Microwaved assisted synthesis Ag₂O/TiO₂/CeO₂ for highly efficient photocatalyst

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Abstract. Photocatalyst Ag₂O/TiO₂/CeO₂ composites were prepared using the microwave assisted method. The concentration of CeO₂ was varied from 25 weight percentage (wt.%) to 75 (wt.%), and the physical properties of the composites were studied by X-ray diffraction, thermogravimetric analysis and different thermal analysis, and UV-Vis spectroscopy. The composites were confirmed by the existence of the cubic phase from Ag₂O and CeO₂ and the anatase structure of TiO₂ nanoparticles. The thermal degradation analysis confirmed the weight lost at 400°C followed by the heat released around 200°C due to the phase transformation from Ag₂O into Ag nanoparticles. The photocatalytic activity of Ag₂O/TiO₂/CeO₂ composites were investigated to remove methylene blue from the aqueous solutions under alkaline condition. The degradation of methylene blue was analyzed by investigating the absorbance around 633 nm. Furthermore, the photocatalytic activity results show that the Ag₂O/TiO₂/CeO₂ composites exhibit good photocatalytic performance for removing methylene blue from the aqueous solution, indicating that the Ag₂O/TiO₂/CeO₂ composites are promising materials for waste water treatment.

1. Introduction

Recently, it is considerably important to modify semiconductor photocatalysts to improve the photocatalytic efficiency [1]. The conventional photocatalyst such as TiO₂ has been known as a promising photocatalyst due to its outstanding photocatalytic performance [2]. However, TiO₂ nanoparticles still have limited efficiency due to the high recombination rate of electrons and holes. Moreover, the single phase TiO₂ can only be activated under UV light irradiation, only requiring 5% of total solar irradiation [3]. Therefore, it is necessary to find a photocatalyst that has high efficiency and wide irradiation range to activate the photocatalyst.

Combining TiO₂ with other materials, the low band gap semiconductor can commonly extend the activation energy from photocatalyst from UV light irradiation to visible light irradiation [4]. Recently, Ag₂O (silver oxide) nanoparticles has become suitable for supporting the photocatalyst to extend the activation of photocatalyst into visible light range [5]. Several studies have studied the combination of TiO₂ and Ag₂O nanoparticles in the form of Ag₂O/TiO₂ composites and shown that the photocatalytic performance under visible light irradiations has increased [6]. The enhanced photocatalytic performance is due to the p-n junction formation from Ag₂O p-type and TiO₂ n-type semiconductors. The p-n junction formation is helpful in facilitating electron hole migration, efficiently retarding electron hole recombination [7].

Recently, cerium oxide (CeO₂) has also attracted considerable attention in the photocatalytic process due to several unique properties such as the following: CeO₂ is a rare earth metal oxide with good chemical stability. The mutation of the oxidation states of Ce⁴⁺ and Ce³⁺ in this metal oxide could create oxygen vacancies. The band gap of CeO₂ can be narrowed by adjusting the level of Ce³⁺ ions,
which will effectively increase photocatalytic activity under visible light irradiation [8]. Therefore, combining AgO/TiO nanocomposites with CeO nanoparticles produces novel materials that are promising for photocatalytic applications.

Therefore, this study evaluates the formation of AgO/TiO/ceO composites with different CeO loading weight percentages as photocatalysts for waste water removal. In this study, AgO/TiO/ceO nanoparticles are investigated by X-ray diffraction (XRD), UV-Vis absorbance, differential thermal analysis, and thermogravimetric analysis. The photocatalytic activities were investigated for methylene blue solution through observation of its degradation. The influence of pH, initial dye concentration, catalyst dosage, and the addition of the scavengers were investigated to understand the photocatalytic behavior of AgO/TiO/ceO composites.

2. Experimental

2.1. Materials
Cerium sulfate pentahydrate [Ce(SO)2·5H2O, 99% Merck], silver nitrate (AgNO3, 99% Merck), titanium dioxide (TiO2, 99% Merck), sodium hydroxide (NaOH, 99% Merck) were analytical grade and purchased from Merck without further purifications.

2.2. CeO nanoparticles synthesis
The CeO nanoparticles were synthesized using the sol-gel method. In the typical process, CeSO4·5H2O was dissolved in water (solution A) and stirred for several minutes. After CeSO4·5H2O being completely dissolved, then the solution is added with NaOH solution. The mixture was then kept stirred using a magnetic stirrer with a constant temperature of 80 °C for 4h. The precipitate was obtained from the results of the centrifugation process followed by drying in a vacuum, then proceed with calcination at a temperature of 800 °C.

