutral A exciton via Coulomb interaction \cite{61, 62}. Presumably, the A\(^-\) transition is promoted by charge transfer from the medium to the 1L-MoS\(_2\) shell \cite{63, 64}. Alternatively, it was shown earlier that MoS\(_2\) closed cage NPs are able to retain not only the excitons but also a LSPR at \( \sim 730 \) nm \cite{65}. Thus, the appearance of shoulder-like peaks at 715 nm could also possibly be ascribed to the plasmonic resonance of the MoS\(_2\) shell (see the supporting information for further details).

We note that in addition to the AuNP@1L-MoS\(_2\) NPs, the product may also contain variable amounts of other

---

**Figure 4.** (a) Normalized low-frequency Raman (Stokes) spectrum of the shear mode measured on bulk 2H-MoS\(_2\) (upper red line) and AuNP@1L-MoS\(_2\) core–shell NPs (lower black line). (b) The extinction spectrum of the AuNP@1L-MoS\(_2\) NPs (solid black) and AuNPs (pink) dispersed in aqueous solution. The local maxima in the extinction spectra are marked with vertical gray lines. The literature values are shown for comparison: MoS\(_2\) closed cage NP \cite{66}, blue dots; 1L-MoS\(_2\) \cite{67}, red dots; 2L-MoS\(_2\) \cite{67}, green dots; bulk MoS\(_2\) \cite{67}, brown dots; resonance of the A exciton in a MoS\(_2\) single layer \cite{62}, blue circled cross; MoS\(_2\) single layer \cite{42}, green dotted line. (c) Illustration of the possible coupling between the C exciton of 1L-MoS\(_2\) and LSPR of AuNP. Here, the black lines correspond to the A, B and C excitons, the red lines (on the right side) correspond to the plasmon bandwidth peak and the gray lines (upper left side) represent the bandwidth of the C exciton.
by-products (10%), such as isolated MoS$_2$ platelets and uncoated AuNPs in relatively small amounts. Moreover, some of the AuNPs are covered by only one layer of MoS$_2$. Hence, multiple mechanisms of light–matter interaction occur in the dispersed mixture and are detected during the extinction measurements. Indeed, the extinction spectrum changes significantly once the amount of by-products increases (see online supplementary figure S3 in section SI4.3).

Studies of the optical properties of individual AuNP@1L-MoS$_2$ NPs are under way and will hopefully shed more light on the complex behavior of these new hybrid NPs.

Conclusions

This work presents a systematic study of a synthetic method for single-layer MoS$_2$ sheathing of AuNPs in a core–shell structure. The conformal coating of a single layer of MoS$_2$ on top of the AuNPs can pave the way for a new type of hybrid material with new optical, electronic and catalytic properties. The characterization of the AuNP@1L-MoS$_2$ structure by Raman and electron microscopy confirmed that AuNPs are indeed coated by a single-layer of MoS$_2$. Extinction measurements show that the hybrid NPs represent genuine optical properties belonging to neither the AuNPs nor the MoS$_2$ coating. These properties can be tuned by varying the size and shape of the AuNPs, the nature of the 2D layer (e.g. replacing MoS$_2$ by WSe$_2$) and the number of layers in the 2D material. The present work paves the way for a new generation of hybrid semiconductor–metal NPs with tunable physico-chemical properties and potential applications in the fields of sensors, (photo)catalysis, medical imaging, etc.

Acknowledgments

The authors thank Tsachi Livneh and Iddo Pinkas for help with Raman analysis. High-resolution electron microscopy was performed at the Irving and Cherna Moscowitz Center for Nano and Bio-Nano Imaging of the Weizmann Institute of Science. The authors gratefully acknowledge the support for atomic resolution electron microscopy at the Max-Born Institute, Berlin, under the 6th Framework Programme (FP7/2007-2013) under grant agreement no. 312483 (ESTEEM2). We acknowledge financial support of the German-Israeli Foundation-GIF (research grant no. I-1233-302.5/2014).

References

[22] Sobhani A et al 2014 Enhancing the photocurrent and photoluminescence of single crystal monolayer MoS$_2$ with resonant plasmonic nanoshells Appl. Phys. Lett. 104 031112
[26] Wu S et al 2014 Control of two-dimensional excitonic light emission via photonic crystal 2D Mater. 1 011001
[27] Liu X et al 2015 Strong light–matter coupling in two-dimensional atomic crystals Nat. Photonics. 9 30–4
Butun S, Tongay S and Aydin K 2015 Enhanced light emission from large-area monolayer MoS2 using plasmonic nanodisc arrays Nano Lett. 15 2700–4

Akselrod G M et al 2015 Leveraging nanovalence harmonics for control of optical processes in 2D semiconductors Nano Lett. 15 3578–84

Lee B et al 2015 Fano resonance and spectrally modified photoluminescence enhancement in monolayer MoS2 integrated with plasmonic nanoantenna array Nano Lett. 15 3646–53


Cao W et al 2015 Gold nanoparticles on MoS2 layered crystal flakes Mater. Chem. Phys. 158 89–95


Lavie A and Tenne R 2016 Particles coated by inorganic layered compounds US provisional patent # 62/312,486


Barthel J, Houben L and Tillmann K 2015 FEI Titan G3 50-300 PICO J. Large-Scale Res. Facilities 1 34

Kovács A, Schierholz R and Tillmann K 2016 FEI Titan G2 80-200 CREWLEY J. Large-Scale Res. Facilities 2 43

Achiya N 2016 Exploring Non-Linear Effects due to Ultrafast Dynamics in Plasmonics (Tel Aviv: Tel Aviv University)


Häkkinen H 2012 The gold–sulfur interface at the nanoscale Nat. Chem. 4 443–55


Zhang X et al 2013 Raman spectroscopy of shear and layer breathing modes in multilayer MoS2 Phys. Rev. B 87 115413


Zhao W et al 2016 Exciton–plasmon coupling and electromagnetically induced transparency in monolayer semiconductors hybridized with Ag nanoparticles Adv. Mater. 9 733–7

Khon E et al 2011 Suppression of the plasmon resonance in Au/CdS colloidal nanocomposites Nano Lett. 11 1792–9


Li Y et al 2016 Au@MoS2 core–shell heterostructures with strong light–matter interactions Nano Lett 16 7096–702

Mak K F et al 2013 Tightly bound trions in monolayer MoS2 Nat. Mater. 12 207–11


Yadgarov L et al 2014 Dependence of the absorption and optical surface plasmon scattering of MoS2 nanoparticles on aspect ratio, size, and media ACS Nano 8 3575–83
