Photoreduction of palladium nanoparticles on ZnO nanorods for enhancing photocatalytic decolorization of methylene blue

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Abstract. The high recombination rate of zinc oxide (ZnO) limits its photocatalytic activity and performance. Depositing noble metal nanoparticles (NPs) onto ZnO nanorods (NRs) is a promising approach that could facilitate interfacial charge-transfer processes, thereby increasing its photocatalytic activity. Generally, silver and gold NPs are used in conventional powdered structure, but in this work, due to the unique chemical and optical properties, palladium (Pd) NPs were utilized. Pd NPs were successfully deposited onto the surface of ZnO NRs by photoreduction process using a UV (365 nm) and a simulated solar light (Xe lamp). Irradiation by a Xe lamp produced a high number of Pd NPs with a particle size average of 52 nm. Compared to the pristine of ZnO NRs, the modified Pd/ZnO NRs (Xe) enhanced the photocatalytic activity about 21%. This improvement might be due to the effect of Pd NPs that increase the light absorbance and the number of free radicals to degrade the methylene blue structure.

Keywords: ZnO/Pd; photocatalyst; ultrasonic spray pyrolysis; hydrothermal; photoreduction

1. Introduction

Huge researchs on semiconductor-based photocatalytic material to degrade organic pollutants in water have been carried out since last four decades [1,2]. Besides titanium dioxide (TiO₂), zinc oxide (ZnO) is widely developed as photocatalytic material as well [3,4,5]. ZnO is a II–VI type of semiconductor with 3.37 eV bandgap and 60 meV exciton binding energy at room temperature [6,7]. Furthermore, ZnO is an environmentally friendly material and relatively cheap [4]. However, ZnO still has some disadvantages as a photocatalyst, such as limited irradiation absorption (in the UV region only) and easy recombination of electron-hole pairs [8,9]. Researchers have made many efforts to overcome these problems, such as developing ZnO nanocomposites with other nanomaterials, for example, carbon nanotubes, graphene, conductive polymers, and noble metal nanoparticles [5]. Noble metal nanoparticles, such as silver (Ag) and gold (Au), function widely as an electron sink that could trap the photogenerated electrons of ZnO to inhibit recombination. In addition, they also have the advantage of increasing the visible light absorbance by its localized surface plasmon resonance (LSPR) [10,11,12]. Some studies have utilized palladium (Pd) NPs to enhance the chemical and optical properties of ZnO...
NPs in sensor and photocatalyst application [13-17]. The isotropic Pd NPs have an LSPR wavelength in the UV region [18] and have good catalytic activity in several chemical reactions [19-22]; some properties of Pd that are expected to improve ZnO/Pd photocatalyst performance. Herein, we report the use of modified ZnO NRs surface by Pd NPs (ZnO/Pd nanocomposites) as a photocatalyst, which is still rare. In this work, ZnO/Pd nanocomposite was synthesized by photoreduction method using a 365 nm UV lamp [13] and a Xenon (Xe) lamp. This study analyzes the effect of light on the formation of Pd NPs on the surface of ZnO NRs as well as compares the photocatalytic performance of ZnO NRs before and after Pd NPs modification.

2. Experimental Method

2.1. Materials
Zinc acetate dihydrate, hexamethylenetetramine, palladium chloride (PdCl₂), methylene blue and ethanol were purchased from Merck. Zinc nitrate hexahydrate was obtained from Sigma-Aldrich. All materials were used without further purification.

2.2. Fabrication of ZnO/Pd nanocomposites
In this experiment, glass substrates (10 mm × 25 mm × 1 mm) and all glassware were washed in ultrasonic cleaner by acetone, ethanol, and aquabidest, sequentially, and then dried in the oven. A thin ZnO film was made on the surface of glass substrates by the ultrasonic spray pyrolysis method as follows: 0.2 M of zinc acetate dihydrate was sprayed onto the surface of the heated glass substrate (450 °C) for 15 minutes by ultrasonic nebulizer (GEA 402 AI, GEA Medical, Indonesia), after that followed by annealing the sample at the same temperature for 1 hour. ZnO films was then grown by immersing the treated glass substrate in 10 mL of mixed solution of 0.05 M zinc nitrate hexahydrate and 0.05 M hexamethylenetetramine and heating them at 95 °C for 6 hours. The obtained ZnO NRs was then dried at 50 °C for 1 hour.

