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Well-Controlled Generation Process of Bimetallic Ag//Au Colloidal Nanoparticles by Non-Thermal Plasma DC Glow Discharge

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Abstract

In this paper, an inexpensive, simple and well-accurate process of the generation of bimetallic silver Ag//gold Au core//shell is colloidal metal nanoparticles (MNPs). This is achieved via an atmospheric pressure non-thermal plasma glow discharge between two electrodes. One of these electrodes is a capillary tube placing over solution about (1 cm) that acts as the cathode, while the other electrode is a metal disk immersed in the solution and acts as an anode. Glow discharge process carried out at room temperature using a home-made cell with (6 KV) applied voltage and direct current (DC) about (1.8 mA) for different discharge periods. A wide range of bimetallic Ag//Au colloidal MNPs was rapidly synthesized as a result of non-thermal plasma formation between a capillary tube and the surface of AgNO₃ solution for (5 min) and a mixture of AgNPs-HAuCl₄ solution for (5, 10 and 15 min). Field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM) and X-ray diffraction were used to investigate the structural properties of the bimetallic Ag//Au colloidal MNPs. While optical properties were investigated using a UV-Vis spectrophotometer. Results show that the discharge time plays a crucial role in modifying the bimetallic nanoparticles properties such as grain size, surface area, and optical stability. Moreover, TEM and FE-SEM confirm the formation of Ag//Au core//shell structure with uniform sizes and shapes.

Keywords: Bimetallic, Ag//Au NPs, Non-thermal plasma Discharge treatment

عملية جيدة التحكم توليد الجسيمات النانوية الغروية ثنائية المعدن للفضة//ذهب عن طريق بلازما التفريغ المتوهج الغير حرارية

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الخلاصة

في هذا البحث ، عملية غير مكلفة، بسيطة، ودقيقة لتوليد الجسيمات النانوية ثنائية المعدن للفضة//ذهب نواة//قشرة. يتم تحقيق ذلك عن طريق التفريغ المتوهج عند الضغط الجوي بين قطبين. أحد هذه الأقطاب هو أنبوب شعري يوضع فوق المحلول (حوالي 1 سم) يمثل الكاثود ، في حين أن القطب الآخر عبارة عن قرص معدني مغمور في المحلول ويمثل الأنود. يتم تنفيذ عملية التفريغ المتوهج عند درجة حرارة الغرفة باستخدام خلية محلية الصنع بجهد مطبق حوالي (6 كيلو فولت) وتيار مستمر حوالي (1.8 مللي أمبير) لفترات تفريغ مختلفة. تم تصنيع مجموعة واسعة من الجسيمات نانوية ثنائية المعدن الغروية للفضة//ذهب بسرعة نتيجة لتكوين البلازما غير الحرارية بين أنبوب شعري و سطح المحلول لمعالجة نترات الفضة (AgNO₃) لمدة (5

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دقائق) ومحلول يتكون من خليط من جسيمات نانوية للفضة-كلوريد الذهب (AgNPs-HAuCl_4) لمدة (5 ، 10 و 15 دقيقة). تم استخدام المجهر الإلكتروني الماسح، المجهر الإلكتروني النافذ و حيود الأشعة السينية لفحص الخواص الهيكلية للجسيمات النانوية الغروية ثنائية المعدن للفضة//ذهب. بينما تم التحقيق في الخصائص البصرية باستخدام مقياس المطياف الضوئي. أظهرت النتائج أن وقت التفرغ يلعب دوراً حاسماً في تعديل خصائص الجسيمات النانوية ثنائية المعدن مثل حجم الحبوب ومساحة السطح والاستقرار البصري. علاوة على ذلك ، يؤكد المجهر الإلكتروني النافذ على تشكيل هيكل نواة//قشرة للجسيمات النانوية الغروية للفضة//ذهب بأحجام وأشكال موحدة.

Introduction

Preparation and characterization of bimetallic nanoparticles like silver Ag//gold Au core//shell configuration have greatly attracted significant attention in the last years. This is due to their specific impacts of electronic and catalytic as well as their good stability, the convenience of electron transfer, biocompatibility [1] and a large surface of Plasmon absorption spectrums [2]. It has different potential applications, such as, photo-thermal cancer therapy [3], drug delivery [4], and chemical sensor [5-6]. The core//shell bimetallic might reveal a promising electro catalytic activity, happening on the shell of the nanoparticle. But the core of nanoparticle intensely affects the performance of whole nanoparticle [7]. The bimetallic Ag//Au core//shell NPs are produced by different approaches, like (chemical synthesis [8], laser ablation [9], micro-emulsions [10], ionic liquids [11], etc.). However, all these methods are expensive and involve a special technique.

Stable formation of non-thermal plasmas at atmospheric pressure by DC glow discharge to co-reduce Ag and Au ions is a comparatively green process, simple method, safety, and low cost rather than others formation process [12-15]. Bimetallic nanoparticles offer superior catalytic rendering than the monometallic nanoparticles. Which is attributable to an interactive impact between two various metals and superior control in structures and installation of chemicals [16]. In the plasmonics application of bimetallic core//shell configuration, the Plasmon of the core portion can efficiently interact with the electromagnetic waves due to that the shell is not thick. But when the shell is adequately dense, only the Plasmon corresponding to shell can be observed [9]. Any changing either in the thickness of shell or the size of the core will be responsible for altering the size of the core//shell nanoparticles and their effective optical properties. In the current research, the well-controlled production of bimetallic Ag//Au core//shell nanoparticles by optimizing the glow discharge time has been reported.

