Fabrication of ZnO nanorods decorated Au nanoparticles by hydrothermal and magnetron sputter techniques

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ABSTRACT

In this study, ZnO nanorods decorated with gold (Au) nanoparticles with the desired size parameters were fabricated using a simple, low-cost, and highly efficient method. The ZnO nanorod structure was fabricated using a hydrothermal method on a ZnO seed layer with hydrothermal solution concentrations varying from 20 mM to 90 mM. Au nanoparticles were coated on the ZnO nanorod structure by magnetron sputtering with a sputtering time from the 40s to 70 s. The characteristics of the fabricated samples were investigated through SEM images and optical absorption spectroscopy. The results show that the fabricated ZnO nanorods are relatively uniform, with a cylindrical shape and hexagonal cross-section when the solution concentration is less than 70 mM. Au nanoparticles were attached to the surface of the ZnO nanorods with average sizes of 30-50 nm. The optical absorption spectroscopy results showed that the ZnO nanorods' absorption edge appeared at a wavelength of approximately 395 nm. In addition, the exciton absorption peak of Au nanoparticles was between 550 nm and 600 nm and there was a shift towards shorter wavelengths as the size of the Au nanoparticle decreased. This result opens up potential applications of this material such as increasing photocatalytic efficiency and its, use in photonic devices, etc.

Keywords: Au nanoparticles; Hydrothermal; Magnetron sputtering; ZnO nanorods.

1. INTRODUCTION

ZnO is a metal oxide semiconductor that has many applications in life such as sensors [1-7], photodetectors [8-12], water splitting [13-14], and photocatalytic [15-19]. These applications of ZnO mainly appear when it exists at the nanometer scale. ZnO on the nanoscale can be fabricated in many shapes and structures such as nanowires, nanodisks, nanotubes, and nanoflowers. ZnO nanostructures are fabricated by various methods but are usually divided into physical and chemical methods. Most physical methods have the advantages of producing high crystalline and uniform ZnO structures but require expensive and modern equipment. The chemical methods have the advantages of low cost, do not require modern equipment, and fast sample manufacturing speed. We choose hydrothermal as the chemical process in this paper to create ZnO nanostructure.

ZnO materials have significant applications in photocatalytic but the efficiency with visible light is still low due to the large optical bandgap and fast electron-hole pairs recombination rate. Using the plasmonic effect of Au nanoparticles attached to ZnO structures, the photocatalytic effect has been enhanced [20-22]. In this paper, we show how to make ZnO nanorods embellished with Au nanoparticles, describe them, and then adjust their size to meet application-specific requirements.

2. FABRICATION PROCESS

2.1. Fabrication of ZnO nanorods

The fabrication process of ZnO nanorods is presented in figure 1. Firstly, $Zn(COOCH_3)_2 .2H_2O$ and Isopropanol (IPA) were mixed in a magnetic stirring machine to make a seed solution and then spin-coating on a clean glass substrate to form a ZnO seed layer. Then, the layer was heated in the air at 500 ^oC for 1 hour. Besides that, $Zn(NO_3)_2$, $C_6H_{12}N_4$, and H_2O were mixed in different concentrations to create the ZnO grow solution. Then, the glass substrate with the ZnO seed layer above was put into the autoclave with ZnO grow solution. For the purpose of producing ZnO nanorods on a glass substrate, they were all subjected to the hydrothermal process for two hours at 80 °C. After that, the autoclave was slowly cooled down to room temperature and the samples were washed with deionized (DI) water and dried.

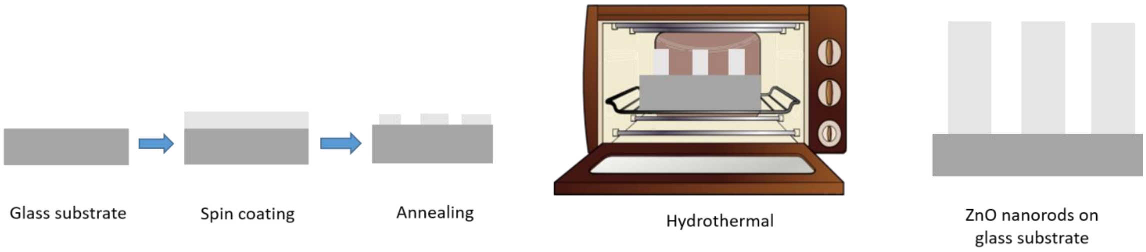

***Figure 1.** Schematic of the fabrication process of structured ZnO nanorods by spin-coating and hydrothermal techniques.*

2.2. Fabrication of ZnO nanorods decorate Au nanoparticles

The process of decorating gold nanoparticles on ZnO nanorods was described in figure 2. A gold nanolayer was deposited onto the ZnO template structures by using the magnetron sputtering technique. The discharge current was 20 mA and the sputtering time was changed from 40 s to 70 s. After that, the samples were annealed at 500 ^oC in the air for 15 min and naturally cooled down to room temperature. The Au nanolayers were melted and formed Au nanoparticles well distributed on ZnO nanorods.

