

## Growth of Gold Nanostructures on the MoS<sub>2</sub> Surface Modified with Polyvinylpyrrolidone

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(Received 10 October 2020; revised manuscript received 15 February 2021; published online 25 February 2021)

Here we report on the synthesis of plasmonic gold nanostructures, preferably nanoprisms, having clean surface. They were grown on the molybdenum disulfide (MoS<sub>2</sub>) modified with polyvinylpyrrolidone (PVP). The synthesis of such nanostructures was carried out in two stages. At the first stage, a modified MoS<sub>2</sub>/PVP surface was obtained, and then gold nanoprisms were synthesized on this surface in growth solution without PVP. To confirm the cleanliness of nanoprisms, scanning electron microscopy and atomic force microscopy, as well as micro-Raman spectroscopy were applied.

**Keywords:** Gold nanostructures, Nanoprisms, Polyvinylpyrrolidone, MoS<sub>2</sub>.

DOI: [10.21272/jnep.13\(1\).01018](https://doi.org/10.21272/jnep.13(1).01018)

PACS numbers: 61.46.Hk, 81.10. – h

### 1. INTRODUCTION

Tunability of plasmonic nanoparticles (NPs) through a cheap chemical procedure has strongly excited nanomatter research in recent years due to their possible application in photochemistry and sensing fields. The size and shape of NPs of noble metals can be controlled using different surfactants. These surfactants perform the function of stabilizers for preventing NPs aggregation. The polyvinylpyrrolidone (PVP) is the most widespread non-ionic surfactant for these purposes [1].

In the case of using Au and Ag NPs in sensing technology, such as surface-enhanced Raman spectroscopy (SERS), the layer of surfactant creates a physical barrier for free access of analyte molecules to a surface of the metal particle. It was shown that the intensity  $I$  of the Raman mode strongly depends on the distance  $r$  between the adsorbate and NP surface [2]. This dependence can be described as  $I = (1 + r/a)^{-10}$ , where  $a$  is the size of the enhancing NP feature. Moreover, in the case of using Au NPs as a catalyst, active centers of particles are blocked with polymer [3]. Thus and so, these particles have to be free of a stabilizing agent.

Niu and Li consider some methods of cleaning the surface of such plasmonic particles [4]. The authors suggested as a convenient way to remove PVP from the surface of Au or Pt NPs based on the multiple washing in water or acetone/ethanol with using centrifugation at the final stage [5-7]. This method was chosen for the purification of gold nanocrystals from PVP in order to use them as the enhanced substrates for micro-Raman spectroscopy [6]. However, if the particles are completely washed from the stabilizer, they prefer to aggregate. These aggregates show only weak amplification of the Raman signal.

Other techniques of NPs purification from PVP are also used. For instance, the PVP layer is replaced by a thiol layer on the surface of silver NPs [8]. Desorption of PVP has also been carried out at room temperature by treating Pt-Pd nanocubes with sodium borohydride in the presence of tertbutylamine [9]. The result of such

purification was confirmed by Raman and Fourier-transform infrared spectroscopies. It is worth to note that the shape, size and crystallinity of the particles did not change during this treatment.

Removal of the polymer from the surface of Pt-Ag particles goes through the heat treatment in O<sub>2</sub>/He/N<sub>2</sub> [10]. However, this approach does not always produce free particles from PVP. Heat treatment leads to the carbonization of the polymer, changes its structure, as well as promotes to the partial melting of particles.

It is well known that intense UV irradiation in the ozone atmosphere causes the purification of Pt NPs from PVP without changing the shape of the particles, but it provokes the formation of partially oxidized metal atoms on the surface [11]. In addition, during such an interaction, the products of PVP decomposition locate on the surface [12]. Thus, at nowadays the problem of cleanliness of the NPs surface remains not fully resolved.

