Formation peculiarities of silver dendritic structures for photocatalysts of the visible radiation range

A P Sigaev¹, I A Averin¹, I A Pronin¹, A A Karmanov¹, N D Yakushova¹, V A Moshnikov¹,²
¹Department of Nano- and Microelectronics, Penza State University, 440026, Penza, Russia
²Department of Micro- and Nanoelectronics, Saint-Petersburg Electrotechnical University, 197376, Saint-Petersburg, Russia

Abstract. The techniques for synthesis of silver structures in the form of a polyhedral array, as well as in the form of self-similar objects, spatially organized by the type of dendrites, are presented. The mechanisms that potentially determine the formation peculiarities of such structures are considered. Prospects of using this type of structures alongside with wide band gap semiconductor oxides, as highly efficient photocatalysts of the visible radiation range, are demonstrated.

1. Introduction

In recent years, much attention has been paid to the development of new materials, which, when transitioning to nanoscale characteristic sizes, acquire unique photocatalytic properties [1, 2]. In this case, nanomaterials that demonstrate high photocatalytic activity in light irradiation, both of ultraviolet and visible wavelength ranges, are of particular interest [3, 4]. To create photocatalysts of this type, various methods and approaches have been proposed, including those based on the use of surface plasmon polaritons (SPPs), excited at the interface boundary with different dielectric constant. The main idea here is to use a composite metal structure (platinum, palladium, gold, silver, etc.), namely, a wide band gap semiconductor (titanium dioxide, zinc oxide, etc.) to generate, collect and separate high-energy charge carriers causing high photocatalytic activity of the nanomaterial. According to this approach, with strong light and matter interaction in the nanostructured materials, binding of incident light in plasmon resonances can be observed. Under certain conditions, these photogenerated plasmon polaritons break up into a collective of non-equilibrium high-energy charge carriers, which later can be used to stimulate a chemical reaction [5]. For example, in the well-known work [6], this phenomenon was used to increase the efficiency of hydrogen generation process in light irradiation of nanostructured photocatalysts with near-zero dielectric constant.

However, as is well known, plasmon resonance for nanomaterials of a simple geometric shape, for example, for spherical metal nanoparticles, corresponds to a certain frequency, and as a consequence, to the fixed wavelength of incident radiation. In accordance with this, research related to the study of SPPs generation in nanomaterials with a complex spatial structure, including self-similar ones becomes relevant [7-9]. The purpose of this work was to study the formation peculiarities of silver dendritic structures for photocatalysts of the visible radiation range. In this case, the self-similar structure of the samples provides the fundamental possibility of generating surface plasmon polaritons not at a strictly defined frequency, but in the frequency range that covers both the ultraviolet and the visible area.
2. Experiment
In the framework of this work, the synthesis of structures based on Ag was carried out according to two main techniques, taking into account the known experimental works [10, 11]. According to the first technique, a solution of silver nitrate was prepared by dissolving 1 mmol salt in 100 mL of nitric acid with a concentration of 0.1 mol. Next, the solution was continuously stirred using a magnetic stirrer, and 3 mmol L-ascorbic acid dissolved in 10 mL of distilled water was added. As a result of the reaction carried out at a temperature of 25°C, silver particles were formed, being precipitated for 60 minutes. At the last synthesis stage, sediment separation by centrifugation, its double washing with water and acetone, and also drying at room temperature were carried out.

According to the second technique, solutions A and B were prepared at the first stage. At the same time, to prepare solution A, 0.2 mmol AgNO₃ was dissolved in 0.5 mL of distilled water, followed by the addition of 9.5 mL of acetone. Solution B was obtained by dissolving 0.4 mmol L-ascorbic acid in 0.5 mL of distilled water, and then 9.5 mL of acetone was added. At the second stage, solution B was dripped into solution A for 3 minutes at a temperature of 25°C. At the third stage, the resulting mixture was kept for 10 minutes at room temperature, after which the sediment was separated by centrifugation and washed with distilled water several times.

3. Results and Discussion
Figure 1 presents the data of scanning electron microscopy (SEM) of samples synthesized in accordance with the first technique. Figures 1a and 1b correspond to an increase of 10.000x and 50.000x, respectively.

![Figure 1(a, b). SEM images of silver structures in the form of a polyhedral array with an increase of (a) 10.000x and (b) 50.000x](image)

An analysis of the images presented in Figure 1 shows that in the solution of water and nitric acid, Ag structures are formed as a polyhedral array, the average size of which does not exceed 2 μm. Moreover, small size dispersion is characteristic for individual particles inside the array; silver particles have the highest concentration, the size of which is ≈ 1.2 μm along the longest axis. For such nanomaterials, even if they have a complex geometrical shape, plasmon resonance is observed in a narrow frequency range corresponding to the characteristic size of polyhedra with allowance for dispersion. This significantly limits the spectrum of the incident radiation, in which the composite metal-wide band gap semiconductor structures exhibit photocatalytic activity. In particular, for composite structures based on zinc oxide and an array of silver polyhedrons, photocatalytic
decomposition of model pollutants is observed mainly under radiation of the ultraviolet wavelength range.