2. Experiments

Stably non-thermal plasma DC glow discharge at the atmospheric pressure in a fixed concentration of AgNO_3 and in the AgNPs-HAuCl_4 mixture was employed for rapid formation of different forms of colloidal nanoparticles. The glow discharge was carried out in an electric discharge cell consisting of two electrodes. A stainless steel capillary electrode (act as cathode) with a diameter of about (700 μm), and the argon gas flows through it and placed at (1 cm) above the liquid. Whereas the other electrode is a platinum (Pt) wire of thickness of about (1mm) is immersed in the solution to fix to the ground, as shown in (Figure-1). The glow discharge conditions include an applied high voltage of about (6 KV) DC with a discharge current of about (1.8 mA) for different discharge times (5, 10 and 15 min) with aqueous concentration solution of (1mM) for AgNO_3 and HAuCl_4 .

The presence of fructose solution as a stabilizing agent prepared with a concentration of (0.01 M). It is utilized to reduce any agglomeration process of the resulting bimetallic nanoparticles.

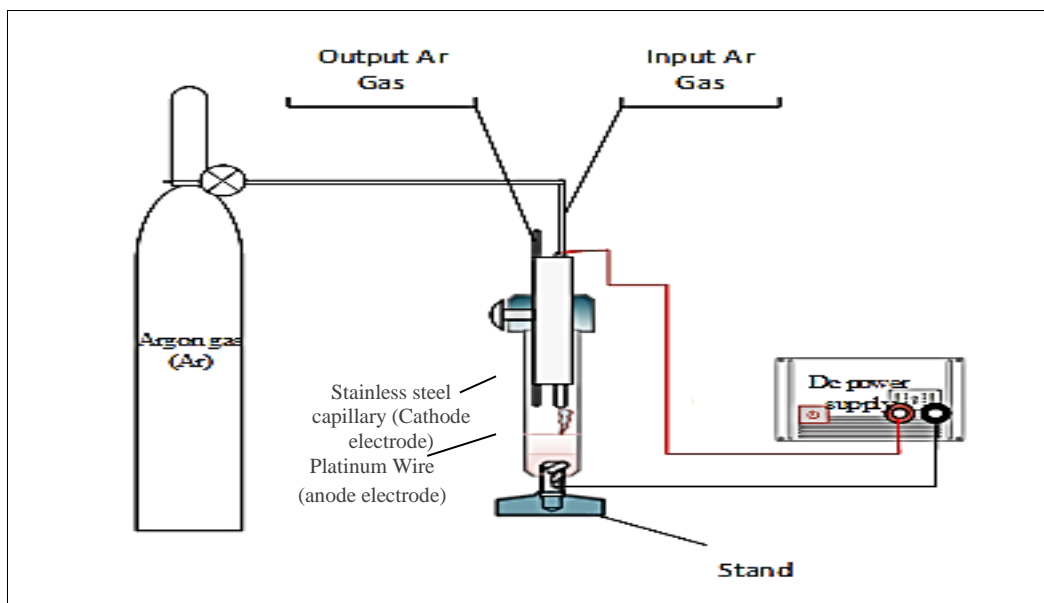


Figure 1-Experimental Set-up of non-thermal glow plasma discharge

Firstly, the silver nanoparticles AgNPs were prepared by atmospheric pressure non-thermal plasma DC glow discharge with the same discharge current and voltage for (5 min) in AgNO₃ solution. Then, the well-controlled production of bimetallic Ag//Au core//shell nanoparticles was synthesized by adding HAuCl₄ solution above AgNPs solution. And then applying the glow discharge above the mixture for different discharge times (5, 10 and 15 min). The colour of the mixture varied according to the discharge time, Figure-2(a-c).

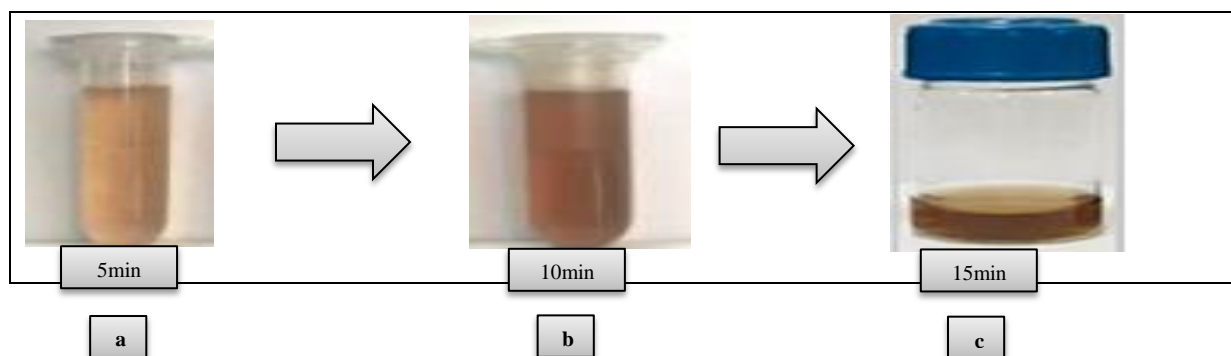


Figure 2-The Ag//Au core//shell nanoparticles colours at different times

The Au and also Ag ions reduction process was carried out by the electrons to synthesize the gold and silver monomers as shown in the following equations [11, 17, 18]:



In this process, the growth and nucleation of Ag//Au NPs depend on the number of Ag⁰//Au⁰ core-shell monomers, which, in turn, depends on the amount of the electrons. The schematic representation approach used in the synthesis of bimetallic Ag//Au core//shell nanoparticles, by an atmospheric pressure glow discharge. Which is non-thermal plasma created between glow discharge and electrolytes of AgNO₃, and in the (Ag NPs-HAuCl₄), is shown in Figure-3:

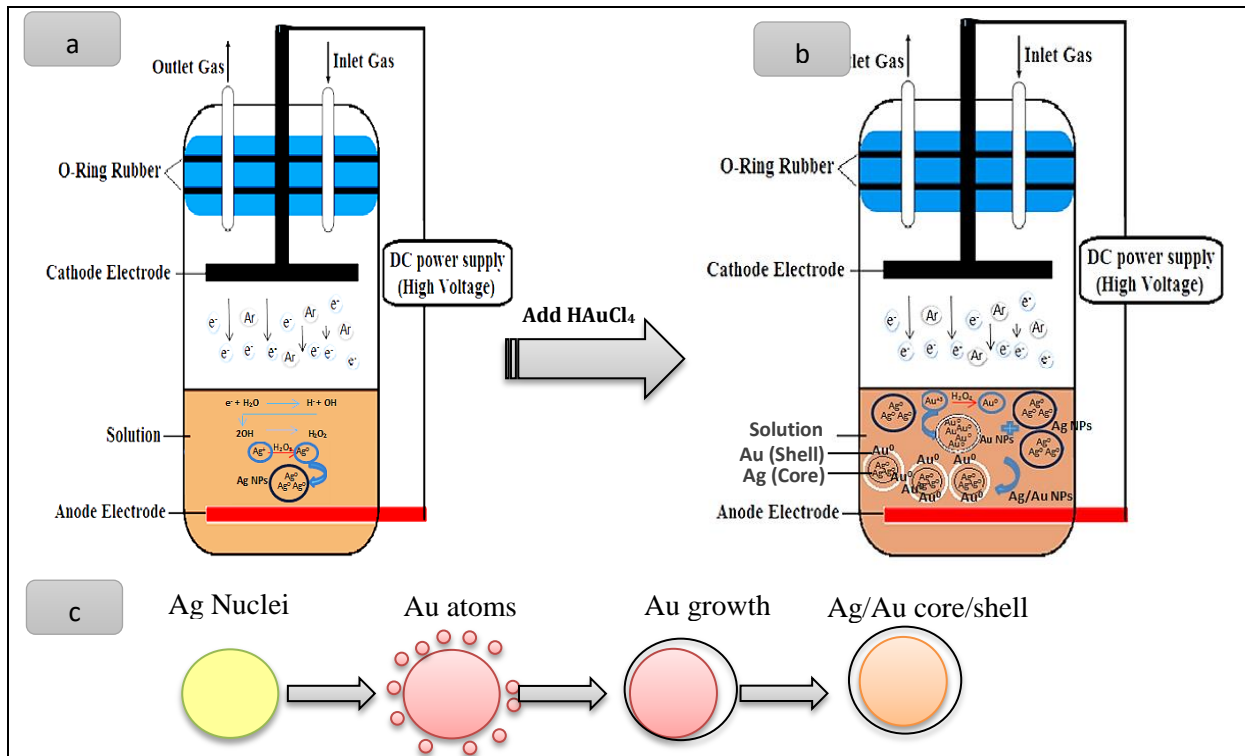


Figure 3-Schematic representation of formation bimetallic Ag//Au core//shell NPs, a) Preparation (Ag NPs), b) Adding HAuCl_4 above AgNPs to create Ag//Au core//shell NPs, c) Schematic depiction of the synthesis approach used in the synthesis of Ag//Au core//shell NPs.

3. Results and Discussion

3.1 UV–visible (UV- Vis) absorbance

The UV–Vis absorbance spectra of Ag//Au core//shell NPs colloidal solutions at different discharge times (5, 10 and 15 min) are displayed in Figure-4 (a-c). The appearance of all the single absorption peaks for the core// shell nanoparticles was situated at the middle wavelengths between the absorption peaks of (Ag) nanoparticles and (Au) nanoparticles at (460, 472 and 480 nm) for the discharge times (5, 10 and 15 min), respectively. Showing that the Ag//Au core//shells nanoparticles were formed. The Plasmon bands of (Ag and Au NPs) were found to be at (412 and 521 nm), correspondingly. This deviation of the plasmonics absorption peaks is due to the fact that the shell of Au layer is thin or incomplete.