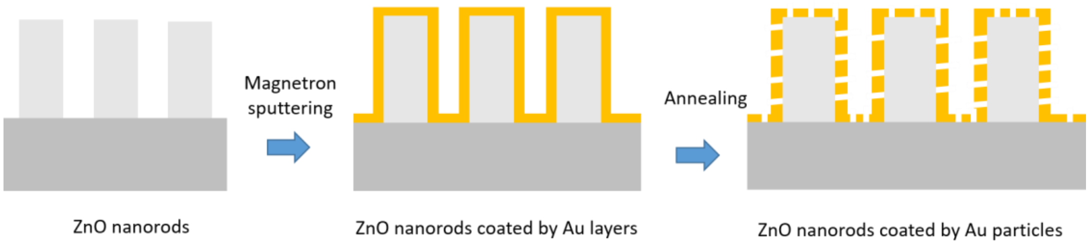

***Figure 2.** Fabrication process of Au nanoparticles decorated ZnO nanorod by magnetron sputter and thermal annealing.*

3. RESULTS AND DISCUSSION

Initially, ZnO nanorods were well-formed on grass substrate. The rods have a diameter from 0.13 µm to 0.713 µm, a height from 0.63 µm up to 2.093 µm, and are perpendicular to the base when the seed solution has a concentration of 1M. Varying the concentration of the solution results in the change in size and density of ZnO nanorods.

In fact, the diameter and length of the rods decreased to 30 nm and 200 nm, respectively, when we reduced the concentration of the seed solution to 0.1M. The number of rods also drastically increased. ZnO nanorod SEM pictures at various seed solution concentrations are shown in figure 3.

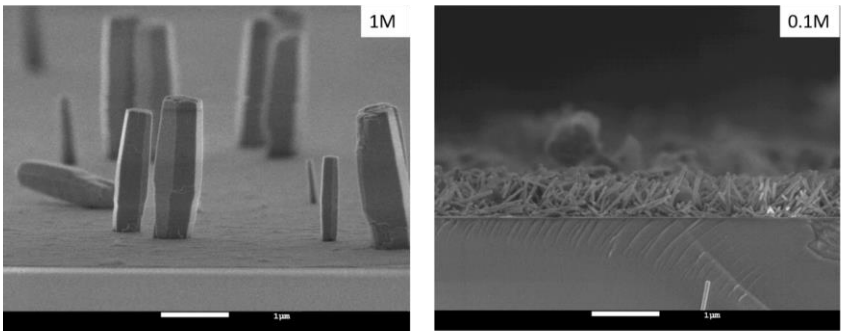

Figure 3. *SEM images of ZnO nanorods in different seed solution concentrations.*

With a target to create structures at the nanometer scale, we decided to keep the seed solution concentration of 0.1M and optimize the ZnO structure's parameters by changing other reaction conditions. We investigate the influence of hydrothermal solution concentration on ZnO structures. **Figure 4** shows the SEM side-view images of ZnO nanorods in different hydrothermal solution concentrations. Each sample's structure is relatively uniform in bar-shaped, and its size strongly depends on the hydrothermal solution. When the hydrothermal concentrations increased from 20 mM to 70 mM, the diameter of the rods increased from 50 nm to 300 nm, and the height of the rods increased from 200 nm to 900 nm as shown in **figure 5**.

