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Synthesis and Characterization of Gold Nanoplates onto Solid Substrates by Seed-Mediated Growth Method

Iwantono[1,a], A. A. Umar[2,b], E. Taer[1,c], V. Asyana[1,d]

[1]Physics Department, Riau University, Jl. HR Soebrantas KM 12,5 Simpang Baru 28293 Pekanbaru Riau-Indonesia

[2]Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor-Malaysia

[a]iwan_tono@yahoo.co.uk, [b]akrajas@ukm.my, [c]erman_taer@yahoo.com, [d]vepyphysics@yahoo.com

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Abstract. A simple technique of seed-mediated growth has successfully been performed to grow gold nanoplates onto solid substrates. The growth of gold nanoplates have been carried out at temperature of 28-30°C in the presence of a binary surfactant mixture: CTAB (cetyl trimethyl ammonium bromide) and PVP (poly-vinyl pyrrolidone) with their various concentrations. Characterizations of the samples have been carried out by using UV-Vis spectroscopy, XRD and FESEM. UV-Vis spectra showed that the gold particles have grown with a various geometrical forms, such as spherical and others. XRD results informed that the presence of two peaks at 2θ: 38.195° and 44.393° indicated the gold nanoplates, with their crystal orientation of (111) and (200). FESEM images showed the edge-length size of nanoplates was dominated in the range of 11 nm to 50 nm, with various morphologies of nanoplates, such as hexagonal, truncated hexagonal, triangular, square and spherical shapes.

Introduction

During the last decade, metals nanoparticles have been an active area of research due to their wide potential applications including catalysis [1-3], optics [4-6] and optoelectronics [7]. Among the metals, gold nanoplate is one of the most interesting materials, because of their special characteristics, such as having an intrinsic characteristic to form various geometries, including triangular and hexagonal nanoplates. Despite there are many available methods for synthesis of gold nanoplates [8-13]. However, almost all of these methods grew the gold nanoplates in solution and only a few techniques grew the gold nanoplates on solid substrates, which wider potential applications, such as on ITO (indium tin oxide) [14] which resulted triangular, hexagonal or truncated-hexagonal and irregular rounded-shape nanoplates.

In this current report, we described a new method of producing gold nanoplates on the ITO surface by using a binary surfactant mixture: CTAB (cetyl trimethyl ammonium bromide) and PVP (poly-vinyl pyrrolidone) with their various volume ratio and annealed the samples at 200°C. We expected that if the optimum volume ratio of the binary surfactant mixture obtained, the yield of the gold nanoplates could be improved with additional shapes (square and spherical shapes). X-ray diffraction performed on the grown gold nanoplates showed two peaks which were represented gold nanocrystals planes of Au (111) and Au (200). These two peaks confirmed the formation of gold nanoplates on the substrates with two nanocrystal planes. FESEM (field emission scanning electron microscopy) images of the best sample (optimum volume ratio of CTAB and PVP) showed that the gold nanoplates covered almost all area of the surface. Much smaller nanoplates of 11-50 nm in edge-length size compared to the previous result [14] were dominated to almost all samples.

Experimental Procedures

Materials. CTAB (cetyl trimethyl ammonium bromide), PVP (poly-vinyl pyrrolidone) and Hydrogen tetra chloro aurate ($HAuCl_4$ $3H_2O$) were purchased from Sigma Aldrich. Trisodium citrate and NaBH4 were purchased from Wako Pure Chemicals, Ltd. The pure water obtained from Autopure WR600A, Yamato Co. Ltd system, with resistivity higher than 18.2 MΩ, was used to produce the solutions of all materials. The ITO substrates were purchased from CBC Ings Co. Ltd.

