

Photocatalytic Performance of CdS/(Pt-TiO₂)-Pumice for E. Coli Disinfection in Drinking Water

Ratnawati, Singgih Hartanto, Yuli Amalia Husnil, Christin Rina Ratri

Abstract: Photocatalytic removal of *E. coli* pathogen bacteria existing in drinking water was studied in this paper. CdS/(Pt-TiO₂) nanocomposite was produced by depositing Pt/CdS on TiO₂ nanoparticles with chemical reduction and hydrothermal method. On the other hand, CdS/(Pt-TiO₂)-Pumice was fabricated by immobilizing of titania composite onto pumice with dip coating method to become photocatalysis without causing problem in the separation titania from solution. The Field Emission Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) were utilized to characterize the photocatalyst samples. Based on the morphology characterization, it was observed that successful deposition of Pt and CdS on TiO₂ occurred. Furthermore, decorating Pt/CdS on TiO₂ can reduce bandgap energy compare to the bare TiO₂ according to the UV-Vis DRS analysis. The treatment of *E. coli* inactivation with CdS/(Pt-TiO₂), CdS/(Pt-TiO₂)-pumice and without photocatalyst had performed in the photoreactor that irradiated with mostly visible light in 90 min. The amount of photocatalyst and the contact mechanism between the photocatalyst and bacteria in the water would effects the performance of E-coli photocatalytic disinfection in drinking water.

Keywords : , CdS/(Pt-TiO₂), *E. coli*, Photocatalysis), Pumice.

I. INTRODUCTION

The lacking of clean freshwater is one of the environment issues that faced in Indonesia. The serving of clean water especially for drinking water that free from microorganisms still a problem that must be overcome. Nowadays, many people are sickened caused by the availability microorganisms such as E coli and viruses in drinking water. As a consequence, many efforts concerning the public health problem should be find out in the decontaminated water which is cheap, effective and environmentally friendly.

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* Correspondence Author

Ratnawati*, Chemical Engineering Department, Institut Teknologi Indonesia, Tangerang Selatan, Indonesia. Email: rnmw63@yahoo.co.id

Singgih Hartanto, Chemical Engineering Department, Institut Teknologi Indonesia, Tangerang Selatan, Indonesia. Email: singgih.hartanto@iti.ac.id

Yuli Amalia Husnil, Chemical Engineering Department, Institut Teknologi Indonesia, Tangerang Selatan, Indonesia. Email: yuli.husnil@gmail.com

Christin Rina Ratri, Physical Research Laboratory, Indonesia Institut of Science, Tangerang Selatan, Indonesia. Email: christinrina@gmail.com

Traditionally, water disinfection is performed by chlorination process, ozonation, or UV-irradiation, but it still has drawback [1]. In recent years, photocatalysis, a green technology, that utilize solar energy to drive the semiconductor photocatalyst, is an advanced oxidation processes (AOP) which can enhance disinfection capability to solve the environment pollutions [2,3,4] and it has attracted great attention. TiO₂ is one of the semiconductors photocatalyst that promise with its outstanding performance in environment application [5]. It is widely used since its properties such as cheap, non-toxicity, high oxidation ability and chemical stability [3,6]. However, TiO₂ still has drawback in its applications since it has wide band gap that can only active in UV light region and high recombination rate of electron-hole pairs [7]. Furthermore, titania also has problem due to the difficulty in separation process from the solution after used.

To reduce the drawback, many efforts have been done to sensitize titania with other semiconductors that have narrower band gap, for instance CdSe and CdS for improving the visible-light response [7,8] and to load metal such as Ni, Au, Pd and Pt, to diminish the rapid recombination of electron hole pairs that results from photocatalytic process [6,7]. Pt with the largest work function among noble metal, is one of the excellent electrons trapper [6], and therefore the abundance of holes available can undergo oxidation reaction that greatly enhances the photocatalytic performance. Synthesizing CdS/(Pt-TiO₂) would give synergy effect that enhance photocatalytic performance. In addition, immobilizing this photocatalyst on pumice as a solid support can reduce the difficulty in separation after used [4,9].