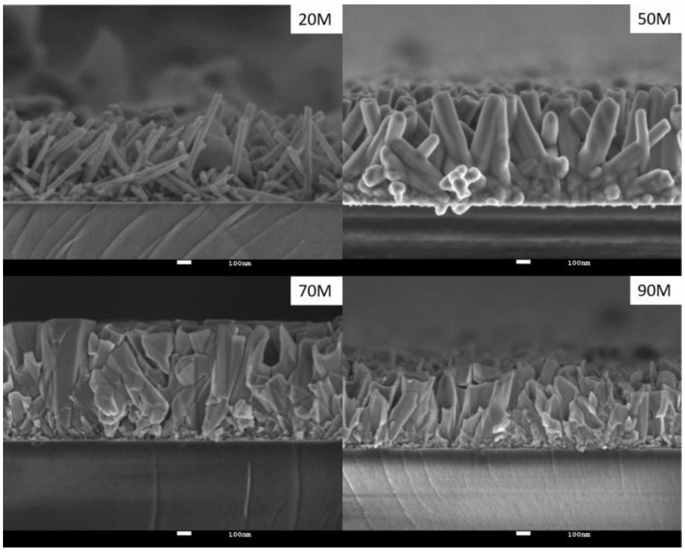

Figure 4. *SEM images of ZnO nanorods side view in different hydrothermal solution concentrations.*

When the hydrothermal solution concentration is 20 mM, the orientation perpendicular to the substrate surface of the ZnO nanorods is poor, the diameter of the ZnO nanorods is small and the density of the rods is large. As the hydrothermal solution concentration increased to 50 mM, the orientation perpendicular to the substrate surface increased, the diameter and height of the nanorods increased, and the density of the nanorods decreased. When the hydrothermal solution concentration was 70 mM, the ZnO nanorods appeared to be voided and filmed due to the large diameter of the rods. This is more evident when the hydrothermal solution concentration is 90 mM. Therefore, the ZnO one-dimensional structure begins to break down when the hydrothermal solution concentration is 70 mM and the best ZnO one-dimensional structure can be obtained in this study when the hydrothermal solution concentration is 50 mM, the hydrothermal temperature is 80 ^{o}C, hydrothermal time is 2 h, hydrothermal solution volume is 50 ml.

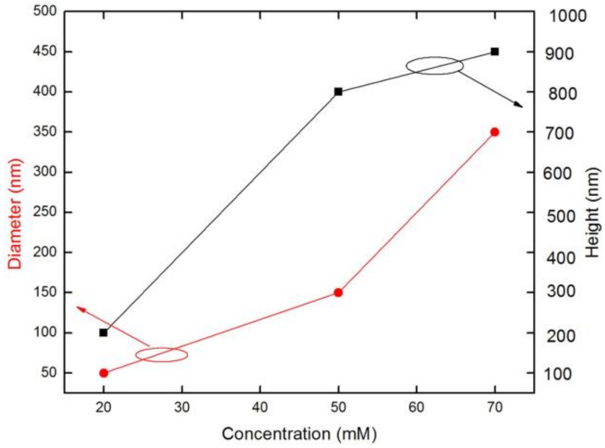

Figure 5: *The change of ZnO nanorods' height and diameter with the hydrothermal solution concentration.*

We decided to coat a gold nanolayer on the best ZnO nanorods obtained above. **Figure 6** shows the SEM images of ZnO before (a) and after (b-c) coated with a gold nanolayer by magnetron sputtering technique. The Au nanolayer was covered relatively uniformly on ZnO nanorods substrate.

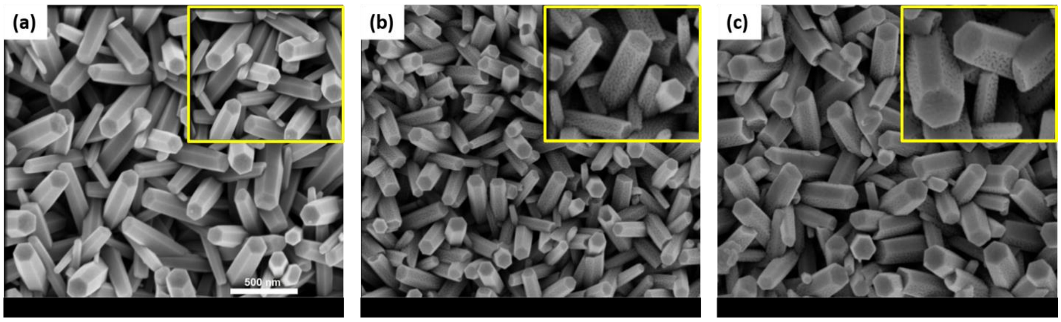

Figure 6. *SEM images of ZnO before (a) and after (b-c) coated with a gold nanolayer by magnetron sputtering technique.*

After coating, the gold nanolayer was annealed at 500 ^{o}C for 15 min to break and form gold nanoparticles. These particles are evenly distributed on ZnO nanorods as displayed in **figure 7**. Au nanoparticle size increases linearly with sputtering time. The greater the particles, the longer the sputtering time. To concretize, as the magnetron sputtering time increased from 40 s to 70 s, the average size of the Au nanoparticles increased from 10 nm to 80 nm.

