Deposition of Au/TiO\textsubscript{2} Nanocomposite on ITO Surface by Seed-Mediated Liquid Phase Deposition Method

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Abstract. An efficient, simple and new procedure has been performed to synthesis Au/TiO\textsubscript{2} nanocomposite thin film on solid surface of ITO by seed-mediated of liquid phase deposition (LPD) method. The deposition of Au seed was applied by our previously reported seed-mediated growth procedure. The solution was prepared by mixing HAuCl\textsubscript{4} and (NH\textsubscript{4})\textsubscript{2}TiF\textsubscript{6} successfully deposited on to ITO substrate containing Au seed. After one hour well adhered film was obtained by mentioned approach of synthesis and nanocomposite with spherical rod like networks has been successfully grown. The resulting nanocomposites were confirmed by ultraviolet-visible (Uv-Vis) absorption spectroscopy. Further characterization and morphology was checked by field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD).

1. Introduction
Nanocomposite of metal and metal oxide have been intensively studied due their good optical, photocatalytic, electrical, magnetic and mechanical properties [1]. These metal and metal oxide nanocomposites are widely applied in gas sensor [2], catalyst [3],[4] and anti bacterial [5]. Nanocomposite of metal and metal oxide have been intensively studied due their good optical, photocatalytic, electrical, magnetic and mechanical properties such as.. Many studies have been reported in the literatures on the effect of doping metal like Au, Pd, Ag and Pt on the TiO\textsubscript{2} [5],[6]. TiO\textsubscript{2} is one of the most attractive semiconductor materials due to the lowest cost, non-toxicity, biologically and chemically stable properties [7]. The presence of metal in the TiO\textsubscript{2} facilitates electron transfer from photoexcited semiconductor to the surroundings and decreases recombination rate between the electrons-holes so that good for application in photoelectrochemical and photocatalytic [8]. In recent years, various methods has been used in synthesis of composite TiO\textsubscript{2}-metal nanoparticles such as photoreduction [5], magnetron sputtering [1, 9], dip coating [10] and sol gel method [6, 11]. Owing to

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the simplicity of the process, catalytic and optical properties, the presence method could be potential approach for producing Au/TiO$_2$ nanocomposite for application in photocatalysis, optical sensing and non-linear optical application.

Liquid phase deposition method (LPD) is widely used in the deposition of TiO$_2$ on solid surface. In particular, LPD is promising technique for direct preparation of TiO$_2$ thin film on to solid substrate using boric acid as scavenger. However, metals such as -Al and Fe has also been reported to be used as scavenger for fluoride ion[12]. In this study, we aims to develop a simple and efficient method to synthesis Au/TiO$_2$ nanocomposite thin film by seed-mediated grow procedure using LPD technique. The obtained composite thin films were characterized by using Uv-Vis absorption spectroscopy, field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD).

2. Experimental

2.1. Materials

Analytical grade chemicals in this work were used without further purification. HAuCl$_4$ and (NH$_4$)$_2$TiF$_6$ were purchased from Sigma Aldrich while trisodium citrate was purchased from Wako Chemical and NaBH$_4$ was from Fluka. The ITO substrate was purchased from CBC Ing. Co. Ltd., Japan. The ITO substrate was cleaned by distilled water and sonicated in acetone followed by 2-propanol for 30 minutes according to the standard procedure. The depositions of Au/TiO$_2$ nanocomposite on to ITO substrate practically involved two steps, namely seeding process and growth process. The ITO substrate immersed into Au seed solution as reported in our previous work [13].The growth process was carried out by immersing the sample in standard growth solution which containing 5 ml of H AuCl$_4$ 1 mM and 5 ml of (NH$_4$)$_2$TiF$_6$ 50 mM. The reaction was performed in bath deposition to keep temperature unchanged during the reaction. The sample was then washed several times by distilled water and dried under nitrogen flow.