Depositing CdS on TiO₂ nanotube arrays (TNTA) and TiO₂ nanoparticles/TNP has been performed for the solar H₂ production [8], degradation of pollutant rhodamine B [3] and methylene blue [10]. Some studies also executed by decorating Pt on: TNTA for H₂ reduction [11], TiO₂ nanotube/TNT for fuel cell and H₂ production [12,13], TNP for hydrogen production [14]. Depositing Pt and CdS on TNTA was studied for reduction of rhodamine B [15]. Meanwhile, photocatalyst CdSe/CdS/Pt/TNTA is used for immunoassay of octachlorostyrene [7]. However, to the best of our knowledge, photocatalytic performance of CdS/(Pt-TiO₂)-pumice for *E. coli* disinfection in drinking water is still rarely studied.

In this study, we fabricate CdS/(Pt-TiO₂) nanoparticles

using H₂PtCl₆ with reducing agent NaBH₄ and CH₄N₂S/CdCl₂ as precursor respectively. The as-prepared composites are characterized by the use of TEM/FESEM and UV-Vis DRS Spectrophotometer.

The efficiency of *E. coli* photocatalytic disinfection in drinking water on CdS/Pt-TiO₂ and CdS/Pt-TiO₂-pumice were tested.

II. MATERIALS AND METHOD

A. Materials

TiO₂ (79% anatase, 21% rutile) with the crystalline size of 20 and 23 nm was purchases from Evonic Industry. Chloroplatinic acid (H₂PtCl₆ 6H₂O), sodium borohydride (NaBH₄), thiourea (CH₄N₂S, 98%), cadmium chloride (CdCl₂, 99%), ethanol (96%) and Tetra Ethyl Ortho Silicate (TEOS) with chemical formula: Si(OC₂H₅)₄, purity 98% were obtained from Sigma Aldrich. There is no further purification for all chemicals. All solutions and media for growing *E. coli* were prepared using high purity distilled water. Natural pumice was supplied from Bali.

B. Synthesis of CdS/(Pt-TiO₂) and CdS/(Pt-TiO₂)-pumice

Solution containing CH₄N₂S and CdCl₂ were used as S and Cd precursor respectively. After reaction, precipitate of CdS formed was then washed and dried. The sol of 1 g TiO₂ with 1w% of CdS were mixed ultrasonically to produce CdS-TiO₂ via hydrothermal method until the paste of CdS-TiO₂ was obtained, and followed by calcination at 550 °C in the muffle furnace.

Pt-TiO₂ was made by added NaBH₄ in excess to the suspension of 2 g TiO₂ in 400 ml aqueous solution that contained precursor H₂PtCl₆ (Pt = 1 w%) under stirring for 1 h. Subsequently, centrifugation of the solution was performed and water/ethanol were used to wash the filtrate. After that, the slurry was dried for 3 h at 90 °C and heated for 1 h at 130 °C. Finally, the sample underwent calcination for 1 h at 500 °C.

To prepare photocatalyst CdS/Pt-TiO₂, CdS (1 %w) was mixed ultrasonically with the solution of Pt-TiO₂ for 30 min and followed by drying at 110 °C. The sample was then experienced calcination process for 1 h at 500 °C. After that, the photocatalyst used for photocatalytic disinfection of *E. coli* and also underwent characterization.

The dip coating method is used to prepare immobilized composite CdS/(Pt-TiO₂) on pumice. First of all, pumice experienced size reduction to around 4 – 5 cm, followed by ultrasonic cleaning for certain time and heated at 400 °C in the furnace for 1 h. Subsequently, dip coating of pumice in sol of photocatalysts (1% and 2.5% w/w of CdS/(Pt-TiO₂) on pumice) with TEOS (0.5 ml TEOS for 1 g) was performed. This composite was then evaporated at 350 °C for 1 h. Finally, the photocatalysts were characterized and used for photocatalytic disinfection test of *E. coli* in drinking water.

