Synergistic effect of a cobalt dopant and Au nanoparticles on the photocatalytic activity of ZnO nanorods

A E Putri¹, V Fauzia¹*, and L Roza²

¹Departemen Fisika, Universitas Indonesia, Kampus UI Depok 16424, Indonesia.
²Program Studi Pendidikan Fisika, Universitas Muhammadiyah Prof. Dr. Hamka, Jakarta Timur 12130, Indonesia

*vivi@sci.ui.ac.id

Abstract. The photocatalytic performance of zinc oxide nanorods (ZnO NRs) still needs improvement. In this regard, the addition of noble-metal nanoparticles (NPs) and doping with transition metals can be employed. In this study, nanocomposites of ZnO NR/Au and Co-doped ZnO NR/Au NPs were synthesized by ultrasonic spray pyrolysis and hydrothermal method and subsequently used as photocatalysts for the degradation of methylene blue. Results revealed that pure ZnO NRs exhibit a degradation rate of only 28.8%, while ZnO NR/Au NPs exhibit a degradation rate of 37.3%, and Co-doped ZnO NR/Au NPs exhibit the highest degradation rate of up to 46.5%. Based on these results, the presence of Au on the ZnO NR surface can enhance the photocatalytic activity due to its key role as an electron sink, which reduces the recombination rate of electrons and holes, while the incorporation of Co into ZnO NRs can also enhance the number of crystal defects, which can widen the visible-light absorption spectrum.

1. Introduction

Zinc oxide (ZnO) is one of the wide band-gap semiconductor materials that demonstrates promise as a semiconductor photocatalyst. At room temperature, pure ZnO has a band gap energy of 3.37 eV and an exciton binding energy of 60 meV [1]. The electronic structure of ZnO can be modified by the addition of small amounts of impurity atoms into the host crystal structure [2,3], such as transition-metal elements of Ni [4,5], Mn [6], Fe [7], and Co [8,9], which can affect the band gap, microstructure, optical properties, and photocatalytic activity of ZnO [10]. In addition, dopants can induce the formation of ZnO defects for the adsorption of oxygen ions and OH− to produce H2O2 and hydroxyl radicals (·OH), which are beneficial for photocatalysis [11].

However, the photocatalytic performance of ZnO is still limited by the high recombination process, inhibiting the production of free electron and holes. Nanocomposite formation between ZnO nanostructures and noble-metal nanoparticles is one of the promising strategies to enhance the photocatalytic activity, where the interface between the noble metal and ZnO can facilitate the transfer of charges, reduce the recombination, and enhance the photocatalytic activity of ZnO [12–15]. Noble-metal NPs on ZnO serve as electron sinks that trap electrons, which in turn can improve the separation of electrons and holes. Some of the noble metals used for decorating ZnO include Pt [16], Ag [17], and Au [18–21], due to their high chemical stability as well as facile synthesis. Thus, in this study, the synergistic effect of the use of cobalt as a dopant for ZnO to widen the light-absorption spectrum and
the deposition of Au NPs on the ZnO NR surface to improve the photocatalytic activity of ZnO was examined.

2. Experiments
ZnO NRs were synthesized by a wet chemical method according to recently reported studies [22] [23]. The process was initiated by the deposition of a ZnO thin film on glass substrates (1.5 cm × 2.5 cm) via ultrasonic spray pyrolysis. First, a seed solution of 0.2 M zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) was sprayed on heated glass substrates for 15 min at 450°C [22]. Second, after seeding, each sample was immersed in 10 mL of a ZnO growth solution containing 5 mL of 0.05 M zinc nitrate tetrahydrate (Zn(NO₃)₂·4H₂O) and 0.5 mL of 0.05 M hexamethylenetetramine (C₆H₁₂N₄) and heated in an oven at 95°C for 6 h. Meanwhile, Co-doped ZnO NRs were prepared by a similar approach by the addition of 5 mol% of 0.05 M cobalt(II) acetate tetrahydrate (C₆H₆CoO₂·4H₂O) in the ZnO growth solution as described in our previous study [24].

