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The Fabrication of Cu/Ag, Core/Shell Nanoparticles Dispersed in Various Aqueous Media Using Laser Ablation

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Abstract

By using the pulsed laser ablation in liquids (PLAL) method, bimetallic liquid colloidal (Cu/Ag) (core-shell) nanoparticles were created, excised in liquid environments double deionized distilled water (DDDW) and sodium borohydride ($NaBH_4$), where this research aims to produce nanoparticles by the effect of surfactant ($NaBH_4$) compared with (DDDW), and then subjected to optical (UV-VIS), structural (XRD) and morphology (TEM) tests. The results revealed that the absorption spectrum displayed the peak value of surface plasmon resonance (SPR) where it was (419 and 410) nm for (Cu_{core}/Ag_{shell}) produced in solutions (DDDW and $NaBH_4$) respectively. The (XRD) test revealed that the (Cu/Ag) solution synthesized in (DDDW) has a cubic crystal structure (cubic), while the (TEM) assay revealed that the NP_s have spherical and semi-spherical forms, with average particle size ranges of (47.938nm) for DDDW and (61.832 nm) for $NaBH_4$ solutions.

Keywords: Cu/Ag core-shell, pulsed laser ablation, UV-VIS, XRD, TEM.

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تصنيع الجسيمات النانوية (Cu/Ag) لب/ قشرة المشتتة في اوساط مائية مختلفة باستخدام الاستئصال بالليزر

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الخلاصة

بأستخدام طريقة الاجتثاث بالليزر النبضي في السوائل (PLAL) ، تم تصنيع جسيمات نانوية سائلة ثنائية المعدن (Cu/Ag) (لب/قشرة)، المستأصلة في بيئات سائلة (ماء مقطر منزوع الأيونات مزدوج (DDDW) وبوروهيدريد الصوديوم ($NaBH_4$)) ،حيث يهدف هذا البحث لانتاج جسيمات نانوية بفعل تأثير الفاعل بالسطح ($NaBH_4$) مقارنة مع (DDDW), ثم أخضعت الى الأختبارات البصرية (UV-VIS), التركيبية (XRD) والمورفولوجية (TEM), أظهرت النتائج أن قيمة طيف الامتصاصية لقمة رنين البلازمون السطحي (SPR) كانت (410 ,419) نانومتر لـ (Cu_{core}/Ag_{shell}) الناتجة في محاليل DDDW و $NaBH_4$ على التوالي. أظهر اختبار (XRD) أن محلول (Cu_{core}/Ag_{shell}) المصنع في محلول (DDDW) له تركيب بلوري (مكعب)، بينما كشف اختبار (TEM) أن الجسيمات النانوية (NP_s) لها أشكال كروية وشبه كروية، وبمتوسط حجم جسيمات يبلغ (47.938 نانومتر) لـ DDDW و (61.832 نانومتر) لـ$NaBH_4$.

الكلمات المفتاحية: Cu/Ag لب- قشرة، الاجتثاث بالليزر النبضي، مطيافية الضوء المرئي/فوق البنفسجي، حيود الاشعة السينية، المجهر الالكتروني النافذ.

Introduction

In the past decade, bimetallic and alloy nanoparticles (NP_s) have attracted interest in a variety of fields, including photonics, catalysis, solar cells, information storage, and surface-enhanced raman scattering spectroscopy (SERS) [1-3], due to their superior optical and optoelectronic properties compared to those of the individual/pure metals (e.g. Au, Ag and Cu). Bimetallic nanoparticles, which are made up of two different metals, have sparked more attention than monometallic nanoparticles, both scientifically and technologically. The properties of bimetallic nanoparticles are determined by the constituent metals and their nanometric size.