C. Characterization of CdS/Pt-TiO₂

FESEM (JEOL Multibeam System 4610F type), TEM and

selected area electron diffraction/SAED (FEI Tecnai type G2-STWIN 200 kV) were applied to study the surface morphology of the photocatalyst samples. UV-Vis DRS analysis was employed using Spectrophotometer Shimadzu 2450 type. The reflectance and absorbance of the photocatalysts were recorded under the ambient condition in the wavelength range of 200-600 nm.

D. Criteria Photocatalytic disinfection of E. coli in drinking water

The removal of *E. coli* experiments by photocatalytic process was performed in the Pyrex glass reactor with 400 ml of solution (nutrient broth that contains of *E. coli*) with 20 g of CdS/(Pt-TiO₂)-pumice and it equipped with magnetic stirrer to make homogeneous system and Philips lamp (83% visible and 17% UV light) to trigger the photocatalytic reaction. Incubation of *E. coli* was performed in the nutrient broth media for 24 h, 37°C on the rotary shaker with 150 rpm. The amount of composite on the pumice were varied at 1 and 2.5 % w/w. The photoreactor system was placed inside a reflector box. Another experiment was also performed with composite that uncoated on pumice to get comparative study. To evaluate the photocatalytic performance, every 10 min for 90 min process, the total number of bacteria were determined using a viable plate counting method with ten-fold dilution.

III. RESULTS AND DISCUSSION

A. FESEM/TEM analysis

FESEM images of CdS/(Pt-TiO₂), pumice and CdS/(Pt-TiO₂)-pumice are depicted in Fig. 1. Fig. 1C pointed out that pumice has covered on CdS/(Pt-TiO₂). It shows that pumice could be impregnated by CdS/(Pt-TiO₂). Although Pt and CdS were not visible in the FESEM image, it can be proven by TEM analysis. Similar results are also stated by Zhu et al. and Van et al. [7, 15]. To make further investigation the microstructure of CdS/(Pt-TiO₂), TEM and selected area electron diffraction (SAED) were employed as presented in Fig. 2. As shown in that figure, Pt and CdS are decorated on TiO₂. TEM image confirms that the light particles are CdS and the dark one is Pt [15]. The diffraction of Pt (1 1 1) and CdS (1 1 1) that detected in SAED confirms the existence of polycrystalline of Pt and CdS. The diffraction spots with d spacing 0.23, 0.33, 0.35 are corresponding to (111) plane of Pt, (111) plane of cubic CdS and (101) crystal plane of TiO₂ respectively [15]. This result further give evidence that Pt and CdS are decorated on TiO₂.

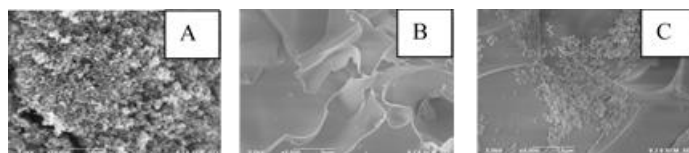


Fig 1. FESEM images of (A) CdS/(Pt-TiO₂), (B) Pumice (C) CdS/(Pt-TiO₂)-pumice

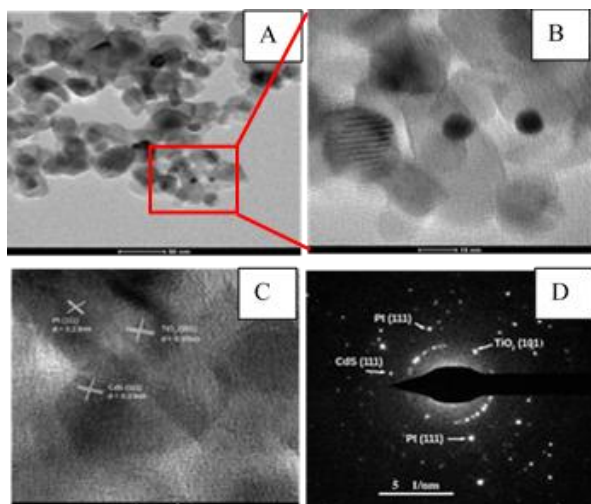


Fig 2. TEM images of CdS/(Pt-TiO₂) at (A) low, (B) high magnification, (C) high resolution and (D) SAED pattern

