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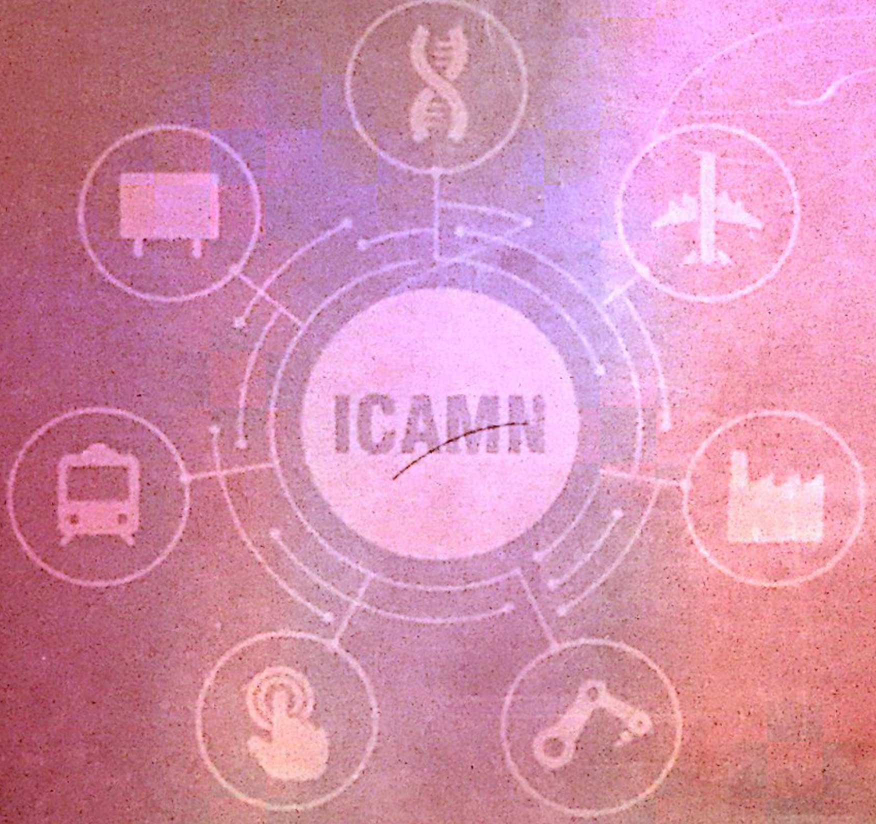

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Photocatalyst of ZnO nanorods decorated with gold nanoparticles

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Abstract— **Zinc oxide is a well - known semiconductor with valuable characteristics: wide direct band gap of 3.3 eV, large exciton binding energy of 60 meV, high efficient photocatalyst... which were applied in many fields such as optical devices (LEDs, laser), solar cells and sensors. Besides, various low dimensional structures of ZnO in terms of nanoparticles, nanorods, nanoneedles, nanotetrapods find many applications in technology and life. This material is also appealing due to the diversity of available processing methods including both chemical and physical approaches such as: hydrothermal, sol-gel, chemical vapor deposition and sputtering. In this report, ZnO nanorods are prepared by hydrothermal method assisted by galvanic - cell effect. The effect of hydrothermal time on the obtained product was studied. The as- prepared nanorods were then decorated with gold nanoparticles by sputtering. ZnO/Au nanostructures show excellent photocatalyst activities which were demonstrated by complete photodegradation of methylene blue under UV irradiation.**

Keywords: ZnO, nanorods, photocatalyst, hydrothermal, galvanic effect.

I. INTRODUCTION

Zinc oxide is an interesting material, which finds numerous applications from daily life to technology such as: cosmetic, medicine, rubber manufacture, sensors, UV absorber. These applications were developed based on unique properties of ZnO: wide direct bandgap of 3.37 eV at room temperature, piezoelectric properties, chemical stability.

In recent decades, ZnO in terms of nanomaterial has attracted more interest from scientists and engineers because many properties of ZnO were enhanced [1–3]. Hence, nanostructures of ZnO were considered as advanced materials.