Growth of Gold Nanoplates on ITO. The seed-mediated growth method was applied to grow gold nanoplates on solid substrates. Before the growth process, two solutions of seed and growth solutions were prepared. The seed solution was prepared using a Murphy procedure, [15] that contains 0.5 ml of 0.01 M $HAuCl_4.3H_2O$; 0.5 ml of 0.01 M trisodium citrate; 20 ml of pure water and 0.5 ml of 0.1 M natrium borohidrida. Meanwhile, the growth solution was prepared by adding 0.1 mL of 0.1 M ascorbic acid (Wako Chemicals) into a solution that contained 0.5 mL of 0.01 M $HAuCl_4$, 19 ml of 0.1 M CTAB (Aldrich), 1 ml of 1 mM PVP (Aldrich), and 2 mL of pure water. The effect of CTAB and PVP concentration in the growth solution was examined by changing the volume of CTAB and PVP, from 19 ml to 10 ml and 1 ml to 10 ml for CTAB and PVP, respectively.

The seed process of gold nanoseeds on the substrates was performed by immersing the substrates into a glass tube that contained 5 mL of the seed solution for 1h 30 minutes. The samples were then removed and gently washed with pure water, dried with a flow of nitrogen gas, and finally transferred into a regular laboratory oven for an annealing process at 200 °C for at least 1 h.

Meanwhile, the growth process was performed by transferring the samples into a glass vial that already contained 10 mL of the new prepared growth solution for about 4 h. After that, the samples were cleaned with pure water, dried with a flow of nitrogen gas, and then transferred into an oven for an annealing at 100 °C for 1 h.

Characterizations. The X-ray diffraction methods using an XRD D8 Advance (Bruker) with Cu KR irradiation operated at 50 kV and 300 mA and a scan rate as low as 2 degrees per minute were performed in order to characterize the structural growth of the Au nanocrystals on the substrates. The morphology of the gold nanocrystals growth was characterized using a field-emission scanning electron microscopy (FESEM) with SUPRA 55VP instrument. UV-Visible optical absorption spectroscopy was performed using UV-160 Lamda 900 (Perkin Elmer) spectrophotometer.

Results and Discussion

Morphology, Structure and Optical Property. The FESEM image of the gold nanocrystals grown on the ITO substrate that was prepared using the present method is shown in Figure 1. The growth time and temperature were 4 h and 28-30 °C, respectively. It was shown that at optimum condition (16 ml CTAB and 4 ml PVP) almost all of the surface area was covered by nanoplates. It was also observed that large number of variable shape gold nanoplates, such as triangular, hexagonal, truncated-hexagonal and square of edge-length size in the range of 11-50 nm was found to favorably grow on the surface.

Figure 2, 3 and 4 show the FESEM images of the samples prepared with different volume ratio of CTAB and PVP. It can be seen from these figures that the 16 ml CTAB: 4 ml PVP sample has resulted the highest density of the gold nanoplates compared to the others. It was observed that the nanoplates yield can be estimated to be more than 70% of the product for all samples. The dominant shape of the nanoplates was hexagonal of about 40% of the product, while truncated-hexagonal, square and triangular shared up to 25% of the product. However, in these samples, it was also found a rounded-shape structure without the presence of clear vertices with a relatively high yield. The
of 30-50 nm of about 50% for almost all
smaller size of nanoplates as volume of PVP