2.3. Synthesis AgO/TiO/ceO composites
AgO/TiO/ceO were synthesized using the microwave-assisted method. There are three prepared solution, AgNO3 (silver nitrate) solution (which is dissolved in 40 mL water), SDS (sodium dodecyl sulfate) solution (which is dissolved with 80 mL water), and 10 mM NaOH solution (which is dissolved in 40 mL water). TiO2 and CeO2 nanoparticles were dispersed in AgNO3 solution with a magnetic stirrer. While still stirring, the SDS solution was then added to the mixture. After that, NaOH solution was added and stirring continued for 10 minutes. After the solution reaches homogeneity, the solution is irradiated with microwave for 2 minutes at 800 W. The precipitate was obtained from centrifugation then it was rinsed with ethanol and DI water, and dried for 5 hours 120°C under air condition.

2.4. Characterization
The structural properties of the samples were characterized by XRD Rigaku Miniflex 600 (30 kV, 15 mA). UV-Vis spectrometer Hitachi UH5300 was used to investigate the optical properties of the samples in the range of 200 nm to 800 nm. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (Rigaku Thermo Plus EVO2 TG-8121) was performed to characterize the thermal properties of the samples. It operated from room temperature to 500 °C with alumina as a reference.

2.5. Photocatalytic measurement
Photocatalytic performance of AgO/TiO/ceO were tested under visible light irradiation to remove methylene blue from the solution using 40 W Xe lamp as an irradiation source. The methylene blue solution was set at 20 mg/L and 0.03 g catalyst dosage. To ensure the solution has reached the adsorption-desorption equilibrium before irradiation, the solution is left for 30 minutes in the dark. At the specified time interval, the methylene blue solution was observed by UV-Vis spectroscopy to examine the degradation process. Degradation can be obtained by the following equation:

\[
\text{Degradation: } \frac{C_t}{C_0}
\]

where \(C_0\) represents the initial dye concentration and \(C_t\) represents the dye concentration after time \(t\).
Table 1. Lattice parameters and grain size of AgO/TiO/CoO composites with different molar ratios.

| Sample       | Lattice parameters | Grain Size (nm) |
|--------------|--------------------|-----------------|
|              | AgO a=b=c | Ag a=b=c | CeO a=b=c | TiO a=b=c | Ag | Ag | CeO | TiO |
| 25 wt.% CeO  | 4.7238    | 4.0894    | 5.4030    | 3.7844    | 9.5171 | 15  | 12  | 13  | 39  |
| 50 wt.% CeO  | 4.7238    | 4.0894    | 5.4030    | 3.7844    | 9.5171 | 14  | 11  | 12  | 33  |
| 75 wt.% CeO  | 4.7238    | 4.0894    | 5.4030    | 3.7844    | 9.5171 | 11  | 11  | 12  | 24  |

Figure 1. XRD spectra of AgO/TiO/CoO composites with different molar ratio.

Figure 2. UV-Vis absorbance spectra of AgO/TiO/CoO composites with different molar ratio.

3. Results and discussion

The structural properties of Ag2O/TiO2/CoO2 with different CeO2 weight percentages investigated through XRD pattern are plotted in figure 1. As comparison, the XRD spectra of AgO, TiO2, and CeO2 are also plotted in the figure. The figure shows that the XRD spectra AgO revealed several diffraction peaks at 20 ≈ 32.79°, 38.02°, 54.98°, and 65.61°, showing the diffraction planes of (111), (200), (220), and (311), respectively, from cubic structure of AgO nanoparticles. In addition, the XRD spectra of TiO2 shows several diffraction peaks at 20 ≈ 25.30°, 37.60°, 48.02°, 53.55°, 54.93°, 62.53°, 68.75°, and 70.59°, and 65.61° that correspond to the existence of (101), (004), (200), (105), (211), (204), (116), and (220) planes, respectively, of the anatase structure of TiO2. The XRD spectra of CeO2 revealed several peaks at 20 ≈ 28.21°, 32.82°, 47.33°, and 56.08° that correspond to the existence of (111), (200), (220), and (311) planes, respectively, of cubic structures from CeO2 nanoparticles. The formations of Ag2O/TiO2/CoO2 composites with different CeO2 loading concentrations confirm the existence of AgO, TiO2, and CeO2 structure that indicate the successfully synthesized composites. The peak intensity of CeO2 also increased with the increased CeO2 contents. However, with increased CeO2 content, a new peak at 20 ≈ 44.10° appeared that corresponds to the existence of Ag nanoparticles. The lattice parameters and grain size of the samples were investigated using the Rietveld refinement method and the Debye Scherrer equations, and the results are presented in table 1. The results of the table show that the corresponding lattice parameters of AgO, TiO2, and CeO2 remain unchanged after being formed in the Ag2O/TiO2/CoO2 composites. This indicates that the formation of Ag2O/TiO2/CoO2 does not change the structural properties of AgO, TiO2, and CeO2 nanoparticles.

The optical properties of the samples investigated by UV-Vis absorbance spectra are plotted in figure 2. As comparison, the UV-Vis absorbance spectra of AgO are also plotted in the figure.
Figure 3. TGA/DTA analysis of Ag$_2$O/TiO$_2$/CeO$_2$ composites.

Figure 4. Absorbance spectra of methylene blue after photocatalytic reactions.