Pd NPs were deposited on the surface of ZnO NRs by photo reduction process. First, ZnO NRs on the glass substrate were immersed into 50 mL ethanol solution of 0.75 mM palladium chloride (PdCl₂) and irradiated them for 30 minutes in two different conditions. First condition, sample was irradiated under 365 nm UV lamp (Sankyo Denki F6T5BLB, Japan) (measured intensity of 5 mW/cm²) and labeled as ZnO/Pd (UV). The second sample was labeled as ZnO/Pd (Xe), wherein it was irradiated by Xenon lamp of Solar Simulator (Abet 10500, US) (measured intensity of 105 mW/cm²). Intensity measurement was conducted by using IL440 Photoresist Radiometer (International Light, USA). After that, each sample was rinsed off with aquabidest, sprayed with nitrogen gas and dried at 50 °C for 1 hour.

2.3. Structural and optical characterizations
The phase and crystal structure were examined by X-ray powder diffraction (XRD Bruker D8 Advance, Germany) with Cu Ka radiation (λ = 1.5418 Å). The surface morphology and elemental composition were observed by scanning electron microscopy (SEM; JEOL JSM IT-300LV, Japan) operated at 10 kV and energy dispersive spectroscopy (EDS; Oxford X-Max, UK), respectively. The measurement of the ZnO NRs and Pd NPs diameter was carried out by ImageJ software, while the crystallite size of ZnO NRs was calculated from XRD diffractogram by Scherrer equation [23,24]. The optical absorbance and photoluminescence spectrum were recorded by MAYA 2000Pro UV-Vis and photoluminescence spectrometer (Ocean Optics, USA), respectively.

2.4. Photocatalytic performance test
The photocatalytic performance test of ZnO/Pd nanocomposites was conducted by monitoring the photodegradation of methylene blue (MB) under simulated sun light (Solar simulator Abet 10500, US). ZnO/Pd nanocomposite was inserted into 10 mL of 5 ppm aqueous MB solution and then irradiated by the Xenon lamp of a Solar Simulator for 120 minutes. To monitor the MB degradation,
the absorption of the solution was measured using UV-Vis spectroscopy (Agilent Cary60, USA) for every 10 minutes. The degradation efficiency of MB was then calculated by the following equation [25]:

\[
\text{Degradation Efficiency } (\%) = \frac{A_0 - A_t}{A_0} \times 100 (\%)
\]

where \(A_0\) and \(A_t\) are the initial absorbance intensities of the MB solution and after an exposure time \((t)\), respectively.

### 3. Results and Discussions

#### 3.1. Morphological and elemental analyses

In order to determine the morphological properties and elemental composition of synthesized ZnO, SEM and EDS analysis was conducted. As shown in Figure 1a, the pristine ZnO nanorods have a hexagonal shape, while the Pd NPs that formed on the surface of the ZnO NRs have a sphere shape with different diameters (Figure 1b and 1c). The distributions of these diameters are shown in Figure 1d-f. According to that, the average diameter of ZnO NRs was 137 nm (Figure 1d) and the diameters of the Pd NPs in ZnO/Pd (UV) and ZnO/Pd (Xe) were 39 (Figure 1e) and 52 nm (Figure 1f), respectively.

The size of Pd NPs resulted from sunlight-assisted photoreduction process is bigger than that of UV-assisted process. This indicates that the visible and infrared light consisted in solar radiation might contributed as well in accelerating the formation of Pd NPs, thus larger size of Pd NPs was formed. Elemental composition analysis by EDS instrument resulted that Zn and O appear to be the dominant elements (inset Figure 1), as expected. The amount of Pd in the ZnO/Pd (UV) is about 3.64 wt\% (inset Figure 1b), and that is twice lower than that in the ZnO/Pd (Xe) sample (7.68 wt\%) (inset Figure 1c). This result is in agreements with the calculation result of size distribution (Figure 1d and 1f), which demonstrated that the size of Pd NPs on ZnO (UV) is smaller than that on ZnO (Xe).

#### 3.2. XRD analysis

Figure 2 shows the XRD patterns of the ZnO and ZnO/Pd nanocomposites. Based on the ZnO standard pattern (ICDD 00-036-1451), the synthesized ZnO is hexagonal wurtzite with nine peaks at \(2\theta\) of 31.77°, 34.42°, 36.25°, 47.54°, 56.60°, 62.86°, 66.38°, 67.96°, 69.10° indexed as lattice plane (100), (002), (101), (102), (110), (103), (200), (112), and (201) respectively. All samples have the highest intensity peak of plane (002) representing the c-axis as the preferred growth orientation, as shown in Figure 1a. The calculated crystallite size of ZnO was around 100 nm, which was almost the same as the average diameter of the ZnO NRs, as shown in the SEM images (Figure 1a). The ZnO XRD pattern, both the pristine ZnO NRs and ZnO/Pd nanocomposite, did not show any significant differences, indicating that the process of Pd NPs deposition did not change the phase or crystal structure of ZnO. Moreover, there is an additional peak at \(2\theta = 40.12^\circ\) in the XRD pattern of ZnO/Pd (UV) and ZnO/Pd (Xe). This peak is indexed as the Pd lattice plane (111) in the cubic crystal structure (ICDD 00-005-0681) and it demonstrates that the crystalline Pd NPs deposited successfully on the surface of ZnO. However, Pd peaks in ZnO/Pd (UV) XRD spectrum is lower than that in ZnO/Pd (Xe) spectrum, which may be due to the lower number and size of Pd NPs.
Figure 1. (a)-(c) Morphological analysis of ZnO NRs, ZnO/Pd (UV), and ZnO/Pd (Xe) nanocomposites, respectively, by SEM, inset: Elemental composition analysis by EDS. (d)-(f) Calculated diameter distribution of ZnO NRs, Pd NPs on ZnO NRs (UV), and Pd NPs on ZnO NRs (Xe) using ImageJ software.