Effect of concentration (NH$_4$)$_2$TiF$_6$ was performed by preparing four different of variation concentration namely 50, 100, 200 and 250 mM with the fixed concentration of H AuCl$_4$ 1 mM at temperature 90ºC for growth time 1 hour. The investigation of formation Au/TiO$_2$ nanocomposite was then studied by varying the growth time of the synthesized nanocomposite for four different variations namely 15 min, 30 min, 1 hour and 3 hours.

2.2. Au/TiO$_2$ nanocomposite characterization

The optical absorption of the sample for fixed concentration, variation concentration of (NH$_4$)$_2$TiF$_6$, and growth time were studied using Uv-Vis spectrophotometer (Lambda 900 PERKIN ELMER) with the wavelength range 300-900 nm. Morphology of nanocomposite for fixed concentration and variation of growth for synthesized nanocomposite were also studied using FESEM technique (ZEISS SUPRA 55VP). The elemental composition of nanocomposite was studied using energy X-ray dispersive (EDX) method (Oxford instruments INCA) at 30 kV using CuK$\alpha$ radiation ($\lambda = 1.541$ Å). X-ray diffraction spectrum was obtained from X-ray diffractometer (BRUKER D8 Advance) with the diffraction angle of 0-60º.

3. Results and Discussions

Au/TiO$_2$ has been successfully deposited on the surface using the presence approach. As reported by Gutierrez et al. who successly produced TiO$_2$ using trivalent Al(III) and Fe(III), in this work we tried to use trivalent Au(III) as scavenger ion in the absence of boric acid. The chemical reaction can be expressed as follows:

$$\text{TiF}_6^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{TiO}_2 + 4\text{HF} + 2\text{F}^-$$  \hspace{1cm} (1)

$$\text{Au}^{3+} + 4\text{HF} \leftrightarrow [\text{AuF}_4]^- + 4\text{H}^+$$  \hspace{1cm} (2)
In typical process, the Au/TiO$_2$ nanocomposite formed in standard growth solution at temperature of 90ºC for 1 hour. Figure 1a shows a typical FESEM image of Au/TiO$_2$ nanocomposite on the ITO surface via seed-mediated LPD method. From the FESEM image, we can see that the shape Au/TiO2 nanocomposites was more towards spherical rod-like with a diameter of 250 nm. These spherical rod-like particles however tends to agglomerate with one another forming a micron size network. In high magnification (Figure 1b), it can be clearly seen that the roughness among the surface of nanoparticles, indicated that the nanoparticles was not only pure Au, but contain dopant (TiO$_2$). The EDX study was performed on the sample to confirm the existence of TiO$_2$. The EDX spectrum below (figure 1c) showed Au, Ti and O peak. This confirmed the formation of Au/TiO$_2$ nanocomposite thin film. However as can be seen from the spectrum, Ti peak was not as high as Au indicates that the composition of nanocomposite was dominated by Au.

![Figure 1. FESEM image of Au/TiO2 nanocomposite deposite on to ITO surface (a) at high magnification (b) and it’s EDX spectrum (c)](image)

Figure 2 showed the XRD spectrum of Au/TiO$_2$ nanocomposite. The peaks observed match to the JCPDS of Au nanoparticles (file number 04-0784) where the peaks related at (111) and (200) corresponding with the diffraction angle 38.185º and 44.393º. However from the XRD spectrum the presence of TiO$_2$ was not seen. This might due to the fact that the presence of TiO$_2$ in the Au/TiO$_2$ nanocomposite was very small. As also can be seen in figure 1, the distribution of investigated nanocomposite was not dense enough.
Figure 2. XRD spectrum of Au/TiO$_2$ nanocomposite deposited on solid surface.

UV-Vis absorption in figure 3 showed that the absorption of Au/TiO$_2$ nanocomposite centering at wavelength 570 nm. This absorption is slightly different from the absorption of Au nanoparticles which is normally exhibit plasmonic absorption around wavelength 520 – 530 nm [13]. There are two possible reasons that may be responsible for that bathocromic shift. First, the presence of TiO$_2$ in the gold nanoparticles (Au/TiO$_2$ nanocomposite) as it was previously reported that the absorption peak for thin film TiO$_2$ was found to be at 350 nm[14]. Second, it was caused by the link of spherical nanocomposite that was contributed to the red shifted absorption spectrum.