Figure 1 presents the data of scanning electron microscopy of samples synthesized in accordance with the second technique. Figures 1a and 1b correspond to an increase of 20,000x and 100,000x, respectively.

An analysis of the images presented in Figure 2 shows that in the solution of water and acetone, arrays of self-similar Ag structures are formed according to the type of dendrites, the trunk and main branches of which have a characteristic size of 1-5 μm, and the side ones are of 100-500 nm. This size of the side branches of the dendrites, as well as their spatial arrangement, ensures the equivalence of the studied structure of the metal surface with convexities and concavities, which realize the locking of electromagnetic energy in the volume, generating strong quasi-static localization [12]. This localization, in turn, ensures the efficient generation of high-energy charge carriers that stimulate catalytic reactions, for example, photocatalytic decomposition of organic pollutants.

4. Conclusions
Thus, the present work considers the formation peculiarities for two types of silver structures: 1) in the form of a polyhedral array; 2) in the form of self-similar objects, spatially organized by dendritic type. We assume that the growth mechanism for silver dendrites, synthesized in accordance with the second technique, is similar to the mechanism for the formation of nanotrees described in [13]. In our case, acetone performs a function similar to hydroxylamine, i.e. its molecules are adsorbed on the faces corresponding to the crystallographic planes (110) and (100), preventing the growth of Ag particles along the spatial directions corresponding to these faces. Being essentially self-similar, the growth mechanism under consideration determines the existence of dendritic branches of different generations. The results obtained may be of interest in the development of composite photocatalysts on the basis of such structures that are active in the visible radiation range.

Acknowledgments
The work has been financially supported by the Ministry of Education and Science of the Russian Federation within the framework of the project part of the state assignment for Penza State University No. 16.897.2017/4.6, as well as in the framework of the Presidential Grant and the Presidential
Scholarship (project No. MK-1882.2018.8, SP-84.2018.1 and SP-3800.2018.1). The authors also thank Kisin V.V. and Smirnov A.V. from Yuri Gagarin State Technical University of Saratov (SSTU) for assistance in the experimental study of silver structures using scanning electron microscopy.

References

[1] Sun L, Li R, Zhan W, Yuan Y, Wang X, Han X, Zhao Y 2019 Nat. Commun. 10 2270
[2] Pronin I A, Averin I A, Kaneva N V, Bozhinova A S, Papazova K I, Dimitrov D Ts, Moshnikov V A 2014 Kinetics and Catalysis 55 167
[3] Zhang Z, Ma Yg, Bu X, Wu Q, Hang Z, Dong Z, Wu X 2018 Scientific Reports 8 10532
[4] Duan Z, Huang Y, Zhang De, Chen S 2019 Scientific Reports 9 8008
[5] Linic S, Christopher P, Ingram D B 2011 Nat. Mater. 10 911
[6] Tian Y, de Arquer F P G, Dinh C-T, Favraud G, Bonifazi M, Li J, Liu M, Zhang X, Zheng X, Kibria Md. G., Hoogland S, Sinton D, Sargent E H, Fratalocchi A 2017 Adv. Mat. 1701165
[7] Ma X-C, Dai Y, Yu L, Huang B-B 2016 Light: Science & Applications 5 e16017
[8] Moshnikov V A, Maksimov A I, Aleksandrova O A, Pronin I A, Karmanov A A, Terukov E I, Yakushova N D, Averin I A, Bobkov A A, Perymakov N V 2016 Technical Physics Letters 42 967
[9] Pronin I A, Averin I A, Yakushova N D, Karmanov A A, Moshnikov V A, Ham M-H, Cho B K, Korotcenkov G 2017 Arabian Journal for Science and Engineering 42 4299
[10] Martínez-Castañón G A, Niño-Martínez N, Loyola-Rodríguez J P, Patiño-Marin N, Martínez-Mendoza J R, Ruiz F 2009 Mat. Let. 63 1266
[11] Han Y, Liu S, Han M, Bao J, Dai Z 2009 Crystal Growth & Design 9 3941
[12] Silveirinha M G, Engheta N 2007 Phys. Rev. B 76 245109
[13] Yang C, Cui X, Zhang Z, Chiang S W, Lin W, Duan H, Li J, Kang F, Wong C-P 2015 Nat. Commun. 6 8150