These are made by combining distinct architectural structures of metallic nanoparticles. They actually have a tendency to optimize the energy of the plasmon absorption band of metallic mixtures, providing us with a versatile biosensing tool. These characteristics may differ from those of pure elemental particles, and they may include size-dependent optical, electrical, thermal and catalytic effects [4]. Bimetallic nanoparticles' composition, atomic ordering, shape and size can all be altered to change their properties. Despite the fact that bimetallic nanoparticles are made up of only two metals, there are numerous shapes that can be created [5]. By doing this, many new ideas could be tried out in a reliable way to create different experimental conditions. Among these are the laser's parameters (wavelength, pulse duration and energy per pulse), the pressure of the surrounding gas and the distance to the target, these factors can be utilized to alter the form and size of the nanoparticles [6]. Many liquids have been used to make NP_s of Ag and Cu [7,8]. In colloids, metallic alloy NP_s of Au-Ag and Ag-Cu have been made using laser ablation techniques with a single or double pulsed laser [9]. However, Ag–Cu alloy nanoparticles have been infrequently employed in SERS-based detection and sensing. Using density functional theory (DFT) [10], the potential benefit of Ag-Cu NPs is their better structural stability with less oxidation (in comparison to pure Ag/Cu NP_s). The inclusion of Ag could successfully inhibit the oxidation of Cu NP_s and also enhance their stability [11]. (DDDW and $NaBH_4$) were utilized as surfactants to manufacture ultra-fine NP_s by laser ablation of Ag/Cu solid targets in liquid in the present study.

Experimental Details

Materials

A silver and copper plates whose purity was checked by using an energy dispersive x-ray fluorescence (ED-XRF) device (model XEPOS) proved that the purity of the plate (98.99%) and (98.55%) respectively, highly purified non-ionic double deionized distilled water (DDDW) and sodium bromide borohydride ($NaBH_4$), the chemical formula is $NaBH_4$ (Kanto Chemical Co., Inc.), > 96% purity and M.W = 37.83 g/mol. The schematic of the experimental setup for laser- generated NP_s at the target-liquid interface is shown in figure (1).

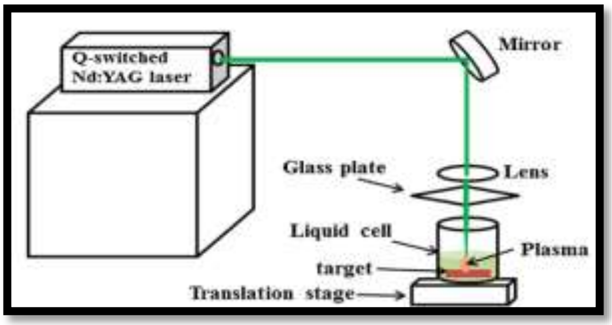

Figure 1: Schematic of the PLAL setup.

Synthesis of Cu/Ag, Core/Shell NP$_s$

The nanostructures (Cu_{core}/Ag_{shell}) were prepared at a wavelength (1064nm) and repetition rate (1Hz), whereby the silver target was placed in a glass bottom containing (2 ml) of solution (DDDW and $NaBH_4$) and bombarded by a laser with a number of (500 pulses). Then we placed the copper target inside the colloidal solution of Ag and bombarded it with a laser (500 pulses). And we will get a (Cu_{core}: Ag_{shell}) nanostructure. Figure (2) shows the samples obtained.

Figure 2: Shows the samples obtained.

Characterization Techniques

The characteristics of (Cu_{core}/Ag_{shell}) nanoparticles have been studied by absorption spectra and surface plasmon resonance (SPR) was recorded for colloids with (UV-ViS) spectroscopy type of (double beam 1800 UV spectrometer) manufactured in (Shimadzu,Japan) for the purpose of knowing the effective aggregates. X-ray diffraction device (type: Lab-X (XRD-6000) Shimadzu Diffactrometer, Japan). Transmission Electron Microscope (TEM) model (ZEISS LED 912 AB-100KV/ Germany).

Results and Discussions

Optical Properties of (Core/Shell) For (Cu/ Ag) System

The composition of the bimetallic colloidal solution was prepared and studied by removing the copper metal placed inside the silver nano colloidal solution when the laser pulses hit the surface of the submerged metal with (2ml), a cloud with a strong vibration wave will be generated that spreads in all directions within impact area this cloud emit light and noise, forming a visible cloud of metal particles that adsorb outside the metal surface and scatter in all directions within the liquid.