Figure 3. UV-Vis absorption of Au/TiO$_2$ nanocomposite.

The works was carried out further to optimize the effect of concentration (NH$_4$)$_2$TiF$_6$ used on the formation of nanocomposite. Four different concentration of (NH$_4$)$_2$TiF$_6$ namely 50, 100, 200 and 250 mM were used in this study. Here, it can be seen when the molarity of (NH$_4$)$_2$TiF$_6$ used increased, the optical absorption of the prepared samples seems to decrease. This might due to the formation of TiO$_2$ complex has hindered the performance of Au in the nanocomposite as it is known better that Au has excellence optical performance contributed by its plasmonic effect. From the spectra profile (figure 4) of UV-Vis absorption, it can be conclude that the optimum (NH$_4$)$_2$TiF$_6$ concentration is 50 mM gave
the best results as it can be seen that the sample growth within this concentration has the highest optical absorption compared to the other sample.

Figure 4. UV-Vis absorption of Au/TiO$_2$ nanocomposite growth in variation concentrations of (NH$_4$)$_2$TiF$_6$.

The optical properties of the Au/TiO$_2$ nanocomposite synthesis at temperature of 90ºC with variation of growth time were further studied by UV-Vis measurement. Four variation of time growth namely 15 minutes, 30 minutes, 1 hour and 3 hours were chosen. By immersing the attached Au seed substrate in the solution containing HAuCl$_4$ 1 mM and (NH$_4$)$_2$TiF$_6$ 50 mM. The color of the thin film changed from colorless to yellow within 3 hours of the reaction. Figure 5 shows the time-dependent spectral response obtained during the deposition of Au/TiO2 nanocomposite. The intensity of the peak increases monotonically with time, indicating the increase in the amount of the Au/TiO$_2$ nanocomposite product. The spectra also recorded that the absorption peak broadens and shifts towards longer wavelength from 540 to 700 nm with the increase of growth time. This broadening and red shift are related to particle size as confirmed from FESEM image (figure 6).

Figure 5. UV-Vis absorption of Au/TiO$_2$ nanocomposite with variations of growth time.
The morphology of Au/TiO$_2$ nanocomposite growth at different time intervals shows was presented by the FESEM image shown below. The shape of the nanocomposite formed was more into spherical shape and was bound to agglomerate towards each other. As the growth time increased, the linked agglomeration of the spherical particle of nanocomposite was elongated. This is due to the fact of the increased deposition time give rise to the formation of this nanocomposite. Thus, it is clear why when the growth time increased, the nanocomposite in micron size network increased. From the FESEM images obtained at the magnification of 20 kx, the grain size of the nanocomposite formed were 149, 172, 278 and 371 nm for the growth time 15 minutes, 30 minutes, 1 and 3 hours respectively.

**Figure 6.** FESEM image of Au/TiO$_2$ nanocomposite with variation growth time i.e. 15 minutes (A), 30 minutes (B), 1 hour (C) and 3 hour (D) in obtained condition. Scale bars are 1 µm.

4. Conclusion

Au/TiO$_2$ nanocomposites thin film has been successfully prepared by seed-mediated LPD technique on the surface of ITO substrate. The UV-Vis spectrum shows band of nanocomposite thin films centering at wavelength 540 – 700 nm. FESEM image showed shape of nanocomposites were spherical like nanorods. EDX analysis confirmed the presence of Au, Ti and O atoms in the Au/TiO$_2$ nanocomposite thin film. From the studies, the optimum growth condition for deposited Au/TiO$_2$ nanocomposite thin films on the surface by seed-mediated liquid phase deposition for HAuCl$_4$ of 1 mM is (NH$_4$)$_2$TiF$_6$ 50 mM with the temperature of 90ºC grown 1 hour.

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