Figure 2. The diffractogram of ZnO (black line) and ZnO/Pd nanocomposites (red and green line), inset: zoom out of the diffractogram of the palladium (111) peak area ($2\theta$ of 38°-42°).
3.3. Optical properties analysis
The optical properties both ZnO NRs and ZnO/Pd nanocomposites were studied by measuring the UV-Vis absorbance and photoluminescence emission as depicted in Figure 3a and b, respectively. According to Figure 3a, all samples have broad absorbance, including in the ultraviolet (< 400 nm) and visible light (400–700 nm) regions. This indicates that the synthesized material contained natural crystal defects that formed especially during the hydrothermal process [26,27,28]. ZnO/Pd nanocomposites show slightly higher intensity at all wavelengths. The higher absorbance intensity in the UV light region may be due to the localized surface plasmon resonance effect of spherical Pd NPs [18], whereas the increasing of absorbance in other regions is probably due to the different light absorption of ZnO itself. The band edges of ZnO/Pd nanocomposites also shifted to higher wavelengths.

Figure 3b shows the photoluminescence spectrum of ZnO and ZnO/Pd nanocomposites. ZnO NRs sample showed a sharp peak centered at a wavelength of 377 nm, which is a consequence of electron-hole recombination between the valence and conduction bands of ZnO [11]. In addition, a broad peak centered at a wavelength of 607 nm was also observed in all samples, wherein that peak is strongly correlated to the radiative transition to the energy levels of the defects of ZnO [29-30]. This result is consistent with the broad peak of UV-Vis absorbance (Figure 3a), which implies a large number of crystal defects in the synthesized ZnO structure. The addition of Pd NPs in ZnO/Pd (Xe) increases the PL intensity, unlike what happened in the ZnO/Pd (UV) sample, which experienced a decrease in PL intensity (Figure 3b). The decrease in PL intensity was generally due to the transfer of electrons from ZnO to Pd NPs, which reduces radiative recombinations [31].

3.4. Photocatalytic performance analysis
The photocatalytic performance of ZnO and ZnO/Pd nanocomposites is presented in Figure 4 and the degradation of the MB solution without a photocatalyst is included as a control. In the same period of 120 minutes, the lowest degradation was achieved by pristine ZnO NRs (% degradation is about 42 %) and then increased to 59 % and 63 % for ZnO/Pd (UV) and ZnO/Pd (Xe) photocatalysts, respectively. These results demonstrate that the addition of Pd NPs on ZnO NRs enhances the photocatalytic activity of ZnO NRs itself. This enhancement may be due to the increasing number of free electrons and holes created by the charge separation between ZnO and Pd NPs [14-17], which can react with the oxygen and hydroxyl ions in the water, lead the production of free radicals to decolorize MB solutions. In addition, the presence of ZnO crystal defects evidenced as broad absorbance in the visible light region also provides more free electrons and holes [11]. The addition of Pd NPs may increase the light absorbance of ZnO NRs due to two factors. First, a localized surface plasmon resonance effect and
second, Pd NPs can trap light in the surroundings of the ZnO NRs, leading to multiple scattering and less reflection over the whole light spectrum [31].

![Figure 4. The photocatalytic performance of ZnO and ZnO/Pd nanocomposites](image)

4. Conclusion
Pd NPs were successfully deposited onto the surface of ZnO NRs by photoreduction process using a 365 nm UV and a simulated solar light (Xe lamp). The SEM images and EDS results showed that irradiation by a Xe lamp produced a higher number and size (52 nm) of Pd NPs. The addition of Pd NPs on ZnO NRs enhanced the UV-Vis absorbance intensity at all wavelengths, shifted the band edge to higher wavelengths and decreased the PL intensity. Compared to pristine ZnO, the photocatalytic activity of ZnO/Pd (Xe) improved 21 % at the same solar irradiation intensity and time (120 min). The enhancement in photocatalytic performance may be due to the charge separation between ZnO to Pd NPs, which increases the number of free electrons and holes as well as free radicals to decolorize MB solutions.

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