The deposition of Au NPs was performed by using the Au precursor solution containing 1.5 mL of a 0.01 M hydrogen tetrachloroaurate (III) trihydrate, 0.6 mL of 0.1 M trisodium citrate, 45 mL of ultrapure water, and 0.18 mL of 0.1 M ice-cold sodium borohydrate. The Au solution was stirred for another 2 h until the color of the solution changed to dark red. Then, the ZnO NR samples were immersed in the Au precursor solution for 2 h and annealed at 200 °C for 1 h.

The morphology and microstructure of the as-prepared materials were observed by field-emission scanning electron microscopy (FESEM) Hitachi SU-8030 and X-ray diffraction (XRD) Rigaku SmartLab 3 kV. Optical properties were recorded on Thermo Fisher Scientific GENESYS 10S ultraviolet–visible and Edinburgh FLS 920 spectrometers (325-nm He–Cd laser). The photocatalytic activity of the composite ZnO NRs was investigated by the photodegradation of methylene blue (MB) under neutral aqueous conditions (pH 7). The photocatalyst was immersed in 10 mL of a 10⁻² mM MB solution under UV-light irradiation (2 UV lamps 40 W), and the MB absorbance peak at 596 nm was observed by using a UV–Vis spectrophotometer at specific periods after removing the photocatalyst from the MB solution.

3. Results and discussion
Figure 1 shows the FESEM images of the ZnO NRs, ZnO NR/Au NPs, and Co-doped ZnO NR/Au NPs. ZnO NRs exhibited vertical growth on a glass substrate surface as well as a homogeneous distribution morphology, in addition to a hexagonal structure in the diameter range of 75–150 nm. A significant difference in the shape and size for the Co-doped ZnO NRs was not observed (Figure 1c). Spherical Au NPs with a diameter of ~40 nm was observed, as well as a relatively uniform distribution on the ZnO NR and Co-doped ZnO NR surfaces (Figure 1b and 1c).

Figure 2 shows their respective XRD patterns: Peaks related to pure ZnO NRs were observed at 20 values of 31.74°, 34.48°, 36.23°, 47.51°, and 56.56°, corresponding to the (101), (002), (011), (012), and (110) crystal diffraction planes of the ZnO wurtzite structure (ICSD 98-009-4004). Meanwhile, in case of Co-doped ZnO NRs, all of the diffraction peaks slightly shifted to higher angles at 20 values of 31.75°, 34.50°, 36.25°, 47.54°, and 56.62°, possibly related to the effect of the substitution of Co²⁺ with the Zn²⁺ sites in the ZnO lattice and the resultant reduction of the unit cell volume.
Figure 1. FESEM images of (a) ZnO NRs, (b) ZnO NR/Au NPs, and (c) Co-doped ZnO NR/Au NPs.

Figure 2. XRD patterns of ZnO NRs, ZnO NRs/Au NPs, and Co-doped ZnO NRs/Au NPs.

This result was consistent with the fact that the ionic radius of Co$^{2+}$ (0.72 Å) is less than that of Zn$^{2+}$ (0.74 Å) [25]. In addition, Co-doped ZnO NRs did not exhibit a secondary phase such as cobalt oxide. Co$^{2+}$ partially replaced the ZnO crystal lattice without the formation of a secondary phase.

In addition, two other peaks were observed at 2θ values of 38.26° and 44.45° for the ZnO NR/Au NP and Co-doped ZnO NR/Au NP samples, corresponding to the (111) and (020) crystal planes of the Au face-centered-cubic structure, respectively (ICSD 98-061-1625).

High-intensity peaks in the ultraviolet wavelength range (320–390 nm) were observed in the absorbance spectra of all samples (Figure 3), confirming that ZnO NRs exhibit a wide band gap [13]. Compared with that of pure ZnO, the absorbance range of Co-doped ZnO NR/Au NPs was apparently extended from 500 nm to 550 nm, possibly related to the increase of the crystal defects such as oxygen vacancies, Zn vacancies, Zn interstitials, or oxygen interstitials that are beneficial for enhancing the photocatalytic activity of ZnO NRs [26]. In addition, the decoration of ZnO NRs by Au NPs led to the increase in the absorbance intensity at 400–550 nm, possibly related to the localized surface plasmon resonance effect of Au NPs [27].
Figure 3. Absorption spectra of (a) ZnO NRs, (b) ZnO NRs/Au NPs, and (c) Co-doped ZnO NRs/Au NPs.