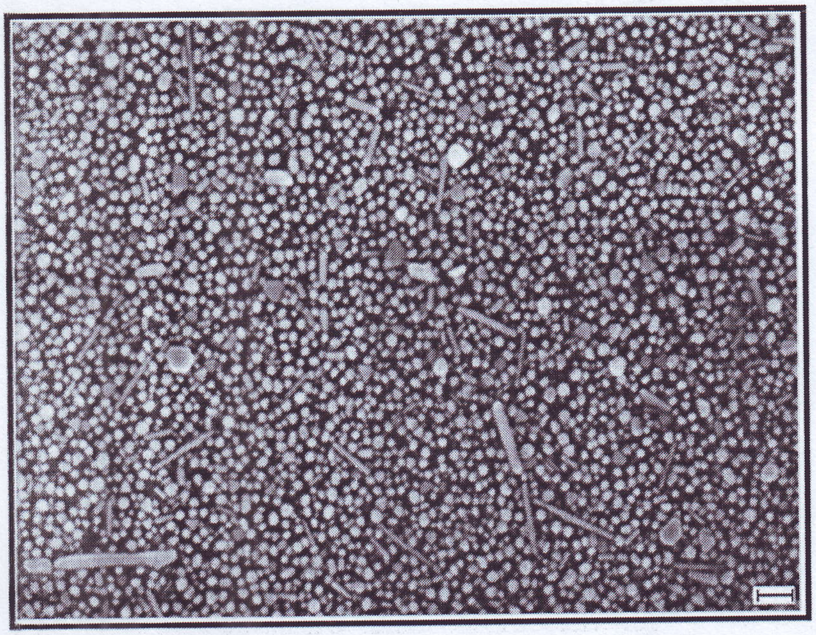

Fig. 1: Gold nanoplates grown onto ITO that covered almost all the surface area

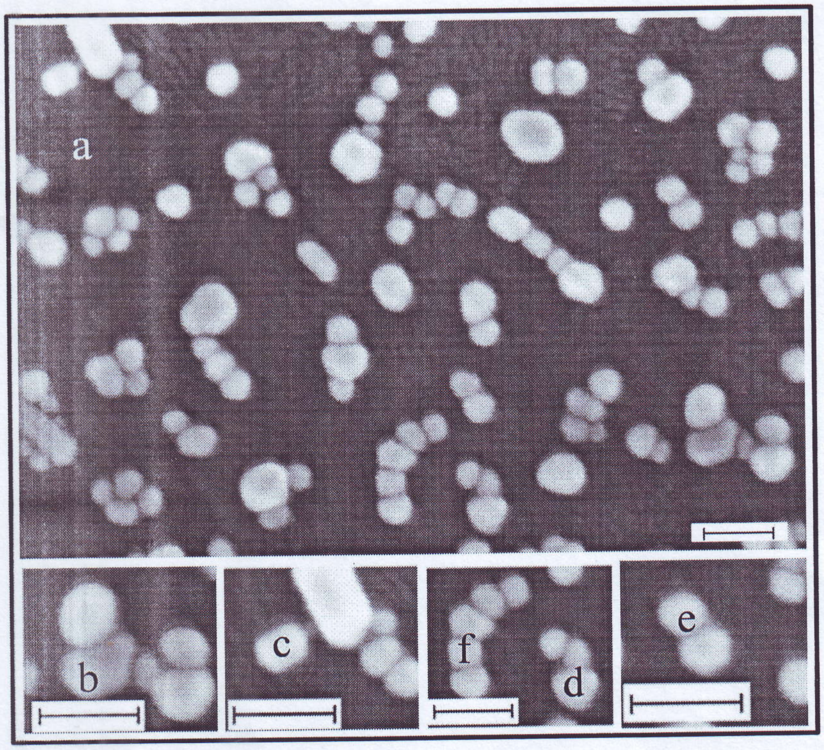

Fig. 2: (a) Grown gold nanoplates with 19 ml CTAB and 1 ml PVP; (b) hexagonal; (c) truncated hexagonal; (d) triangular; (e) irregular-rounded and (f) square shapes

