Formation and Growth of Gold Nanostructures on Atomically Smooth Surfaces of MoS2, Graphite, Mica in the Non-Aqueous Medium

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Abstract* – *A numerous methods of synthesis of gold nanoparticles (NPs) allow to obtain spherical and anisotropic Au NPs in aqueous and non-aqueous media, in the micelles and at the phase interfaces. Here we propose to grow the Au NPs directly on atomically flat surfaces of different monocrystals: MoS_2, highly oriented pyrolytic graphite (HOPG) and mica. Thus, the spherical NPs and monocrystals are being formed preferentially in presence of the mica and graphite surfaces, while on MoS2 −NPs and Au nanowires. The shape, size and thickness of the gold NPs were estimated by scanning electron microscopy. The method of electron microprobe analysis has revealed that the gold NPs have no incidental impurities.

Key words – nanoparticle, monocrystal, atomically smooth surfaces, side defects, dendritic structures, scanning electron microscopy.

I. Introduction

The gold nanoparticles (NPs) is widely used in different applications due to their unique optical and catalytic properties. Physical properties of such NPs strongly depend on their shape and size which can be controlled by tuning of synthesis conditions. A numerous methods of synthesis of NPs allow to obtain spherical and anisotropic Au NPs in aqueous and non-aqueous media, in the micelles and at the phase interfaces. For following characterization nanoparticles are being delivered to the surface of various materials. We propose to grow the Au NPs directly on atomically flat surfaces of different monocrystals: MoS_2, highly oriented pyrolytic graphite (HOPG) and mica.

It has previously been shown [1] that flat triangular and hexagonal gold nanocrystals with thickness less than 100 nm can be formed in free volume of mixture of ethanol (ET), ethylene glycol (EG), $HAuCl_4$ (precursor of gold) and stabilizer polyvinyl pyrrolidone (PVP) at 80° C.

Immersing to the growth medium [1] the plates of freshly cleaved MoS_2, HOPG or mica drastically changes the synthesis conditions and leads to a qualitative and quantitative difference between nanostructures obtained in free volume and on the surfaces. Thus, the spherical NPs and monocrystals are being formed preferentially in presence of the mica and graphite surfaces, while on MoS_2 −NPs and Au nanowires.

We have changed the conditions of synthesis by adding the glycerin in growth medium. Thereby the viscosity of the dispersion medium and the wettability of substrate surface were increased. It was found that the gold NPs have been formed on all immersed substrates at a volume ratio of EG-ET-GL (7: 7: 6) and at concentrations of C_{Au} = 1 mM, C_{PVP} = 0,045M at 80 ° C during 5 hours. Nanoprisms were mainly formed on the mica surface after 48 hours (Fig. 1), on MoS_2 - nanowires, nanoprisms and Nps (Fig. 2 and 3), on graphite - nanoprisms and NPs with more complicate shape (Fig. 4). Such difference in formation of nanostructures on the atomically smooth surfaces of MoS2, graphite and mica is related to the nature of the immersed surface, mobility of gold atoms.

The shape, size and thickness of the gold NPs were estimated by scanning electron microscopy. The method of electron microprobe analysis has revealed that the gold NPs have no incidental impurities. It has been found that the distribution of gold NP is accidental on the mica surface, while the formation of nanowires on MoS_2 surface was observed preferentially close to defects, which are most likely associated to sulfur atoms on the surface.

II. Results and Discussion

When a piece of single-crystalline MoS2 is immersed into growth solution gold NPs can decorate the substrate of MoS2 as shown in the SEM images Fig. 1, *a* and 1, *d*. It was found that a large number of irregular-shaped gold particles formed on the major surface defects of the MoS2 (Fig. 1, *a*). Moreover, a five-fold symmetry of some flower-like particles and clearly defined dendritic outgrowths were observed, growth of which are accompanied preferentially by side defects of MoS_2.

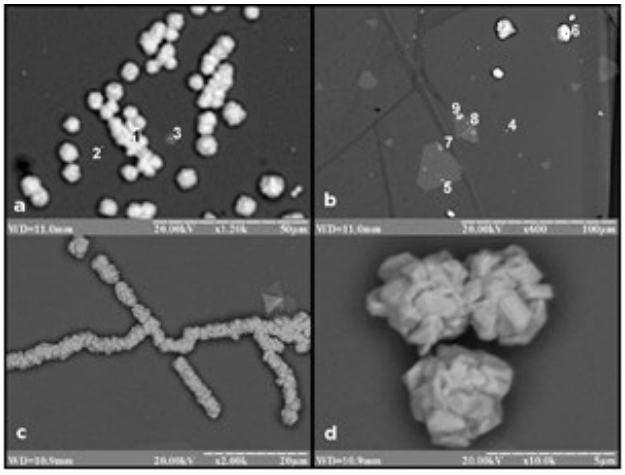

Fig. 1. SEM images of Au structures on MoS_2 after 48 hours of synthesis and washing in distilled water; irregularly shaped particles (a, d), triangular and hexagonal Au crystals (b), dendritic structures (c). *Marked with figures are the points where the electron microprobe analysis was held

Dendritic growth can be explained by specific of capturing of gold atoms. Thus, at the early stages of nucleation the sizes of the adatom capture areas are expected to be much smaller than the general interparticle distances. We noticed that a large density of $HAuCl_4$ in

growth medium preferentially leads to the formation of dendritic structures.