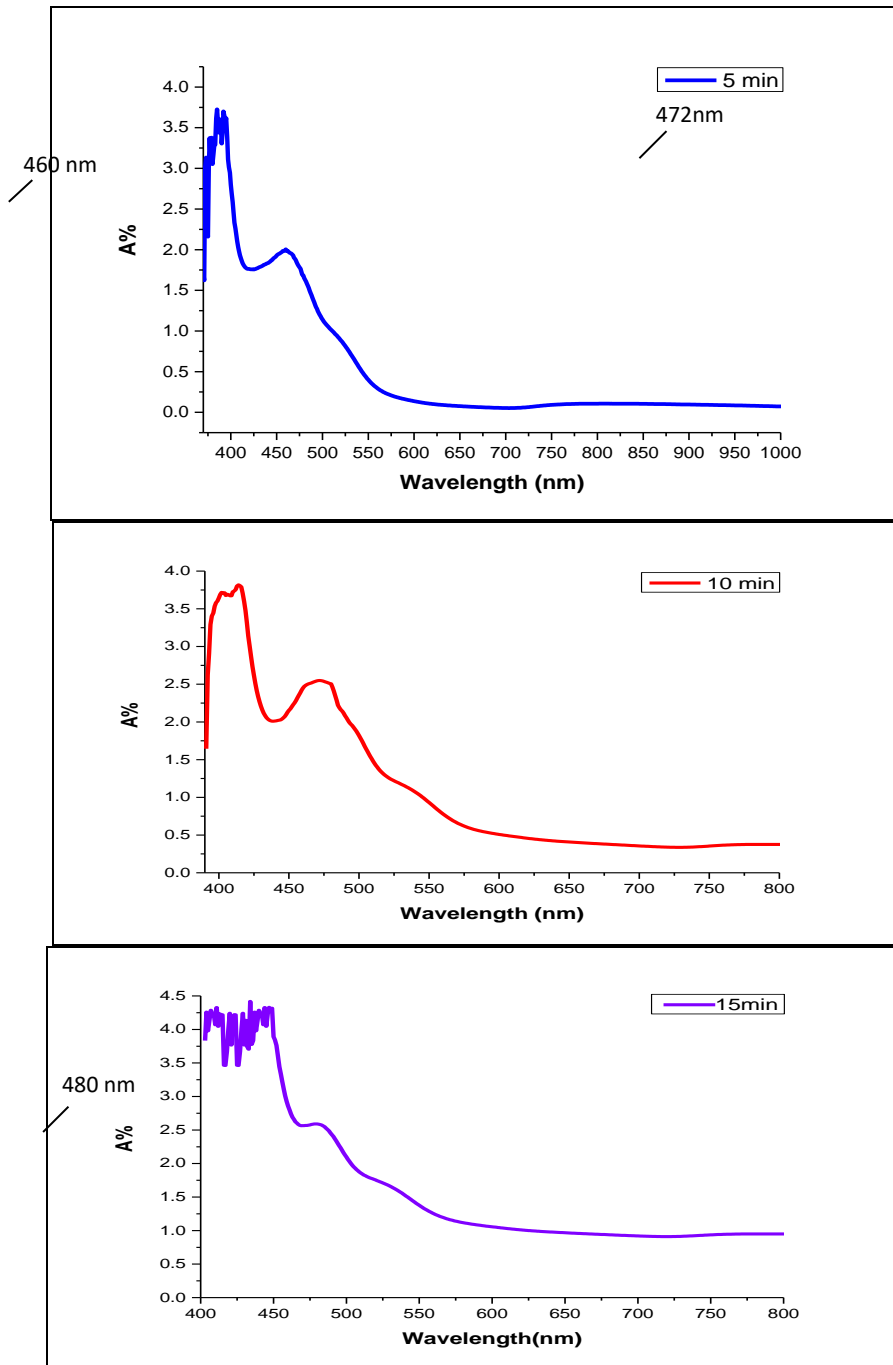


Figure 4-UV-Vis absorbance spectra of Ag//Au core//shell MNPs Colloidal solutions at various discharge exposure times

The stability of the Colloidal Ag//Au core//shell NPs solutions at different discharge times as a function to the stored time in the range from (20 min) to (200 min) is presented in Figure-5(a-c). From this figure, it can be noted that the formed Ag//Au core//shell NPs have a high degree of stability. With a very little variation in the absorbance with time due to the less tendency for the aggregation process.

