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تهیه و مشخصه یابی نانوستاره طلا به عنوان نانوساختارهای جدید پلاسمونی

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چکیده- در این پروژه، نانوستاره‌های طلا به عنوان ساختارهای جدید پلاسمونی با کمک روش شیمیایی تولید و مشخصه یابی شدند. به این منظور، نمک طلا در محیط به تعادل رسیده بازی سنتز شد و پس از تصویربرداری و اطمینان از شکل گیری ساختار، طیف جذبی نمونه‌ها ثبت شد. ساختار و طیف‌های جذبی نانوستاره‌ها در شرایط مختلف از قبیل تغییر پارامترهای سنتز و تاثیر زمان بر نمونه مورد مطالعه قرار گرفتند. نتایج حاصل از تصویربرداری، نشان دهنده رسیدن به ساختار شش ضلعی پس از رسیدن به پایداری می‌باشد و طیف جذب، نشان دهنده مدهای اصلی پلاسمونی در نمونه های تولید شده است.

کلید واژه- نانوستاره طلا، مد پلاسمونی، نانوساختارهای پلاسمونی، سنتز شیمیایی.

Synthesis and characterization of Gold nanostars as new kind of plasmonic nanostructures

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Abstract-In this work, gold nanostarshave been synthesized chemically and characterized as novel plasmonic structures. The synthesis based on reduction of Tetrachloroauric acid in stable basic environment and absorption spectra have been recorded when the imaging confirmed nanostars formed. Morphology and absorption spectra of gold nanostars have been studied under different conditions such as varying synthesis parameters and aging. Imaging results show hexagonal structures have been formed when the samples became stable, and absorption spectra depict fundamental plasmonic modes in synthesized samples.

Keywords: Au nanostar,Plasmonic mode, Plasmonic nanostructure, Chemical synthesis.

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1. Introduction

Plasmonic metal nanoparticles are very interesting both from a fundamental science point of view, and also in applications such as optics, medicine, clinical diagnosis and therapy [1, 2]. These structures are very sensitive because of localized surface plasmon resonances (LSPRs) on their surface [3]. Therefore, the shape and the size of the plasmonic metal nanoparticles can affect their properties and applications. The shape of the nanoparticles can have a wide range such as nanosphere, nanorodes, nanobars, nanostars, nanoprisms, nanosrystals etc. [4- 6]. One of the most important properties that the shape and size of nanoparticles can affect it, is spectral range of the nanoparticles and it can be shifted by varying the size and morphology of the particles, therefore different applications can be defining according to the spectral range. It has been reported metallic nanostars have displayed extraordinary properties and highly enhanced electromagnetic filed with promising applications in biosensing, bioimaging and biodetection [7, 8]. Recently, Tomitaka et al. reported application of magneto-plasmonic nanostars for image-guided and NIR-triggered drug delivery [9].Studies show star shaped nanoparticles largely intensify local electric filed specially around their tips and sharp corners [10, 11] and it has been expected that they show IR-shifted plasmonic resonances. In table I enhancement factor for gold nanoparticles (AuNPs) and nanostars (AuNSs) has been compared.

Table I. Comparison of enhancement factor for AuNPs and AuNSs [12]

Plasmonic structure	Size (nm)	EF
AuNPs	60nm	10^3
AuNSs	50nm	10^4-10^5

In this project, Au Nanostars have been synthesized with simple chemical method and without using surfactant that may affect the nanoparticles properties and limit the optical characteristics. In fabrication, the main reaction was reduction of Au. It is supposed the reductors have the main role in growing of the spikes in nanostars and sharp corner in polygonal nanoparticles. In synthesis of Au nanostars, ascorbic acid was reduction agent. NaOH was used as it was supposed to increase the reaction yield [13, 14]. It should be mentioned aging has very important role in morphology transformation.

2. synthesis of Gold nanostars

In fabrication of gold nanostars (AuNSs), Cetyl trimethylammonium bromide (CTAB), Tetrachloroauric acid (HAuCl4), Sodium hydroxide (NaOH), ascorbic acid (C6H8O), silver nitrate (AgNO3) and acetone (C3H6O) were used. The synthesis method followed in this project was the same as the protocol Trigari et al. used [15].

The synthesis of AuNSs based on reduction of HAuCl4. Au nanostars preparation was started by making a 3 mL solution of CTAB (50mM) and HAuCl4 (2mM) mixture in water. The colour of this solution was dark yellow. Afterward, 80 µL of NaOH (0.25 M) was added (the experiment was performed with different amount of NaOH to investigate the effect of it on AuNSs properties that is discussed in results section). Then 200 µL of ascorbic acid (40 mM) was added to the solution. By adding NaOH and ascorbic acid, the solution became colourless. In the last steps of the synthesis 60 µL of AgNO3 (10 mM) and the 65 µL acetone were added to the solution. All the solutions were prepared in HPLC water. To complete the reduction of AuNSs the solution containing nanostars was kept in 25˚C overnight. The schematic of the sample preparation was shown in figure 1.