Interestingly, particles with prismatic features appear via increasing time of synthesis. The surface of these nanoprisms serves as new centers of nucleation (Fig. 2). The majority of centers are concentrated near the edges of prisms which is confirmed the peculiarity of growth reported in [1]. Such tendency was observed mainly for the sample Au nanoprisms / MoS2 while other samples did not demonstrate it (clean surfaces of nanoprisms in Figs. 3 and 4).

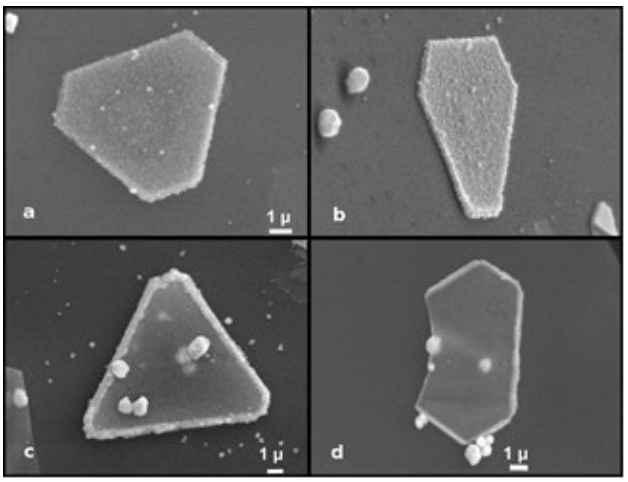

Fig. 2. SEM images of Au prisms on MoS_2

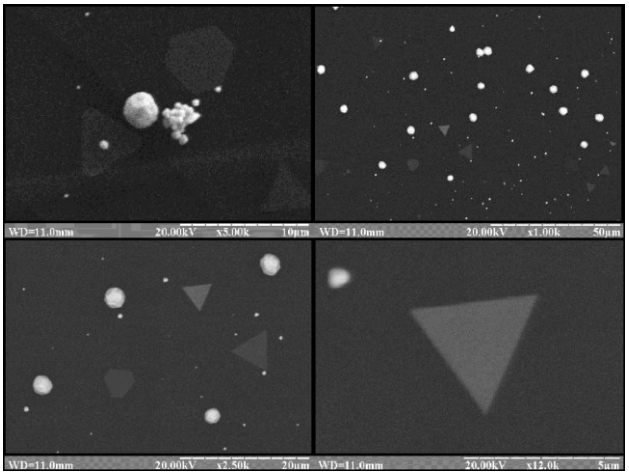

Fig. 3. SEM images of Au structures on HOPG after 48 hours of synthesis and and washing in distilled water

It is not clear whether prisms pre-forme in the volume of the growth medium and settle out on the surface or grow directly on the surface. We highlight three possible options for fastening/forming Au NPrs on investigated surface: (i) prism "sticks" to the defects of the surface, (ii) links with the adatoms, clusters or other particles that previously settled out on the surface and (iii) forms directly from the embryo on graphite surface.

(i) Surface defects of graphite and mica such as monoatomic terraces can act as a nucleation centers for Au nanoprisms. The difference of surface energy between terraces directly influences on the processes of adsorption/diffusion of individual nanostructures of gold.

(ii) It is known that gold particles may grow due to other particles (Ostwald ripening). This fact confirms ability of Au nanoprisms to "attach" to smaller particles, in this case to those that have already adherent to the surface of graphite/MoS2/mica.

(iii) Peculiarity of kinetic of growth of gold nanostructures on the investigated surfaces well-described in literature. It was clearly shown that the growth of well-faceted, three-dimensional crystallites with smooth edges begins from embryo less than 5 nm. We suppose that the majority of Au nanoprisms with sharp edges more likely initially formed in the volume of growth medium and then settled out on the surface of substrate. However, the Au nanoprisms with rounded edges has repeatedly been observed.

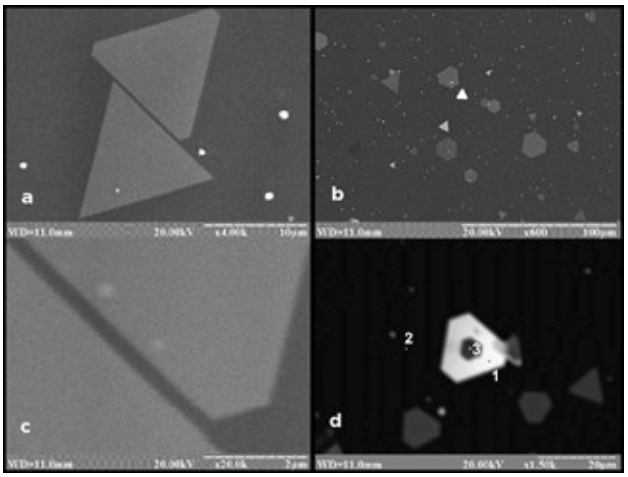

Fig. 4. SEM images of Au structures on mica substrate after 48 hours of synthesis and washing in distilled water. *Marked with figures are the points where the electron microprobe analysis was held

Several experiments with samples washed in distilled water were carried out. Taking into account diffusion of Au structures and not very strong binding with the substrate, in case of graphite, nanoprisms can disconnect from the surface during washing. But, as shown in Figs. 1, 3 and 4 the most of triangular and hexagonal Au crystals leave on surface after washing. This fact confirms that well-faceted Au nanoprisms may settle out on surface as well as grow on it.

Conclusion

The conditions of synthesis and formation of gold nanostructures on the atomically smooth surfaces of MoS_2, graphite and mica have been established. Obtained nanostructures can be used in micro- and nanoelectronics, sensing, catalysis.

References

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