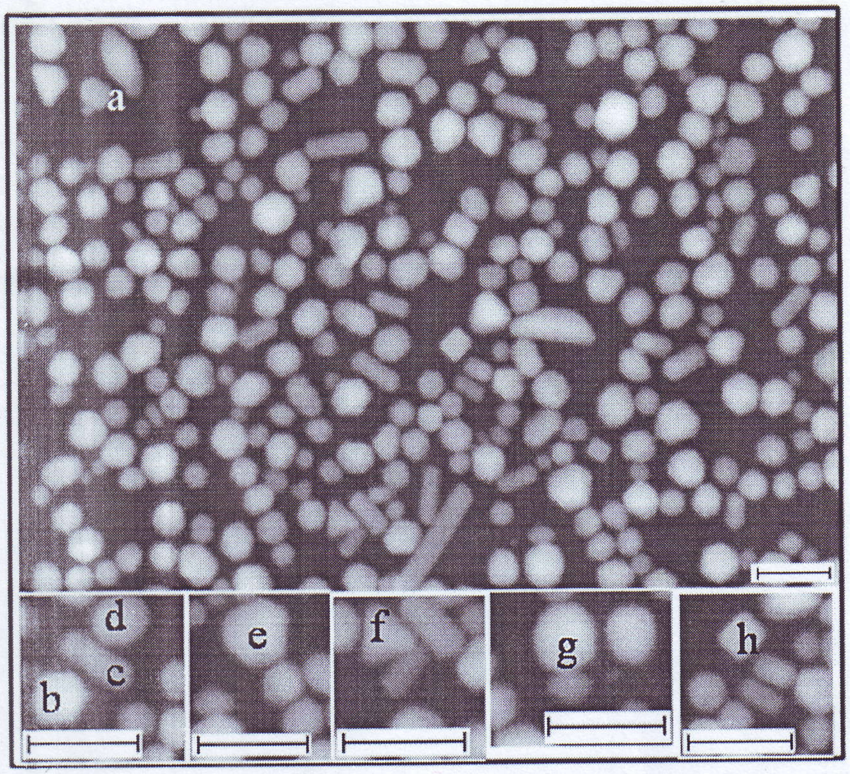

Fig. 3: (a) Grown gold nanoplates with 18 ml CTAB and 2 ml PVP; (b) hexagonal; (c) truncated hexagonal; (d) spherical; (e) pentagonal; (f) triangular; (g) irregular-rounded shapes and (h) square shapes

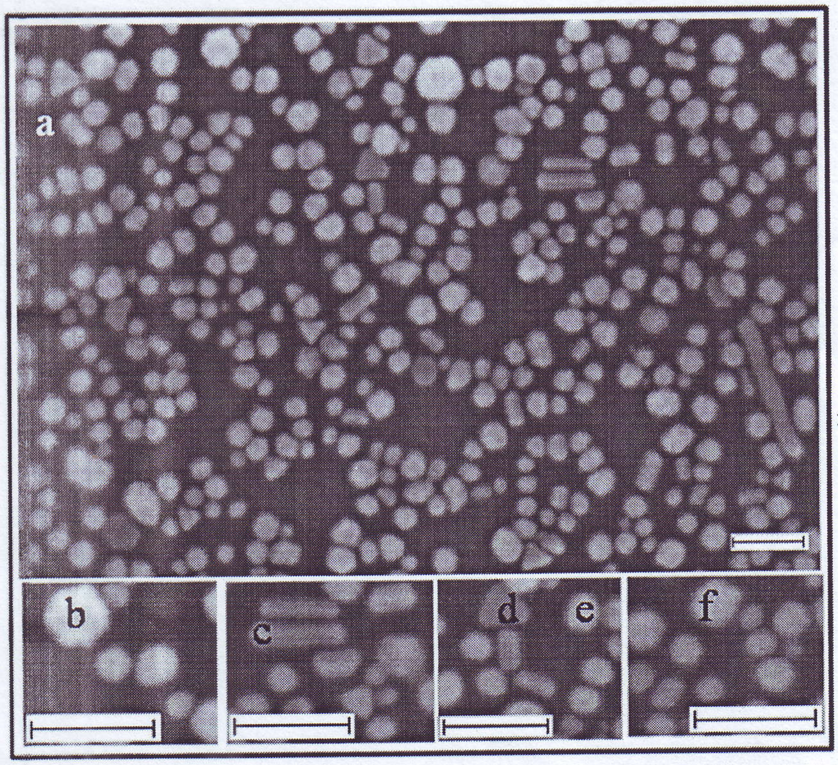

Fig. 4: (a) Grown gold nanoplates with 14 ml CTAB and 6 ml PVP; (b) hexagonal; (c) truncated [illegible] ular-rounded and (f) square shapes

The X-ray diffraction patterns of the gold nanoplates that were grown on the ITO for all samples were shown in Figure 5. Two peaks were clearly observed at 38.185° and 44.393° representing the Au (111) and Au (200) crystallographic planes of fcc gold nanocrystals. The first peak (111) was also observed as previous result reported [14]. The peak (111) was clearly much stronger than the (200) peak. Additional peak of Au (200) may represent of the present of more various shape gold nanoplates.