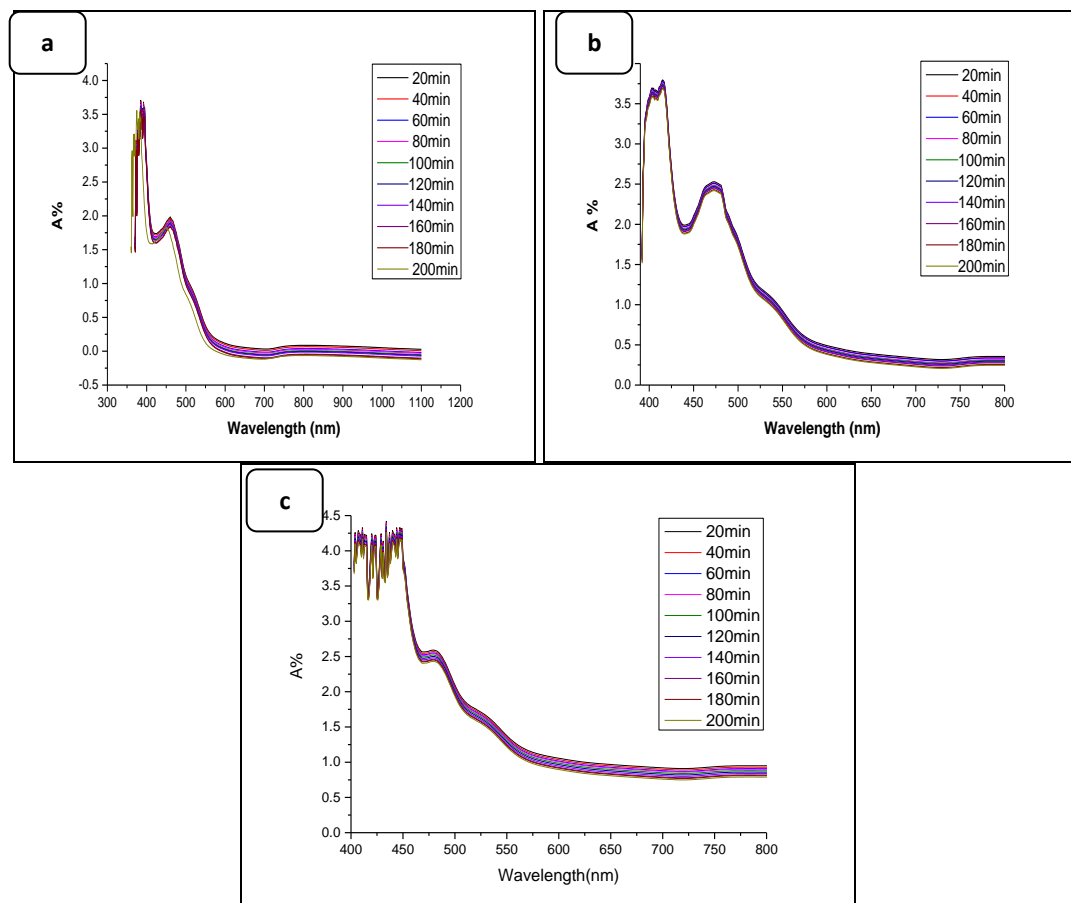
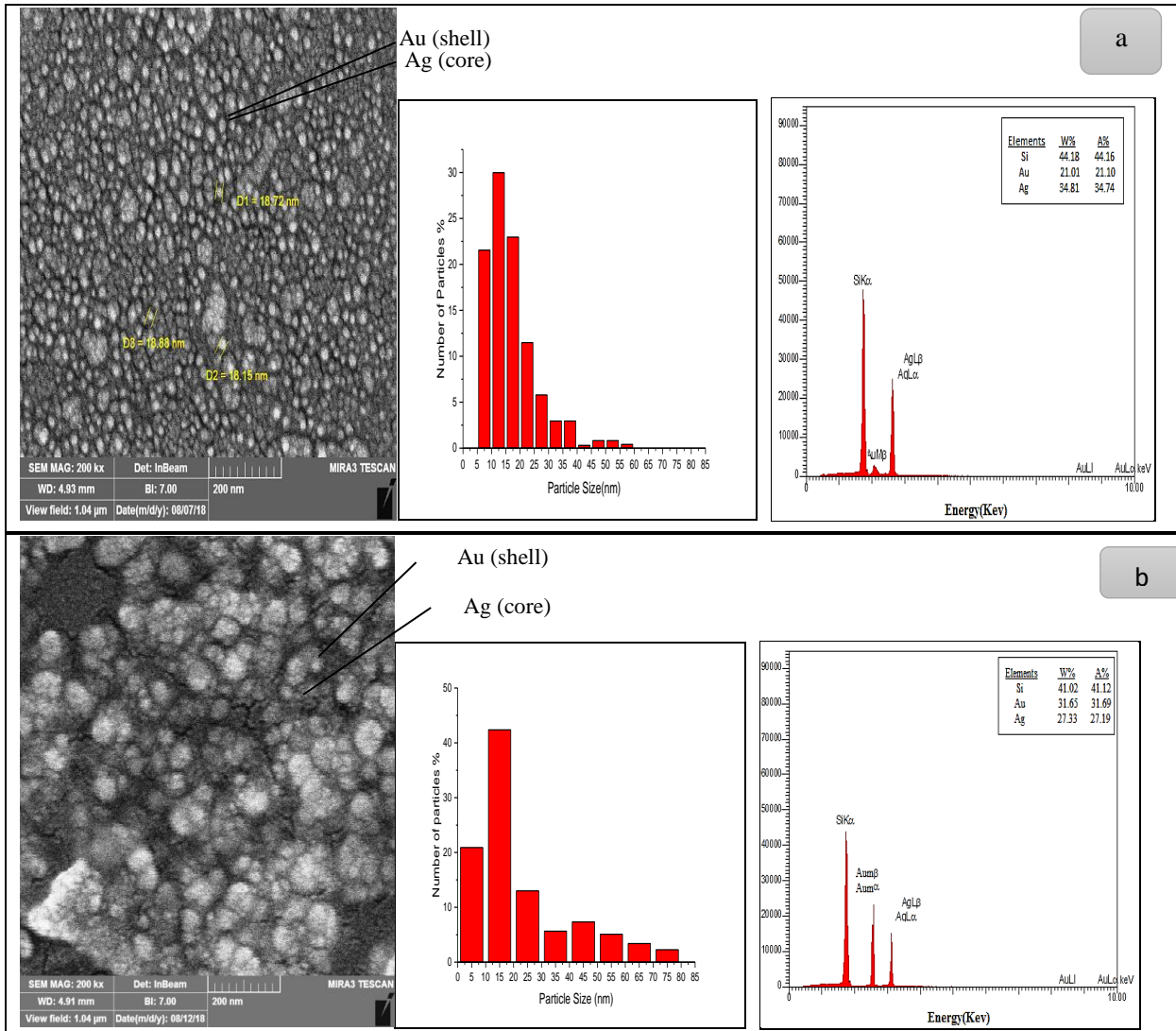


Figure 5-Stability of Colloidal Ag//Au core//shell NPs at different discharging times; (a) 5 min, (b) 10 min, and (c) 15min