Herein we demonstrate another approach to solve the above-mentioned problem. In our study, the flat gold nanoprisms (NPRs) are chosen as test objects. Usually, the PVP concentration is substantial in the growth solution that leads to the formation of a rather thick PVP covering of NP surface. The main idea is to improve the technology of PVP layering. We propose not to remove the PVP layer from the surface of NPRs, but to change the conditions for their synthesis in a way providing the minimal involving of PVP in the process. To obtain NPRs with a clean (not contaminated PVP) surface on the MoS<sub>2</sub> substrate, the changes in the proposed synthesis are: (i) a PVP layer is preliminary adsorbed on the MoS<sub>2</sub>; (ii) the synthesis of NPRs is carried out on the MoS<sub>2</sub>/PVP surface in the growth solution containing no PVP. The detailed description of this method is presented below in the text.

### 2. MATERIALS AND METHODS

For our research, PVP ( $M_w \sim 29$  kDa), glycerin and molybdenum disulfide crystals were purchased from Sigma-Aldrich. Ethylene glycol, ethyl alcohol and chloro-

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auric acid ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) were supplied from “Reakhim”, Russia and Shanghai Synnad Fine Chemical Co., LTD, respectively.

Formation of Au NPRs with clean surfaces is schematically shown in Fig. 1. Stage I includes the modification of  $\text{MoS}_2$  surface by a layer of PVP. Then the sample is washed in ethanol to remove the surplus of PVP. Stage II involves the growth of gold nanostructures on a modified  $\text{MoS}_2/\text{PVP}$  surface in the growth solution that does not contain PVP!

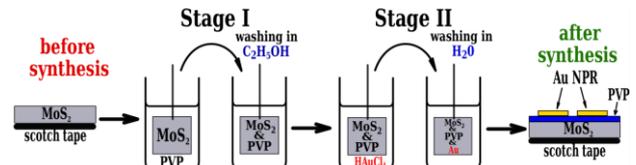
Freshly cleaved  $\text{MoS}_2$  surfaces were prepared by mechanical exfoliation of several layers from a bulk crystal using a scotch tape. These samples were immersed vertically in conical tubes with a mixture of alcohols: ethylene glycol (Eg), glycerin (G), ethanol (Et) (in a volume ratio of 7:7:6) and 45 mM PVP (concentration in terms of one repeating unit). The adsorption of the polymer was proceeded during 48 h at the temperature  $T = 353$  K. Then the modified  $\text{MoS}_2/\text{PVP}$  substrates were washed in ethanol and transferred to the growth medium Eg:G:Et (7:7:6) and 1 mM  $\text{HAuCl}_4$  (without PVP!). The growth of gold nanostructures proceeded during 48 h at  $T = 353$  K. Finally, the samples were washed with distilled water in an ultrasonic bath (1 min, 30 W) and dried at room temperature.

The morphology of the PVP layer and fabricated gold nanostructures was studied using a JSM-6060 scanning electron microscope (SEM) and an atomic force microscope (AFM, Solver ProM, NT-MDT, Russia). Raman scattering spectra were obtained by the Confocal Raman spectrometer (Witex, Focus Innovation, objective  $\times 100$ ). Laser excitation wavelength  $\lambda_{\text{exc}} = 632.8$  nm, laser beam power 1.5 mW, signal accumulation time  $\sim 1$  min were chosen in the experiments.