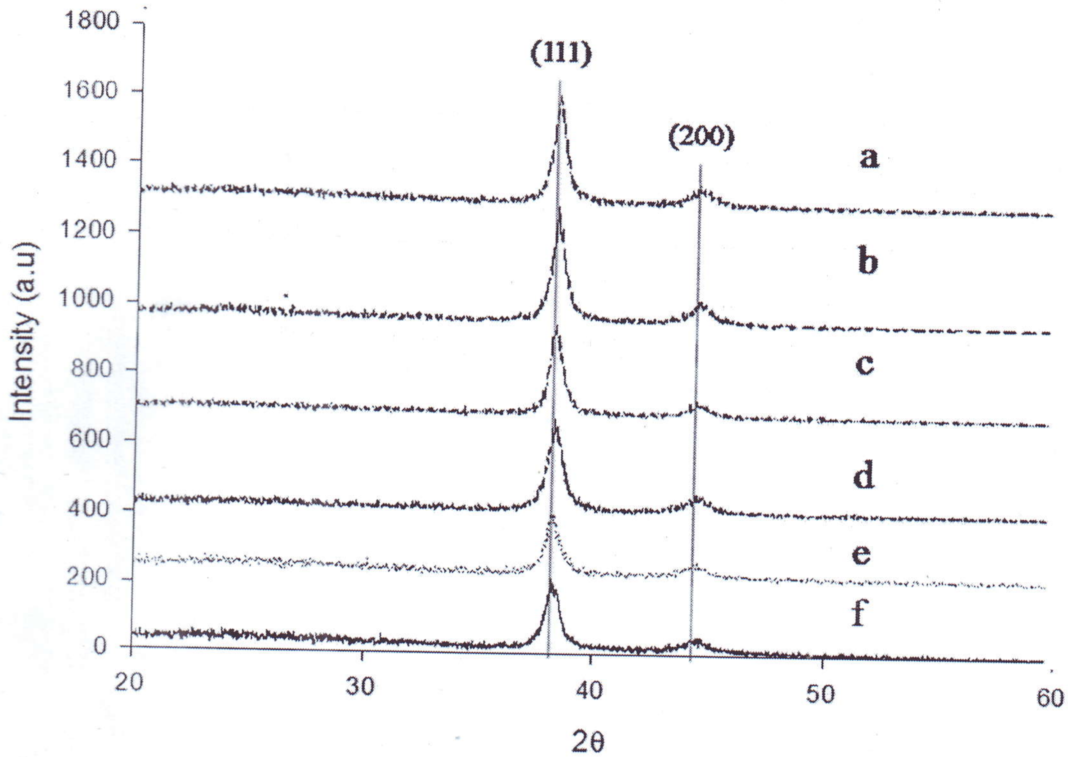

Fig.5: XRD spectra of the gold nanoplates grown on the ITO substrate showing two Au (111) and Au (200) peaks

Figure 6 shows UV-Visible absorption spectra for the samples with different volume ratio of CTAB and PVP. It shows two absorption bands that represented to a transverse and a longitudinal surface plasmon resonances (SPR). The longitudinal SPR (LSPR) is typical for gold nanoplates and blue-shifted when the size of gold nanoplates decreased. The LSPR was found to be broadened when the nanoplates size increased.

Effect of Volume Ratio of CTAB and PVP on the Nanoplates Growth. Shape, size and number of the grown gold nanoplates on the substrates were strongly depended on the volume ratio of CTAB and PVP used in the growth solution. In a decreasing CTAB volume and an increasing PVP volume, the size of grown gold nanoplates decreased and yield of gold nanoplates was observed tend to increase. It was also obtained that the nanoplates shape changed linearly from irregular or rounded shapes to a regular shape, such as triangular and hexagonal with the decrease in CTAB volume and the increase in PVP volume. The FESEM images for the gold nanocrystal grown using different volume ratio of CTAB and PVP, that is, 19 ml CTAB : 1 ml PVP; 18 ml CTAB : 2 ml PVP; 14 ml CTAB : 6 ml PVP and a growth time of 4 h, is shown in Figure 2, 3 and 4, respectively. These figures show that at a lower CTAB volume and a higher PVP volume, for example in Figure 4 (14 ml CTAB and 6 ml PVP), small edge-length size nanoplates of 11-30 nm dominated the sample (70%) with a yield almost 70% of the product were obtained. The sample at this volume combination, about 75% of the nanoplates had morphology of irregular or rounded-shape. Whereas, at a higher CTAB volume of 18 ml and a lower PVP volume of 2 ml (Figure 3), ... ze nanoplates were dominated the sample, that ... nanoplates. The morphology of nanoplates was dominated by regular (hexagonal, truncated hexagonal, triangular, square and spherical) shapes of nanoplates, that was, about 70% of nanoplates. On the other hand, the yield of irregular shape decreased significantly to only about 30% of nanoplates.