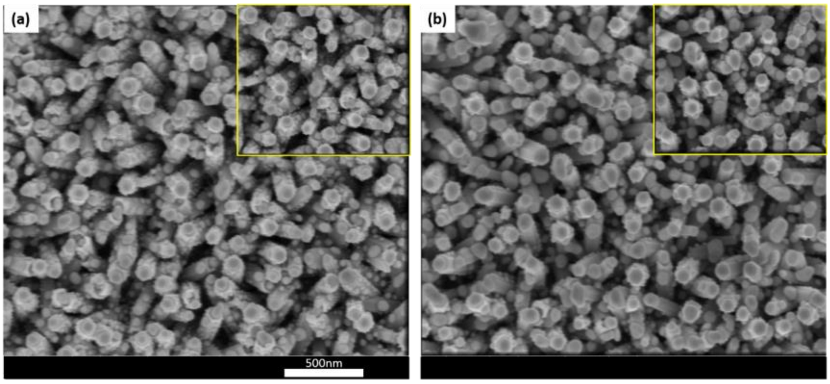

__Figure 7.__ SEM images of Au nanoparticles decorated on ZnO nanorods after annealing, sputtering in the 40 s (a) and 70 s (b).

The influence of gold nanoparticles on the optical properties of the ZnO nanorods structure was investigated through the optical absorption and photoluminescence spectrum presented in **figures 8, 9, and 10**.

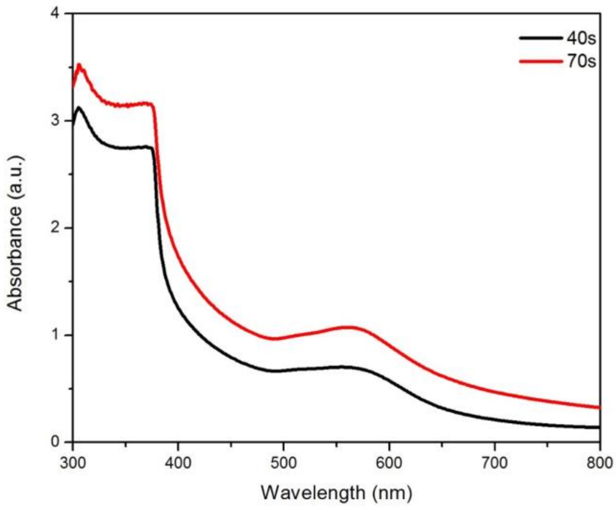

__Figure 8.__ Optical absorption spectrum of ZnO nanorods decorated Au nanoparticles in different sputtering times.

Figure 8 indicated that the absorption edge of ZnO nanorods is 365 nm. The optical absorbance increased markedly as the Au nanoparticle size increased. The exciton absorption peak of Au nanoparticles is between 550 nm and 600 nm and there is a shift towards a short wavelength as the size of Au nanoparticles increases.

In the photoluminescence spectrum of the two samples of ZnO nanorods coated with Au nanoparticles in **figure 9**, the sample with Au particles coated in the 40 s higher than the Au sputtered sample at 70 s different from the optical absorption spectrum in figure 8. The plasmonic effect for smaller particles is higher than for larger particles that agree with proposed theories about the plasmonic effect from other studies. This also reveals the ability to enhance the photocatalytic effect of ZnO nanorods decorated Au nanoparticles compared with ZnO nanorods sample.

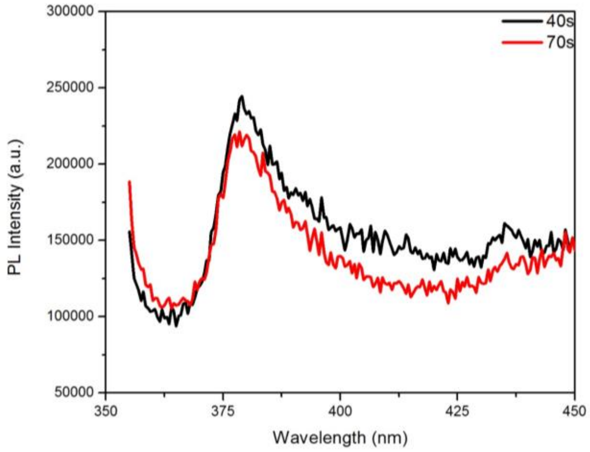

Figure 9. Photoluminescence spectrum of ZnO nanorods decorated Au nanoparticles in different sputtering times.