Among diverse family of ZnO, 1D structures i.e ZnO nanorods and nanowires were reported as potential candidates for sensor and spintronics applications. ZnO is also famous for its good photocatalytic properties. In this paper, we report the synthesis of ZnO nanorods by hydrothermal methods. ZnO@Au nanocomposite was then prepared by sputtering method. The ZnO@Au nanocomposite shows good photocatalytic properties, which allow decomposing totally Mb on the surface of ZnO@Au nanorods after UV treatment.

II. EXPERIMENTAL

ZnO nanorods were grown on print circuit boards (PCBs) as substrates by hydrothermal process. The detailed experiment setup is described in our previous papers [3,4]. In a typical process, substrates were first cleaned thoroughly by ultrasonic bath with acetone, ethanol and deionized water. Then the substrates were dried by nitrogen blow. Galvanic effect was used to enhance the growth of ZnO nanorods. Edges of the substrate was covered by Al foils before being transferred into mixture solution of 75 mM zinc nitrate hexahydrate ($Zn(NO)_3.6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_{42}$). Temperature of the reaction was set at 90 ºC by a temperature controller and reaction time was 1h. ZnO nanorods would be grown in uncovered area of the substrates.

Gold was sputtered onto ZnO nanorods in different amount of time. Morphology of the sample was studied by using Nova Nano SEM 450. Raman spectra were collected on HR 800 Raman spectrometer from Horiba Jobin Yvon with excitation wavelength of 632.8 nm line from He – Ne laser.

Photocatalyst activity of ZnO@Au nanorods was performed by wetting the substrate with DI water and shining the sample by UV irradiation from Philips UV lamp in 60 min. After UV irradiation, the samples were then rinsed with DI water, blown dry by nitrogen gas. The existence/decomposition of Methylene Blue was checked by surface enhanced Raman scattering.

III. RESULTS AND DISCUSSION

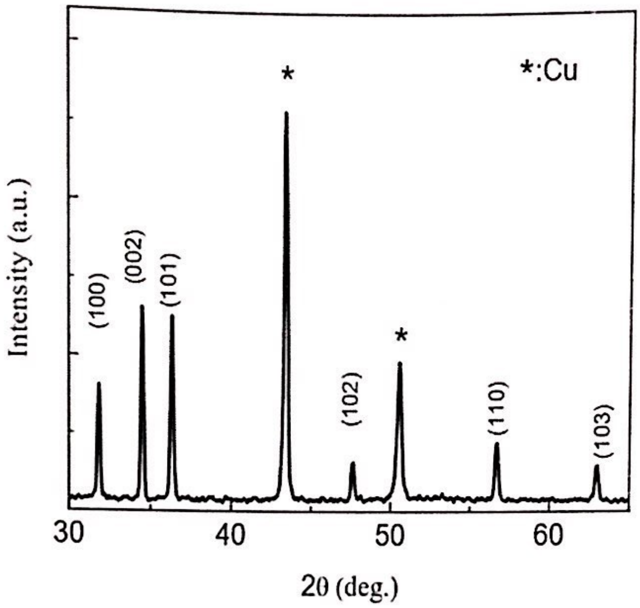

Figure 1. XRD patterns of ZnO nanorods prepared in 3 h at 90 °C.

XRD pattern of ZnO nanorods is shown in Figure 1. The pattern matches well with JSPS card no. 36-1451 of ZnO with hexagonal structure. Lattice constants of the samples were estimated as: a = 0.319 nm; c = 0.521 nm. The lattice parameters of our sample agree well with those reported by other groups [3,4]. Except two peaks of Cu resulted from the substrate, no other peak of impurity or strange phase was observed.