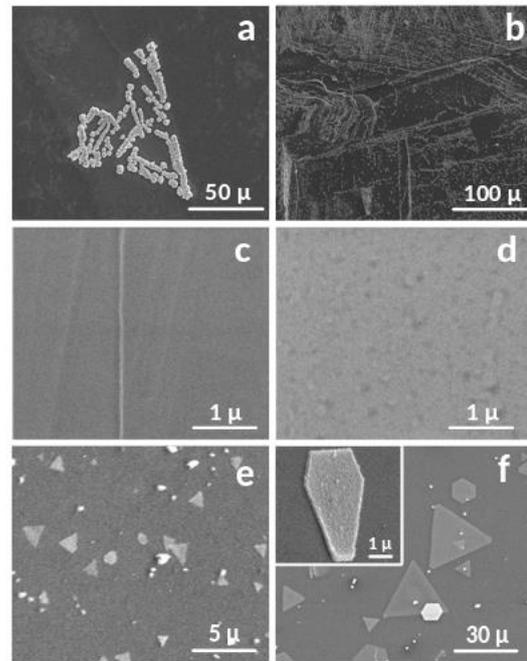
### 3. RESULTS AND DISCUSSION

First, consider the formation of gold nanostructures on a freshly cleaved  $\text{MoS}_2$  surface in growth medium Eg:G:Et (7:7:6), 1 mM  $\text{HAuCl}_4$  (without PVP!). It was shown that gold prisms cannot be formed on the flat  $\text{MoS}_2$  in such a medium (Fig. 2a, b). In this case, only the isolated Au NPs and the extended chains of intergrown NPs are observed (Fig. 2a). Previously, Shi [13] and Sreepasad [14] revealed that Au NPs prefer to grow at substrate cracks and/or defects. We have repeated this observation in our experiments for the sake of clarity. With increasing the time of synthesis, particles spread over the entire surface of the sample (see Fig. 2b), however none shows the shape of the prism.

We emphasize that the presence of PVP in the growth environment is a necessary condition for the formation of prisms in the mixture Eg + G + Et +  $\text{HAuCl}_4$  [3, 15, 16]. This conclusion is confirmed by our previous studies [17-19]. We have identified that the surface of NPRs and NPs has been coated with a PVP layer. Moreover, a variety of shapes of these particles took place due to the specific adsorption of gold ions, PVP molecules, and PVP-Au complexes on the  $\text{MoS}_2$  surface [19]. It was found that the size and shape of the particles are affected by the molecular weight of the polymer, the concentration ratio of PVP and  $\text{HAuCl}_4$ , and the time of synthesis [12, 20-22]. Hereinafter the state of the NPRs is considered in detail after each stage.



**Fig. 1** – The scheme of NPRs formation on the  $\text{MoS}_2/\text{PVP}$  substrate



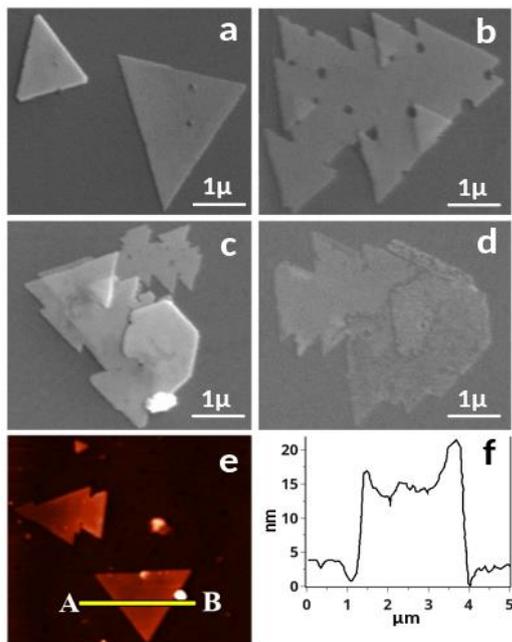
**Fig. 2** – Gold nanostructures on  $\text{MoS}_2$  in the growth medium without PVP after (a) 5 h and (b) 48 h at the temperature  $T = 353$  K. SEM images of (c) freshly cleaved  $\text{MoS}_2$ , (d)  $\text{MoS}_2$  with a PVP layer. The conditions of PVP adsorption: Eg:G:Et (7:7:6),  $C_{\text{PVP}} = 45$  mM,  $T = 353$  K,  $t = 48$  h. SEM images of NPRs formed on (e) the modified  $\text{MoS}_2/\text{PVP}$  surface, (f) pure  $\text{MoS}_2$ . The insert in (f) shows a PVP layer on the NPR surface