Figure (3) shows the absorption spectrum of the prepared nanoparticles (Cu,Ag, Cu_{core} /Ag_{shell}) in (DDDW), where we notice from the figure three peaks of (652, 400,419) nm for each of (Cu, Ag and Cu_{core} /Ag_{shell}) respectively. As the (419nm) peak contains copper and silver particles, the copper peak was (652 nm) and when forming a core/shell structure, the absorption peak shifts towards longer wavelengths (blue shift). Figure (4) shows the absorption spectrum of the prepared nanoparticles (Cu, Ag, Cu_{core}/Ag_{shell}) in $NaBH_4$, where we notice from the figure two peaks of (415,410) nm for each of (Ag, Cu_{core}/Ag_{shell}) respectively.

As the (419nm) peak contains copper and silver particles, this is attributed to the effect of the shell will be more effective on the core, so the absorption value of (SPR) will shift from (415 nm) to (410 nm) by the action of the silver shell, and this confirms with clear evidence that the influential shell effect overshadowed the effect of the core [12]. Figure (5) shows the surface plasmon resonance (SPR) peak of the colloidal solution (Cu_{core}/Ag_{shell}) prepared in (DDDW and $NaBH_4$) solutions.

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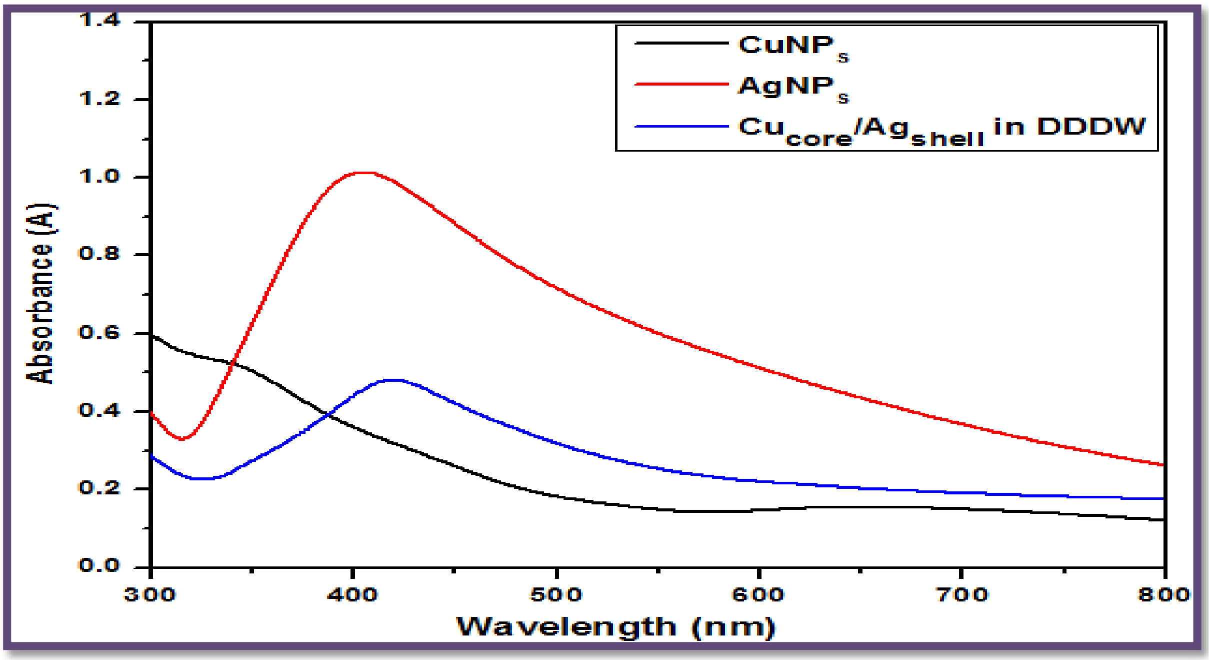

Figure 3: Absorbance spectrum of NP_s (Cu, Ag, Cu_{core}/Ag_{shell}) in solution (DDDW)