Figure 5. Photocatalytic performance of Ag$_2$O/TiO$_2$/CeO$_2$ composites with different molar ratios.

The figure shows that Ag$_2$O nanoparticles composites show low absorbance ability under visible light irradiations. However, after forming the Ag$_2$O/TiO$_2$/CeO$_2$ composites, the broad absorbance under visible light irradiations had a maximum intensity at 400 nm that could be due to the existence of surface plasmon resonance (SPR), i.e., the collective oscillations of conduction electrons in presence of electromagnetic radiation, from the silver nanoparticles. In addition, nanoparticles of noble metal (Au, Ag and Cu) exhibit interesting optical properties that also come from the SPR of the metal nanoparticles.

Thermogravimetric analysis and differential thermal analysis were performed to identify the thermal properties of the samples. The TGA analysis of the Ag$_2$O/TiO$_2$/CeO$_2$ composites is plotted in figure 3, and the figure shows that the Ag$_2$O/TiO$_2$/CeO$_2$ composites pose good stability from room temperature until 400 °C. However, after 400 °C, thermal degradation occurs. The thermal degradation at 400 °C is due to the phase transformation from Ag$_2$O into Ag nanoparticles, and the differential thermal analysis of the Ag$_2$O/TiO$_2$/CeO$_2$ composite confirms that the thermal degradation at 400 °C is an exothermic process.

The methylene blue degradation through photocatalytic process is plotted in figure 4. The figure shows that the methylene blue has a maximum intensity at 630 nm and gradually decreases with increased irradiation time. This indicates that the methylene blue concentration has been reduced after photocatalytic treatment using Ag$_2$O/TiO$_2$/CeO$_2$ composites. The photocatalytic performances with different molar ratio are also plotted in Figure 5. The figure shows that all samples have good
Table 2. Degradation percentage and rate constant of methylene blue degradation using Ag₂O/TiO₂/CeO₂ composites.

| Samples              | Degradation (%) | Rate constant (min⁻¹) |
|----------------------|-----------------|-----------------------|
| TiO₂                 | 54              | 0.00651               |
| 25 wt.% CeO₂         | 80              | 0.01322               |
| 25 wt.% CeO₂         | 91              | 0.01994               |
| 25 wt.% CeO₂         | 97              | 0.02777               |

Figure 6. The influence of pH solution on the photocatalytic performance.

Figure 7. Point of Zero Charge (PZC) measurement.

The photocatalytic performance for degrading methylene blue from the aqueous solution. The composites with 25 wt.% CeO₂ has can degrade methylene blue by approximately 80%. The photocatalytic activity further increases with the increased CeO₂ weight percentages from 50 wt.% and 75 wt.% with the degradation ability being approximately 91% and 97%, respectively. The degradation rate of the methylene blue degradation followed pseudo-first order kinetic reactions with a rate constant, as shown in table 2. The results in the table show that the composite samples with 75 wt.% CeO₂ exhibit faster degradation ability.

The photocatalytic performance of Ag₂O/TiO₂/CeO₂ composites was performed in methylene blue degradation. The influence of pH solution is an important aspect in the photocatalytic process, and the pH of methylene blue solution varied between 3, 5, 7, 9, 11, and 13. The result is plotted in figure 6. The figure shows that it is very difficult under an acidic condition to degrade methylene blue from the aqueous solution. However, after increasing the pH solution from 7 to 13, the photocatalytic performance significantly increased. The figure also shows that the pH solution plays a significant role in the photocatalytic process. Several researchers suggest that the surface charge between methylene blue and photocatalyst is important in the photocatalytic process. Methylene blue is the cationic dye, when it dissolved in water, it will become positively charged. To know the surface charge of the photocatalyst, point of zero charge measurement were performed, and the point of zero charge result is plotted in figure 7. The figure shows that under acidic conditions (pH 3–5), the surface charge of photocatalyst is positively charged and the point of zero charge of the photocatalyst is 6.28. After pH reaches 6.4, the surface of photocatalyst become negatively charged. The low photocatalytic performance under acidic condition is due to the repulsive effect from the positive charge of the photocatalyst and the cationic surface of methylene blue. However, under a pH above the point of zero charge, the attraction between the negatively charged photocatalyst and methylene blue provides better contact between photocatalyst and methylene blue.
4. Conclusions
Ag$_2$O/TiO$_2$/CeO$_2$ composites with different CeO$_2$ loading were successfully synthesized through the microwave-assisted method. The structural analysis revealed that the composites samples pose a heterostructure consisting of a cubic structure from Ag$_2$O and CeO$_2$ and an anatase structure from TiO$_2$. Moreover, the existence of noble metal silver could be detected by the existence of SPR in the UV-Vis absorbance spectra at 400 nm. The photocatalytic activity revealed that Ag$_2$O/TiO$_2$/CeO$_2$ composites with 75 wt.% CeO$_2$ shows the highest photocatalytic performance, and the surface of the catalyst is positively charged above pH 6.28, implying that methylene blue (cationic dye) is efficiently degraded under alkaline conditions.

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