3.2 Structural properties

Field Emission Scanning Electron Microscopes (FE-SEM) images used to study the morphological property of particle size of NPs. Where the Ag//Au core//shell NPs created after the discharge duration at (5 min for Ag colloidal to create AgNPs). And then (5min when adding HAuCl₄ colloidal above AgNPs), (10 min) and (15 min) to form Ag//Au core//shell NPs. Several drops of colloidal nanoparticles deposited on the bare silicon substrate. Figure 6(a-c) manifests the surface morphology and the statistical distributions of Ag//Au core//shell NPs sizes deposited on the bare silicon substrate. The morphological property of particle size was studied by analyzing the FE-SEM images. At (5 min) discharge time, the statistical distribution of the Ag//Au core//shell NPs ranges from (5 to 60 nm). And the highest of the distribution is located at (14 nm) with percentages 30%, as depicted in fig.6 (a). For the increase of the discharge time to (10 min), the statistical distribution of Ag//Au core//shell NPs ranges from (5 to 75 nm). And the highest of the distribution is located at (18 nm) with percentages 28.5%, as revealed in fig.6 (b). Finally, for further increasing of the discharge time to (15 min), the statistical distribution of Ag//Au core//shell NPs ranges from (5 to 80 nm). And the highest of the distribution is located at (15) with percentages 48%, as presented in Figure-6 (c). The results display that the Ag//Au core//shell NPs sizes enlarged with the discharge time. This consequence is largely connected to the affinity of Ag//Au core//shell NPs to agglomerate owing to the progress of growth rate. The shapes of the aggregated groups are approximately having a quasi-regular cylindrical Ag//Au core//shell NPs. The EDX spectra of the Ag//Au core//shell nanoparticles deposited on the bare silicon substrate indicate the presence of silicon, gold, and silver elements on the sample. The existence of silicon element is attributed to the substrate. As exposed from this spectrum, it can be documented certainly that the intensity of silver peak is higher than that of the gold.



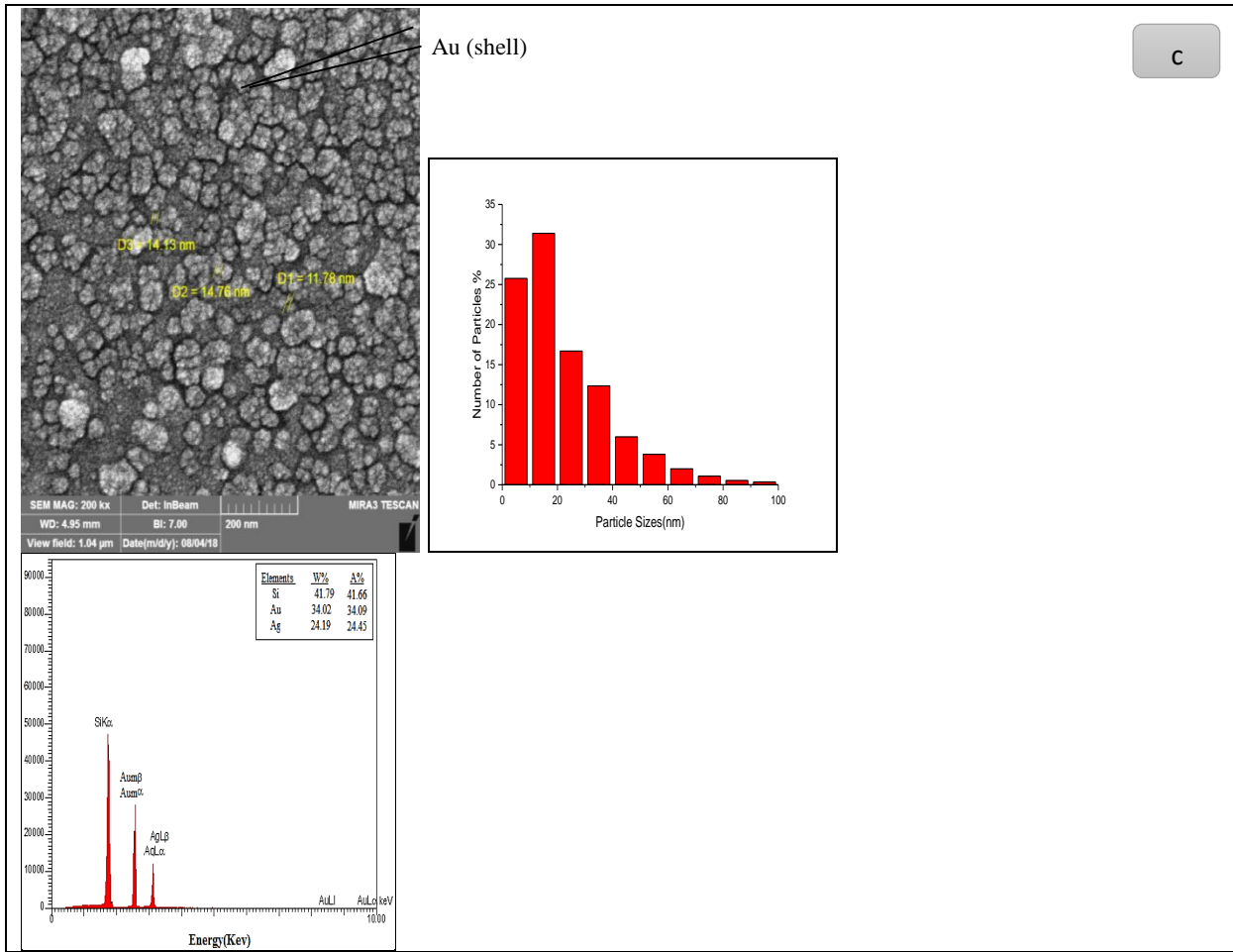


Figure 6-FE-SEM images of Ag//Au core//shell nanoparticles and their statistical distributions and EDX analysis at different discharging times; (a) 5 min, (b) 10 min, and (c) 15 min

Figure-7(a–c) illustrates the high-resolution transmission electron micrographs (HR-TEMs), recorded on samples prepared at the discharging times (5, 10 and 15 min). It ought to be noted that the core//shell structure is recognizable from the transmission electron microscopy HR-TEMs. These data present that it is conceivable to control the crystal structure and this is done by changing the discharging times. The diameter of the core (Ag) nanoparticle was varied from (40 nm) to (95 nm). But the thickness of the shell (Au) nanoparticles was also varied from (12.3363 nm) to (25.1880 nm) and to (54.2843 nm). With an increase the discharge time from 5 to 10 and to 15 min, respectively.