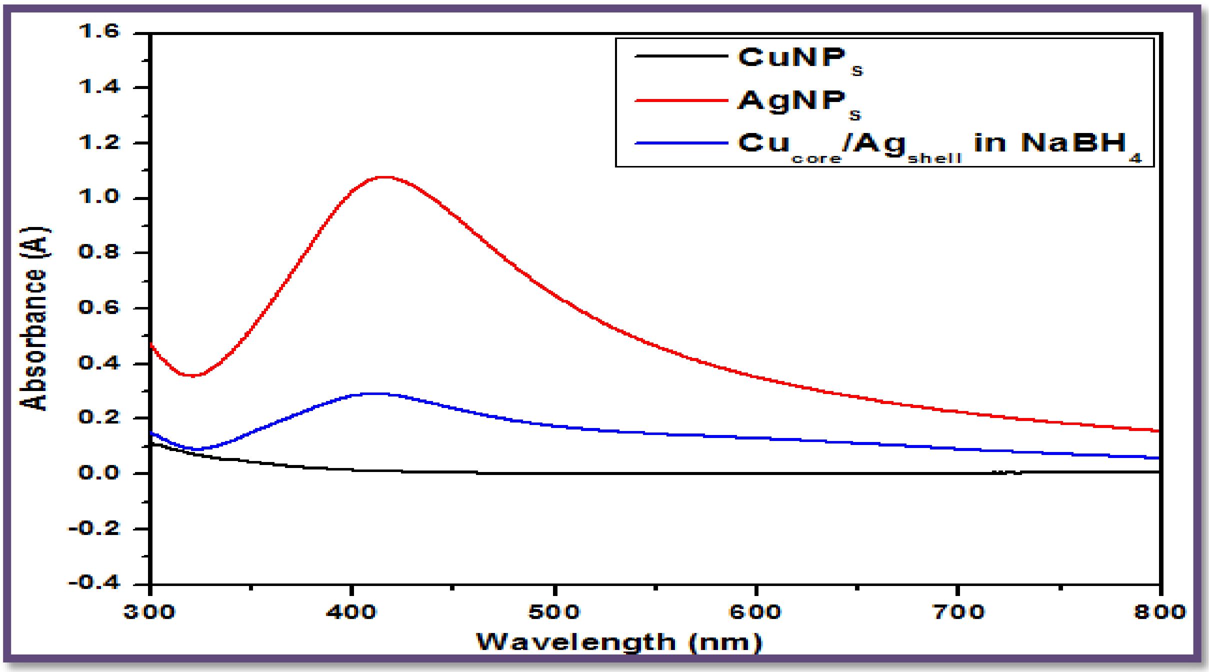

Figure 4: Absorbance spectrum of NP_s (Cu, Ag, Cu_{core}/Ag_{shell}) in solution ($NaBH_4$).