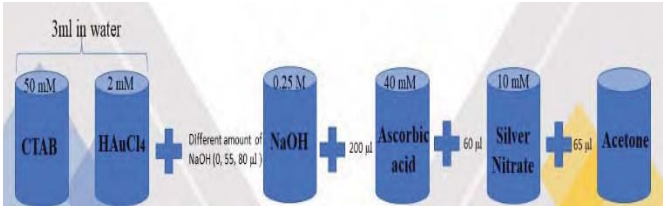

Figure 1. Schematics of the Au and Ag Nanostars. AuNSs

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3. Results and Discussion:

3.1.TEM and SEM of AuNSs

As it was mentioned before AuNSs was kept in25˚C overnight to complete the reduction. To investigate the effect of NaOH on size of the particles, AuNSs was prepared with three different amount of NaOH which were 55 µL and 80 µL of NaOH and without it.

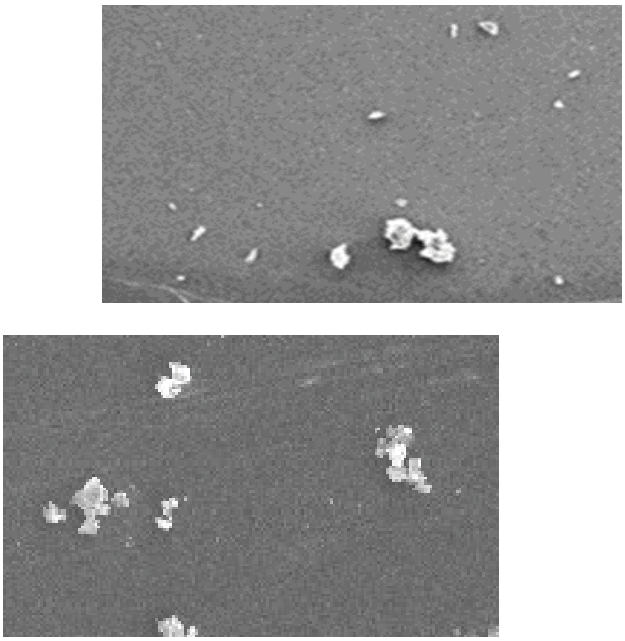

Figure 2. SEM images of Au nanostars with different amount of NaOH. (Top 80 µL, middle 55 µL and bottom without NaOH)

SEM images were recorded 24 hours after synthesis. Figure 2 shows the SEM images for three samples with different amount of NaOH. As it can be seen, sample with the highest amount of NaOH has the smallest size of the nanostars and the sample without NaOH has the biggest particles size.

TEM images for AuNSs samples was recorded a week after fabrication for sample with 80 µL of NaOH and sample without NaOH as they are shown in figure 3.

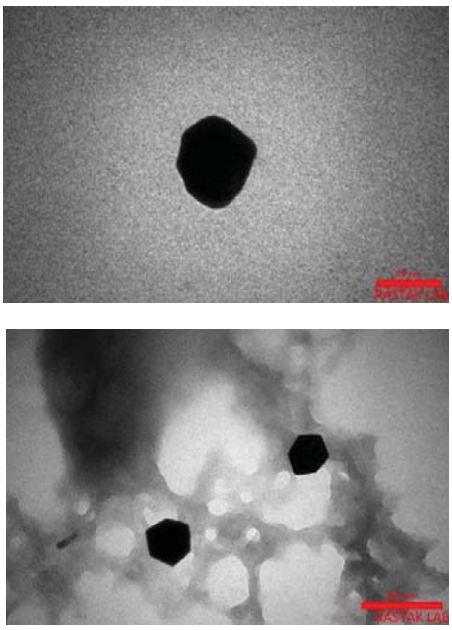

Figure 3. TEM images of Aunanostars a week after fabrication. (TopAuNSs with 80 µL of NaOH and bottomAuNSswithout NaOH)

As it can be seen after one week the arms of the nanostars vanished and they became polygonal with sharp corners. This is the same happening Wu et al. got for their samples. They found after 52h nanostars lost their arms and transformed to spherical nanoparticles [16].

3.2.Absorption spectra of AuNSs

Absorption spectra of AuNSs with three different amount of NaOH have been measured and the results are shown in figure 4.

The main peaks at 530 nm belong to the Au absorption and the shoulders appear due to the sharp corners of polygonal. As it can be seen the signal to noise ratio has its highest value for the sample with 80 µL of NaOH and the sample with 55 µL of NaOH has smaller peak and the sample without NaOHhas the smallest one.

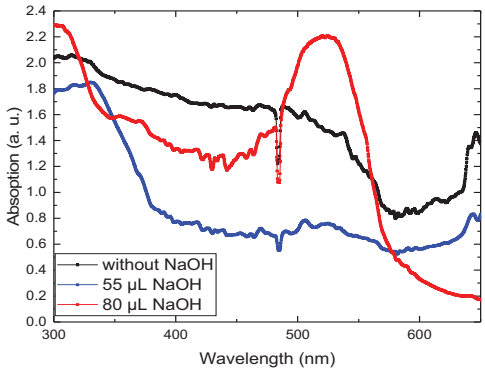

Figure 4. Absorption spectra of AuNSs with different amount of NaOH.

4. Conclusion:

Au Nanostars were synthesized by a simple chemical method. These nanostars were stable for few days without any stabilizer and surfactants but after few days they lost their arms and tips and transformed to polygonal shape. The results show the amount of NaOH can affect reaction yield and change the size and morphology of the nanostars. Also, the amount of NaOH can change the intensity of the absorption peak, by increasing the amount of NaOH the signal to noise ratio was increased.

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