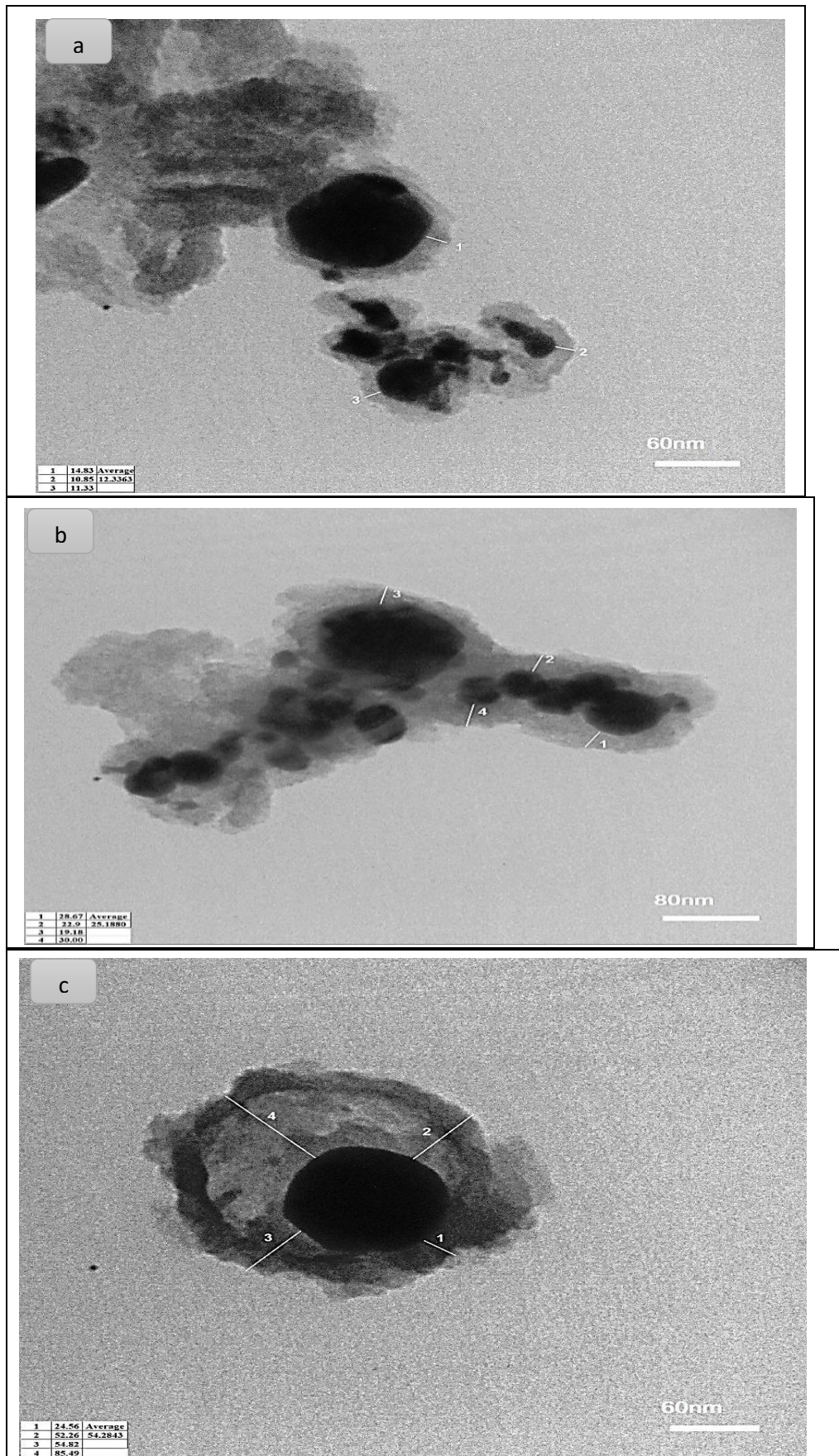


Figure 7-High-resolution TEMs of Ag//Au core//shell NPs created by using a micro-plasma discharge exposure time of a) 5 min, b) 10 min, and c) 15 min