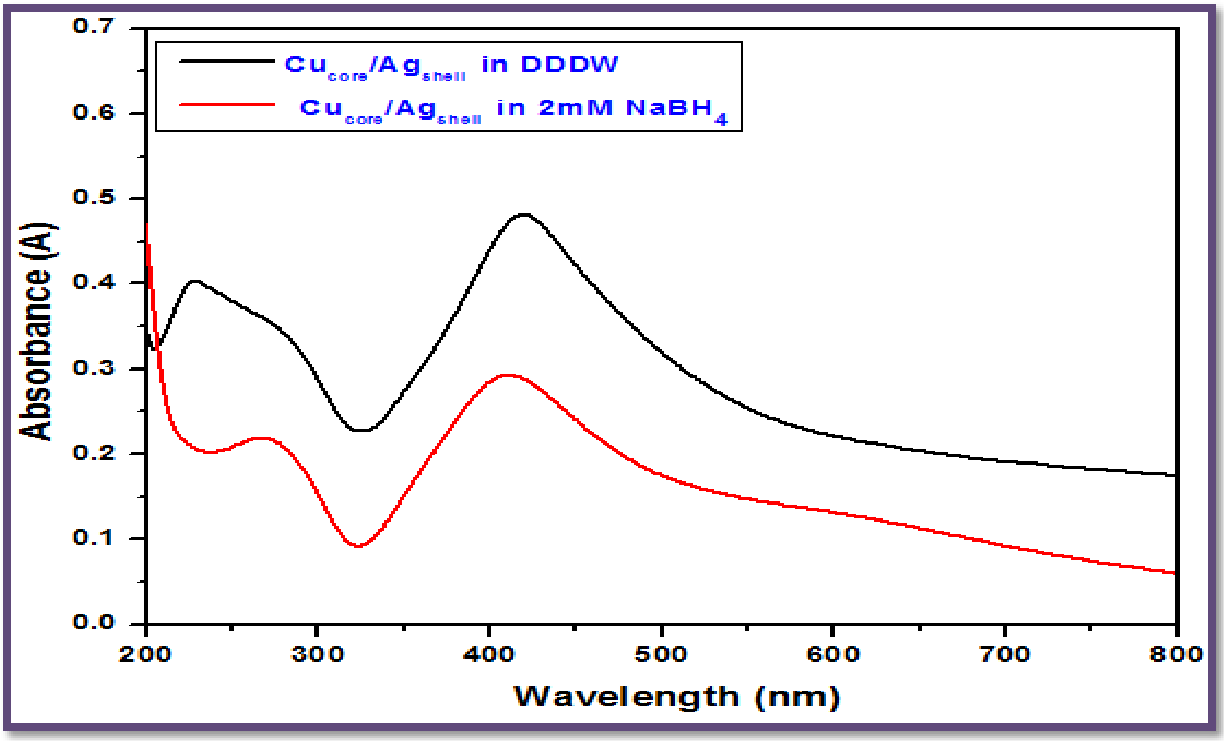

Figure 5: Absorbance spectrum of NP_s for colloidal solution (Cu_{core}/Ag_{shell}) in solutions (DDDW, $NaBH_4$).

The figure (6) shows the energy gap value that we obtained when installing (Cu_{core}/Ag_{shell}). The optical energy gap allowed for the direct transfer of solutions of the composition (Cu_{core}/Ag_{shell}) was estimated. The energy gap is strongly influenced by the chemical bonds of the elements that make up its structure and grain size and by general changes with the change in particle size, as is evident from the energy gap values for each of the different solutions prepared by the pulsed laser ablation (PLAL) method. The energy gap was obtained by plotting the relationship between (αhυ) and (E) using the (Tauc) relationship using the program (Origin pro 8.5). Where we note that the value of (E_g) for (Cu_{core}/Ag_{shell}) prepared in (DDDW) is approximately (2.29 eV) and that this value increased to (2.43eV) for solution $NaBH_4$, the high value of band gap in $NaBH_4$ compared to (DDDW) is due to the presence of smaller sized NP_s [13].

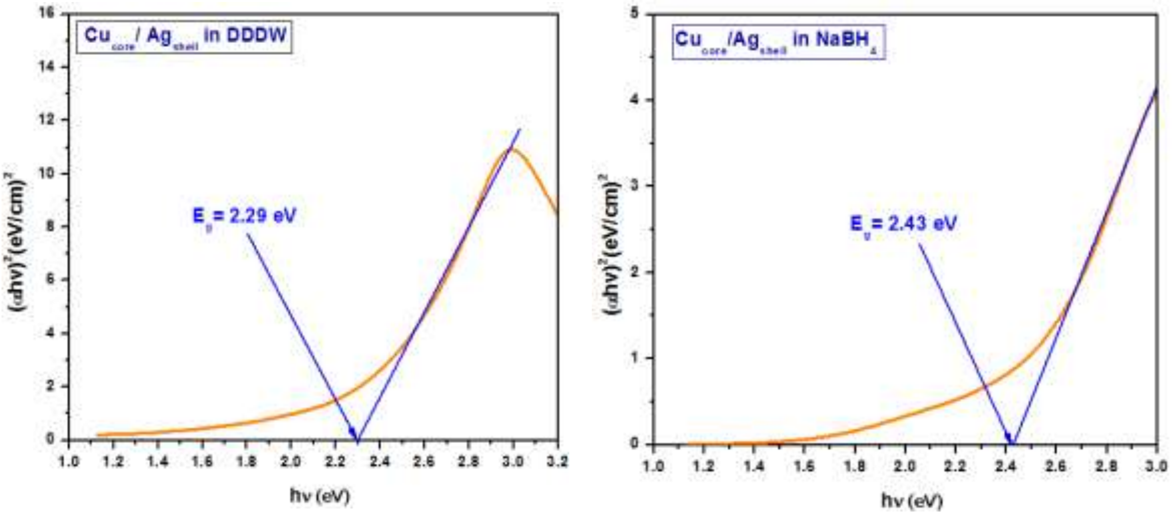

Figure 6: Direct band gap estimations of colloidal (Cu_{core}/Ag_{shell}) nanoparticles samples