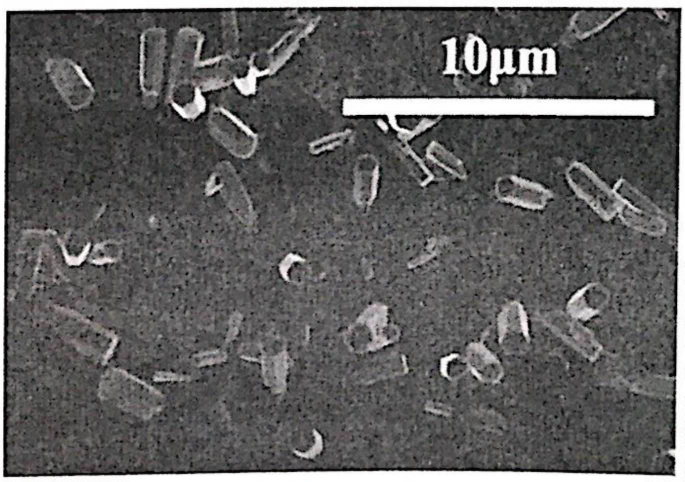

Figure 2. SEM images of ZnO nanorods.

SEM image of ZnO nanorods is presented in Figure 2. ZnO nanorods have quite uniform size and shape. Most of the rods have hexagonal cross-section with diameter of around 200-300 nm and length of 1-2 μm.

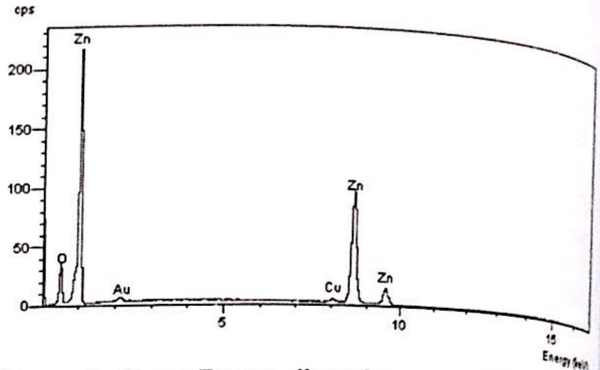

Figure 3. X-ray Energy dispersive spectra of ZnO@Au nanorods

EDS spectrum of ZnO sputtered with Au is shown in Figure 3. The spectrum reconfirms the purity of the sample with only peaks of Zn, O. It should be noted that copper signal comes from the substrates. Clear peak of Au was observed in the spectrum of ZnO sputtered with gold.

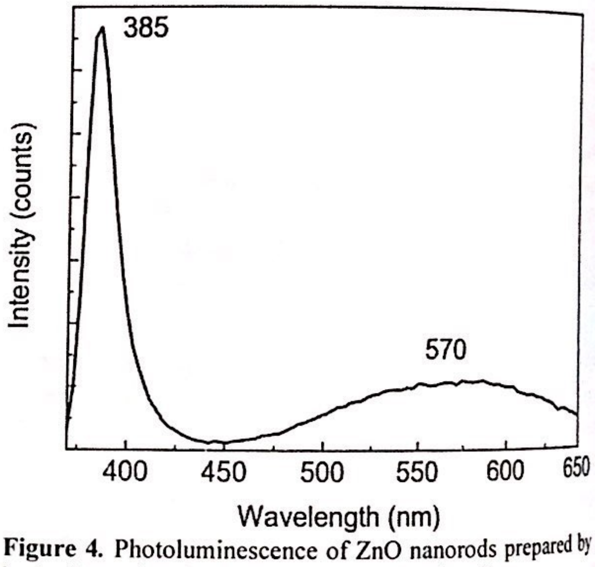

Figure 4. Photoluminescence of ZnO nanorods prepared by hydrothermal method assisted with galvanic effect.

Figure 4 shows the photoluminescence of the as prepared ZnO nanorods. ZnO has two well known photoluminescence peaks. One coresponds to near band edge transition, and the other corresponds to deep levels realted to defects in ZnO nanomaterials such as: oxygen vacancies or zinc interstitials. For our sample, near band edge transition was oberseved as a sharp peak at 385 nm while defect related transitions are characterized by a broad band in the region 570 nm. For photocatalyst activity these defect transition might not be useful because they reduce the number of free electrons and holes which are necessary for photocatalyst.