The X-ray diffraction spectra of Ag//Au core//shell NPs created by non-thermal atmospheric plasma discharge with different discharging times are demonstrated in Figure-8 (a-c). The XRD data elucidate the specific diffraction peaks at $2\theta = 37.985^\circ$ and 45.035° at (5 min), 38.135° and 45.085° at (10 min), also 38.235° and 45.385° at (15 min) for which can be indexed to ((111), (200)) phase of pure gold and silver (ASTM Standard Card). It supports that both of gold and silver are the chief composition of the nanoparticles. The two characterization peaks for Ag//Au core//shell NPs clarify that they are crystallized in (fcc) structure. The particle size of Ag//Au core//shell NPs was determined by using Scherer formula [19, 20]:

$$D = 0.9\lambda/\beta \text{ Cos}\theta \dots\dots\dots (3)$$

The specific surface area (S) is an exclusive significant feature of nanomaterial and is given by [21]:

$$S = 6000/D * \rho_{Ag+Au} \dots\dots\dots (4)$$

Density of monometallic Ag and Au is (10.5 and 19.3) g/cm^3 [22, 23], respectively, and according to the discharge exposure times (5, 10, and 15 min), the density of the bimetallic Ag//Au core//shell NPs is about (13.8, 15.2, and 15.6 g/cm^3), respectively. The value of density for Ag//Au core//shell NPs can be determined using equation (5) depending on the data about the EDS analysis of results of Ag//Au core//shell NPs [24]:

$$\rho_{Ag+Au} = \frac{a*\rho_{Ag}+b*\rho_{Au}}{a+b} \dots\dots\dots (5)$$

Where, ρ_{Ag+Au} is the density of the bimetallic Ag//Au core//shell nanoparticles (g/cm^3), ρ_{Ag} is the density of the Ag NPs, ρ_{Au} is the density of the Au NPs, a = wt. % of Ag and b = wt. % of Au from the EDS data.

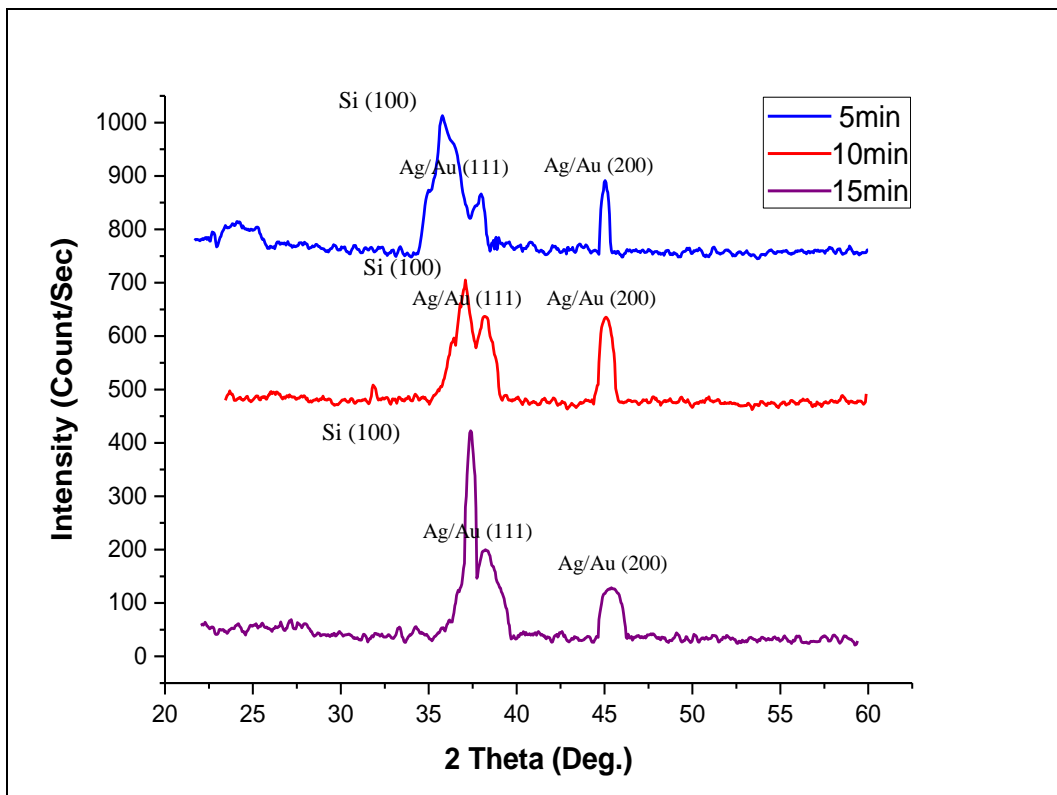


Figure 8-XRD pattern of the Ag//Au core//shell nanoparticles at various discharging times, (a) 5 min, (b) 10 min, and (c) 15 min

The highest value of the specific surface area is about (73.7 m²/gm), and the lowest (D) value is about (5.2 nm) for discharge time (15 min), respectively. The nanoparticles size and the specific surface area are increased with increasing the discharge time. The resulting data are listed in Table-1

Table 1-The grains size (D) and Specific surface area (S.S.A) of Ag/Au core/shell NPs

Discharge times (min)	Plane (111)		Plane (200)	
	D (nm)	S.S.A (m ² /gm)	D (nm)	S.S.A (m ² /gm)
5	7.8	55.7	13.9	31.2
10	6.3	62.5	8.6	45.8
15	5.2	73.7	5.8	66.31

4. Conclusions

Non-thermal atmospheric plasma discharge can be effectively used to create well-controlled bimetallic colloidal Ag//Au core//shell NPs by optimizing the DC glow discharge time. Discharge time can be effectively used to generate Ag//Au core//shell of quasi-regular spherical nanoparticles with different core-shell sizes. The specific surface area of colloidal Ag//Au core//shell NPs increased with increasing the non-thermal plasma treatment time with fixed concentration of AgNPs–HAuCl₄ mixture. Ag//Au core//shell NPs have a high degree of stability with small variation in its absorption due to the small tendency of aggregation with time. Further investigations in the application of these colloidal Ag//Au core//shells demonstrate an innovative view in the line of metallic plasmonics.

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