X-ray Diffraction of (Core/Shell) For (Cu/Ag) System

The results of the x-ray diffraction of a solution of (Cu_{core}/Ag_{shell}) nanoparticles prepared in (DDDW) deposited on a quartz slide with dimensions of (1cmx1cm), showed that the crystal system is cubic in shape. Figure (7) we note the presence of four peaks at the angles (38.18^o, 43.52^o, 50.38^o, 64.51^o, 74.14° and 77.61^o) and corresponding to the levels (111), (111), (200), (220), (220), (311) and these results are in great agreement with the results of the values mentioned in the international numbered card (00- 001-1164 and 00-004-0836) for the substance of gold. In addition, the crystal plane direction (111) is dominant. Table (1) shows the agreement between the standard and experimental data with a small shift in distances for the atomic levels (d).

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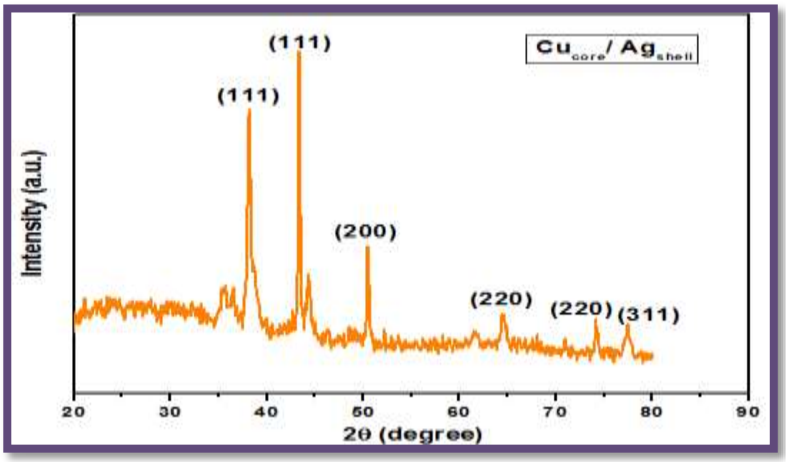

Figure 7: X-ray diffraction pattern of (Cu_{core}/Ag_{shell}) nanoparticles generated by laser ablation.

Table 1: The structural properties of (Cu_{core}/Ag_{shell}) nanoparticles.

2Θ (DEG) Experimental	2Θ (DEG) Standard	FWHM (DEG)	D (NM)	D_{HKL} (Å) Experimental	D_{HKL} (Å) Standard	(HKL)	Geometric Crystal System	Card Number
38.18	37.934	0.3361	25.022	2.355	3.550	111	Cubic	00-001-1164
43.52	43.298	0.5538	15.453	2.027	2.030	111	Cubic	00-004-0836
50.38	50.434	0.1957	44.881	1.8124	1.808	200	Cubic	00-004-0836
64.51	64.64	0.3730	25.196	1.4451	1.440	220	Cubic	00-001-1164
74.14	74.133	0.1773	56.183	1.27784	1.278	220	Cubic	00-004-0836
77.61	77.549	0.4935	20.667	1.4451	1.23	311	Cubic	00-001-1164

Transmission Electron Microscopy (TEM) of (Core/Shell) For (Cu/Ag) System

Figure (8) shows the images (TEM) of the microscope with scale (80nm) and magnification (46.460 KX) and the corresponding part statistical distribution of the size of nanoparticles for the prepared (Cu_{core}/Ag_{shell}) colloidal solution (DDDW and $NaBH_4$). The sizes of the nanoparticles were calculated using the program (Image J). As well as the statistical distribution and average sizes of nanoparticles through the program (Origin pro 8.5). From the figure, we notice that the nanoparticles are almost spherical and with a volume rate of (47.938nm and 61.832 nm) for both (DDDW and $NaBH_4$) respectively.