At stage I, the surface of freshly cleaved  $\text{MoS}_2$  (Fig. 2c) is modified by a PVP layer (Fig. 2d). The ideally smooth areas and the areas with defects were detected after the cleavage of  $\text{MoS}_2$  sheets from a bulk crystal (Fig. 2c). The PVP molecules adsorb mainly in the coil-like and/or in the globule-like conformations on these sheets, forming a loose structure. A coil conformation occurs due to an increase in the hydrodynamic radius of polymer in the presence of alcohols [23], that is, repulsion between polymer chains predominates. Note the fact that the PVP- $\text{MoS}_2$  interaction occurs between the C=O, C–N functional groups of PVP and the active centers of  $\text{MoS}_2$  [24]. Very often the absence of active centers leads to the areas without adsorbate on  $\text{MoS}_2$  (Fig. 2d).

At stage II, Au NPRs form on the  $\text{MoS}_2/\text{PVP}$  surface. Note that, in fact, NPRs synthesized in the growth solution without PVP (Fig. 2e) and those synthesized with involving 45 mM of PVP (Fig. 2f) are completely different. Fig. 2f shows that the clean surface of  $\text{MoS}_2$  as well as NPRs will be finally covered by PVP. Moreover, such prisms enlarge enough to reach sizes up to 30  $\mu\text{m}$ . On the contrary, the NPRs synthesized using 1 mM  $\text{HAuCl}_4$  only (without PVP) are free of PVP on

their surfaces (Fig. 3). In addition, these prisms are substantially smaller (the lateral size is up to 3  $\mu\text{m}$  and height is up to 30 nm) and their amount is much higher per unit area. It can be explained by the fact that the preliminary formation of a PVP layer increases significantly the concentration of nucleation sites and promotes the growth of prisms rather than particles.

The two types of NPRs, single and intergrown, obtained after the second stage, have preferably the shape of a regular triangle (Fig. 3). One can observe such NPRs as unfinished nanostructures (Fig. 3b, c) with "intergrowths" between terraces.



**Fig. 3** – SEM- (a-d) and AFM- (e) images of Au NPRs and nanostructures on the MoS<sub>2</sub>/PVP surface. (f) – profile of a NPR along the AB line. The synthesis conditions are: a mixture of alcohols Eg:G:Et (7:7:6), 1 mM HAuCl<sub>4</sub>, the temperature is 353 K, the time of synthesis is 48 h

Similar terraces had been formed due to the stepped or screw dislocations, and even cracks in sections/faces of the particle during the biosynthesis of Au NPRs in an aqueous solution containing yeast extract [25].

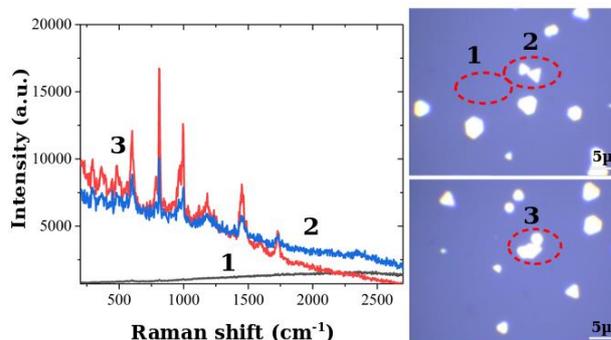
The right side of a flat prism in Fig. 3d consists of single particles. Interestingly, the left part of this prism looks more compact. Formation of such parts is induced by the particle coalescence, which afterwards produces the enlargement of particles in the lateral direction. Finally, step-by-step, a rough surface of NPR appears (Fig. 3e, f). Further formation of a rough surface mainly concerns with the unfinished atomic layers of the (111) face. Every new layer mainly begins the growth from the vertices and edges of the prism, and goes to its center. Therefore, the edges of the prisms have higher walls. We have observed such fortress-like prisms with high walls on MoS<sub>2</sub> surfaces before [19]. The surface profile along the AB line (Fig. 3f) demonstrates the excess of height at the edges by 3-7 nm comparing with the center. The roughness of the prism is about 2.5 nm in the central part.