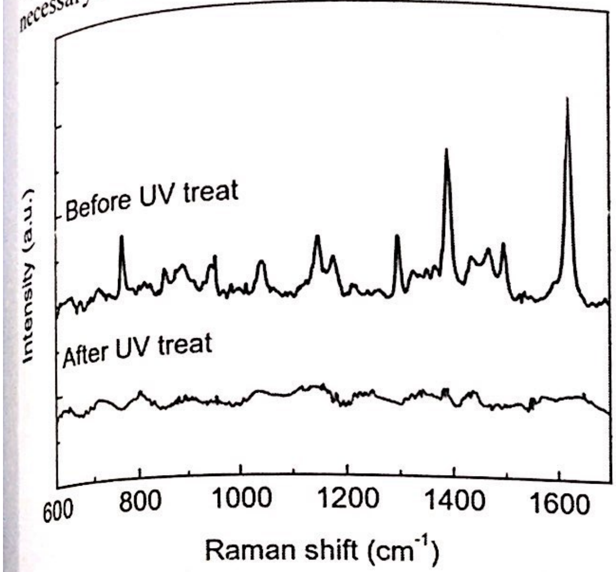

Figure 5. Raman spectra of MB on ZnO@Au nanorods before and after treatment with UV irradiation.

ZnO@Au nanorods also show good photocatalytic activity. Figure 5 shows that ZnO@Au nanorods can decompose Mb effectively under UV irradiation. Characteristic Raman peaks of Mb disappear after UV treatment. The selfcleaning ability of ZnO@Au nanorods is resulted from the excellent photocatalyst of ZnO nanorods, which helps to effectively remove organic molecular from the substrate. Futhermore, the chemical stability of ZnO@Au nanorods gurantees that the cleanning cycles can be performed many times without reducing the quality of the samples. Under UV irradiation, electron hole pairs are generated and move to the surface of ZnO@Au nanorods. Then, the electrons and holes react with oxygen and water vapor to produce active groups such as: $^{*}OH$ and $^{*}O_2$. Such active groups will decompose organic compounds into CO_2 and H_2O [5]. High surface area of nanorods improves photocatalyst reaction rate. In addition, it has been reported that better photocatalyst is obtained when ZnO is decorated with noble metal such as Au or Ag [6–8]. The enhancement is result of the charge transfer from ZnO nanorods to gold nanoparticles. This process reduces defect related recombination not being useful for photocatalytic activity (Figure 6).

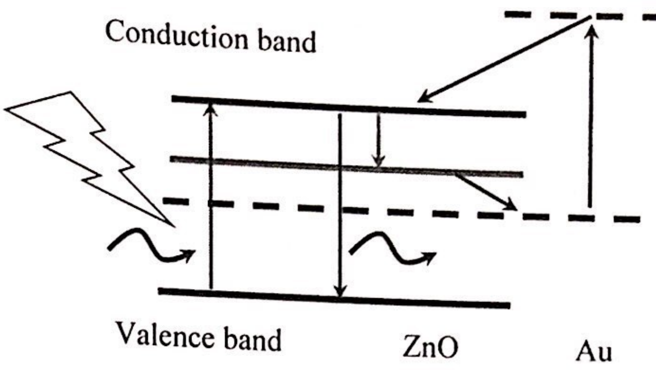

Figure 6. Diagram of mechanism for enhancement of band edge emission in ZnO nanorods.

IV. CONCLUSION

ZnO@Au nanorods were successfully prepared by combination of hydrothermal method and sputtering method. The products are pure and clean as demonstrated with XRD pattern and EDS spectrum. The obtained nanorods have uniform size of 200-300 nm in diameter and 1-2 um in length with hexagonal cross-section as shown by SEM images. The samples show good photocatalyst with ability to decompose completely methylence blue absorbed on the surface of the samples. The mechanism for good catalyst of the product was suggested as the combination of electron hole pair generated under UV irradiation and charge transfer between ZnO nanorods and gold sputtered on the surface of ZnO nanorods.

ACKNOWLEDGMENT

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