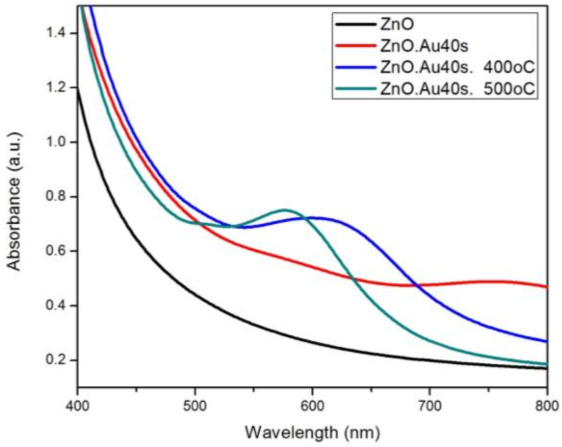

Figure 10. *Optical absorption spectrum of ZnO nanorods in different annealing temperatures.*

F**igure 10** demonstrates the influence of annealing temperature on the optical property of ZnO samples. There was a significant increase in optical absorbance between the ZnO nanorods sample and ZnO nanorods coated with a gold nanolayer without annealing due to the impact of the coating gold film. The ZnO nanorods coated with Au nano-thin film annealing at different temperature of 400 ^{o}C and 500 ^{o}C also reveals an absorption peak of Au nanoparticles in the range from 570 nm to 600 nm, and a blue-shift when the size of Au nanoparticles decreases. The higher the heating temperature, the more the gold layer melts, breaks, and shrinks to form gold particles of smaller size, and the more obvious the plasmonic effect appears. This is consistent with the other conclusions and results mentioned above.

4. CONCLUSIONS

We have successfully fabricated the ZnO nanorods decorated Au nanoparticles on glass substrates by hydrothermal and magnetron sputtering methods. The nanorods reached a hexagonal face, perpendicular to the base, and best size when fabricated with the hydrothermal solution concentration of 50 mM. Then, the gold nanoparticles were decorated on top of ZnO nanorods by magnetron sputtering and thermal annealing techniques. The size of Au nanoparticles depends strongly on sputtering time. Exciton peaks of Au nanoparticles were shown on the UV-Visible spectrum and there was a blueshift when the size of Au nanoparticles decreased. The obtained results in this study are oriented to application in the decomposition of organic compounds of the ZnO one-dimensional structure with Au nanoparticles.

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TÓM TẮT

Chế tạo cấu trúc một chiều ZnO có đính hạt nano Au bằng phương pháp thủy nhiệt và phún xạ magnetron

Trong báo cáo này, chúng tôi trình bày phương pháp đơn giản, giá thành thấp và hiệu quả cao sử dụng để chế tạo vật liệu ZnO nanorods (NRs) có đính hạt nano vàng (Au) với các thông số kích thước như mong muốn. Với phương pháp này, cấu trúc một chiều ZnO được nuôi bằng phương pháp thủy nhiệt trên lớp mầm ZnO, sau đó được phủ Au bằng phương pháp phún xạ magnetron. Tính chất của mẫu được khảo sát thông qua các phép đo SEM và UV-Vis. Kết quả cho thấy các thanh nano ZnO được tạo ra tương đối đồng đều, có tiết diện lục giác và được đính các hạt nano Au trên bề mặt. Trong điều kiện thủy nhiệt ở 800 ^oC và nồng độ dung dịch là 50 mM, các thanh ZnO nanorods được tạo ra với chất lượng tốt nhất có chiều cao 800 nm và đường kính 100 nm. Các hạt nano Au có kích thước trung bình trong khoảng từ 30 nm đến 50 nm với thời gian phún xạ là 40 s và 70 s. Kết quả này mở ra các ứng dụng tiềm năng của vật liệu này như làm tăng hiệu suất quang xúc tác, sử dụng trong các thiết bị quang – quang tử,…

Từ khoá: ZnO nanorods; Au nanoparticles; Hydrothermal.