Figure 4. Photoluminescence spectra of (a) ZnO NRs, (b) ZnO NRs/Au NPs, and (c) Co-doped ZnO NRs/Au NPs.

Figure 4 shows the room-temperature photoluminescence (PL) spectra of pure ZnO NRs and Co-doped ZnO NRs: A UV emission band was observed at 390–410 nm, multiple peaks were observed at 425–500 nm, and an extremely wide peak was observed at 550–800 nm. In addition, the presence of Au NPs led to the significant reduction of the PL intensity of ZnO NRs and Co-doped ZnO NRs, related to the electron-sink effect via which Au NPs trap the photogenerated electrons; hence, the recombination of excitons in the ZnO NRs is significantly reduced [18,28–31].

The photocatalytic performance was investigated by the degradation of MB under UV radiation. Figure 5 shows the mechanism underlying the photocatalytic degradation of MB solution. When ZnO are irradiated by UV light, the electrons excite from the valence band to the conduction band forming the excitons. These electron–hole pairs will react with the oxygen and water to produce hydroxyl and oxide radicals. In the case of the ZnO NRs/Au NPs and Co-doped ZnO NRs/Au NPs, the electrons are transferred from ZnO to Au until reach the equilibrium of the Fermi energy level [23]. These free charges then react with the oxygen in the water to form highly reactive and strongly oxidizing free radicals to react with the MB molecules, thus resulting in the degradation color of MB [32].

Figure 5. Schematic of the photocatalytic activity mechanism of ZnO NRs, ZnO NRs/Au NPs, and Co-doped ZnO NRs/Au NPs.
Figure 6. Photocatalytic activity of ZnO NRs, ZnO NRs/Au NPs, and Co-doped ZnO NRs/Au NPs for the degradation of methylene blue.

The photocatalytic performance results in Figure 6 revealed that pure ZnO NRs exhibit a degradation rate of only 31.8%, while the ZnO NR/Au NPs exhibit a degradation rate of 37.3%. The highest degradation rate of up to 46.5% was observed for Co-doped ZnO NR/Au NPs, possibly related to the presence of Co dopant in the ZnO structure, affording a new energy level between the valence and conduction bands of ZnO NRs, as indicated by the wider absorption spectrum in the visible-light region. In addition, the presence of Au NPs led to the efficient reduction of the recombination rate of the photogenerated electrons and holes; hence, the free electrons (e⁻) and holes (h⁺) react with OH⁻ and O₂ ions to produce hydroxyl and oxide radicals, respectively [26]. These radicals play a key role for the degradation of the MB solution into molecules that are safer for the environment.

4. Conclusion
In this study, the photocatalytic activity of ZnO NRs was improved by using cobalt as a dopant for ZnO and by the deposition of Au nanoparticles (Au NPs) on the ZnO NR surface. Co²⁺ possibly substituted into the Zn²⁺ sites in the ZnO lattice without forming a secondary phase. The cobalt dopant and Au NPs increased the intensity and visible-light range, and the presence of Au NPs also led to the significant reduction of the photoluminescence intensity of ZnO NRs and Co-doped ZnO NRs. For the degradation of methylene blue (MB) under the UV radiation of Co-doped ZnO NR/Au NPs, the highest degradation rate of up to 46.5% was observed, possibly related to the synergistic effect of the presence of a Co dopant and Au NPs. The Co dopant in the ZnO structure afforded a new energy level between the valence and conduction bands of ZnO NRs; hence, the absorption intensity in the visible-light region is widened, and the presence of Au NPs efficiently reduces the recombination rate of the photogenerated electrons and improves the photocatalytic activity of ZnO NRs.

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