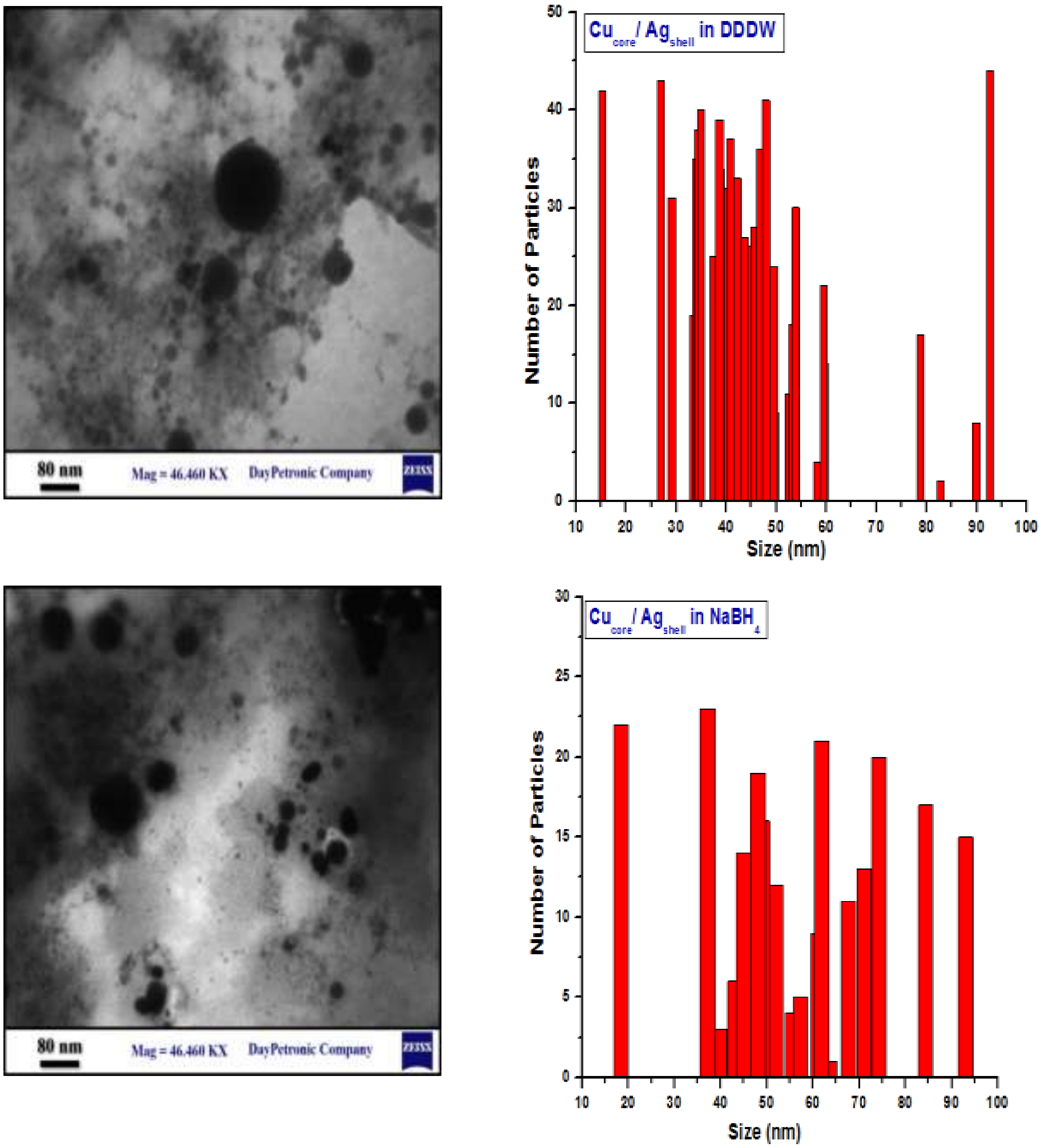

Figure 8: TEM images and statistical distribution of colloidal solution (Cu_{core}/Ag_{shell}) in solutions (DDDW and $NaBH_4$).

Conclusions

It can be concluded that the laser ablation sequence of the metal targets did not change the structure of Cu_{core}/Ag_{shell}, as the production of bimetallic NP_s in DDDW was less successful than in $NaBH_4$ where the prepared NP_s deposited black precipitates in the bottom (pyrex) after (30 minutes). This problem can be attributed to the low stability of NP_s produced in DDDW. It was evident that both the size and (SPR) band properties of (Cu_{core}/Ag_{shell}) were slightly affected by the replacement of the laser ablation of the metal targets and the duration of the ablation. In solutions of (DDDW and $NaBH_4$), ultra-fine (Cu_{core}/Ag_{shell}) with an average size of less than 60nm were made.

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