The surface purity can be checked more precisely by using the micro-Raman spectroscopy. We used a solu-

tion of rhodamine R6G (4  $\mu\text{M}$ ) in anisole, containing 3 % PMMA, that was deposited on the surface of Au NPRs.

The Raman signal was excited by a laser beam focused on the edges of a few closely spaced NPRs (Fig. 4, spectra 2, 3 and the corresponding areas 2 and 3 in the inset photos). Spectrum 1 was obtained under the same conditions from the area 1 (Fig. 4, the photo in the inset), where there are no NPRs. Preliminary studies established that the intensity of some lines had enhanced by several orders of magnitude. This is clearly seen for the peak with the wave number  $\nu = 809 \text{ cm}^{-1}$ . The ratio of intensity  $(\Delta I)_{\nu=809 \text{ cm}^{-1}}$  of spectrum 3, obtained at the edges of the prisms, to  $(\Delta I_0)_{\nu=809 \text{ cm}^{-1}}$  of spectrum 1 (outside the prisms) is  $\sim 10^4$ . We have achieved the similar gain in our previous study [6]. The results obtained indirectly confirm that prisms, growing on the modified MoS<sub>2</sub>/PVP substrate, have a clean surface, because the amplification of the Raman spectra occurs mainly, when a probe-dye connects exactly with gold.

More generally, we consider the very low possibility of PVP adsorption on the NPR surface in the synthesis condition, which we have proposed. Note the fact that the polymer dissolves partially from the modified MoS<sub>2</sub>/PVP substrate in the growth environment containing alcohols [23]. Due to the diffusion, PVP simultaneously adsorbs on and desorbs from the surfaces of the NPRs. However, the concentration of dissolved PVP is negligible to cover the whole NPR, that is, the layer of the polymer is not continuous. We assume that the local concentration of PVP near the NPR is gradually decreasing during the synthesis, and its surface is cleaned in this way.



**Fig. 4** – The Raman scattering spectra of rhodamine R6G with PMMA adsorbed on the MoS<sub>2</sub>/PVP (1) and Au NPRs (2, 3)

#### 4. CONCLUSIONS

We highlight the two-stage method of synthesizing atomically fresh gold nanostructures on MoS<sub>2</sub>/PVP substrate. Incorporating such a straightforward method, one obtains nanoprisms with clean and enlarged (111) face. For these purposes, at the first stage, the PVP layer is adsorbed on the freshly cleaved MoS<sub>2</sub> surface from the mixture of alcohols and PVP. At the second stage, NPRs form in the growth solution without PVP on the modified MoS<sub>2</sub>/PVP substrate. However, the problem of NPRs roughness is not fully resolved due to the formation of fortress-like prisms, which demonstrate the excess of height at the edges.

Micro-Raman spectroscopy confirms that the surface of NPRs stays clean after the second stage of syn-

thesis and enhances strongly the Raman signal. We believe that due to this experimental revealing, nano-prisms are promising objects for the SERS-studies, photochemistry, sensing as well as could be applicable as substrates for further functionalization by organic monolayers and gold nanoparticles [26].

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## Ріст наноструктур золота на поверхні MoS<sub>2</sub>, модифікованій полівінілпіролідом

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У роботі описано спосіб синтезу плазмонних наноструктур золота, здебільшого нанопризми, які мають чисту поверхню. Вони вирощені на модифікованій полівінілпіролідом (PVP) поверхні дисульфиду молибдену (MoS<sub>2</sub>). Синтез наноструктур здійснювався у два етапи. На першому етапі було отримано модифіковану поверхню MoS<sub>2</sub>/PVP, а потім на ній синтезували нанопризми золота у ростовому розчині, що не містив PVP. Для підтвердження чистоти поверхні нанопризми застосовували сканувальну електронну мікроскопію, атомно-силову мікроскопію, а також мікрораманівську спектроскопію.

**Ключові слова:** Наноструктури золота, Нанопризми, Полівінілпіролідон, MoS<sub>2</sub>.