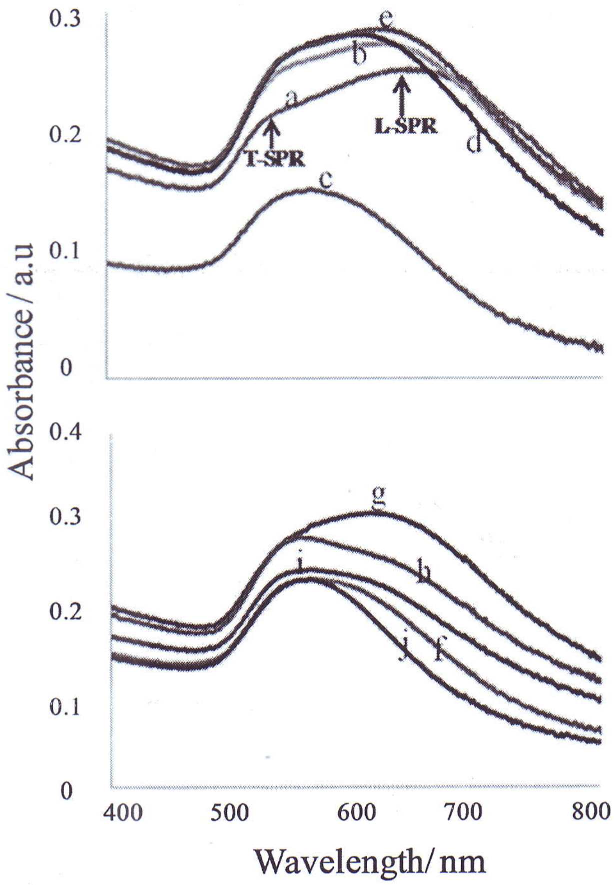

Fig. 6: UV-Visible absorption spectra of various volume ratio of CTAB and PVP: (a) 19 : 1 ml; (b) 18 : 2 ml; (c) 17 : 3 ml; (d) 16 : 4 ml; (e) 15 : 5 ml; (f) 14 : 6 ml; (g) 13 : 7 ml; (h) 12 : 8 ml ; (i) 11 : 9 ml; and (j) 10 : 10 ml

The fact that the use of higher CTAB volume may promote the growth of bigger gold nanoplates, it caused by deterioration of the nanoplates shape symmetry and may be as the result of oxidation of high-energy gold atoms by excess of CTAB molecules. On the other hand, the use of higher PVP volume may promote smaller edge-length size nanoplates. It might be caused by forming a multilayer of PVP on the surface that hampered the gold ions in reaching the growing plane of the nanoplates.

Conclusions

This work has demonstrated a method of seed-mediated growth for growing gold nanoplates onto the solid substrate (ITO) using a binary surfactant mixture of CTAB and PVP. XRD results informed that the presence of two peaks at 2θ: 38.195° and 44.393° indicated the gold-nanoplates, with their crystal orientation of Au (111) and Au (200). Much smaller gold nanoplates were grown on the ITO surface of 11-50 nm in edge-length size. At the optimum volume ratio of CTAB and

d almost all surface area of the substrate, with
s of the nanoplates were hexagonal, truncated-
l nanoplates were also found, such as square and

spherical shapes of nanoplates. The regular shapes of the nanoplates changed to irregular-rounded shape without clear vertices when prepared at a high CTAB volume and a low PVP volume. The unique properties of surface produced from crystallographic planes of gold nanoplates should find use in widespread applications, such as catalysis, analytics, optoelectronics, optics, and sensors

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