B. UV-Vis DRS analysis

Fig. 3 shows the Tauc plots with Kubelka-Munk function that can be used to determine the band gap energy of various photocatalysts [6,8,]. The band gap energy was obtained by extrapolation of the linear portion of the Tauc plot $(F(R).hv)^{0.5}$ to the energy (hv) axis. Pure TiO₂ has the bandgap of 3.17 eV and can only absorb the UV light (< 390nm). On the other hand, the decoration of Pt and CdS on TiO₂ could present strong absorptions in redshift region. As a result, lowering band gap energy of Pt-TiO₂, CdS-TiO₂, and CdS/(Pt-TiO₂) were occurred compare to the based material (TiO₂). It is most likely due to deposition of CdS and Pt on TiO₂ and could come from the electronic interaction among TiO₂, Pt and CdS as reported by previous authors [15]. The lowering band gap of Pt-TiO₂, CdS-TiO₂ and CdS/(Pt-TiO₂) suggests that decoration of Pt and CdS on TiO₂ can promote a red shift of photon absorption.

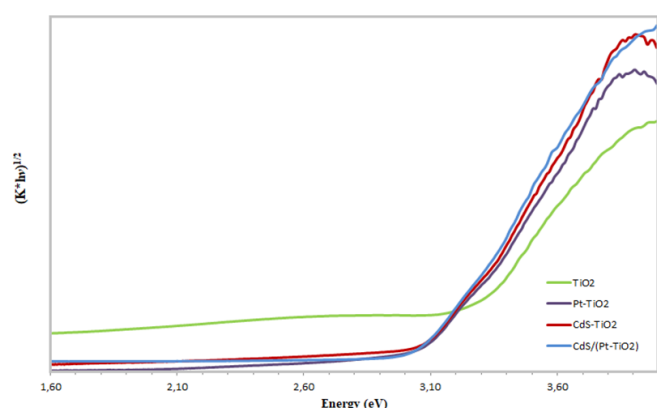
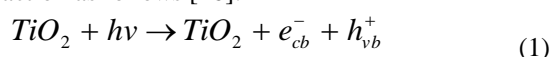


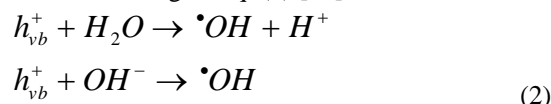
Fig. 3. Tauc plot of transformed Kubelka-Munk function vs energy (hv) for various photocatalysts, where $F(R) = (1-R)^2/2R$, $R =$ reflectance, $hv =$ photon energy

C. Photocatalytic disinfection of *E. coli* in drinking water

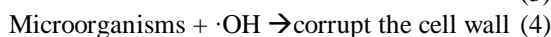
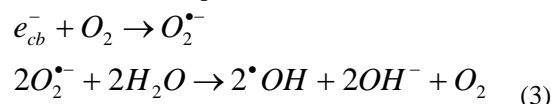
Decreasing the number of *E. coli* as a function of irradiation time were presented in Fig. 4 with different concentration and photocatalyst samples. The mechanism of photocatalytic disinfection could be explained according the reaction as follows [16]:



The reaction of water with hole in the valence band produces $\bullet OH$ (hydroxyl radical) as reactive oxidant with the reaction according to Eq. (2) [16]:



Meanwhile O₂ can react with electrons in the conduction band to become superoxide anion. The superoxide anion reacts with water to produces the $\bullet OH$ as follows [16]:



As shown in Fig. 4, 2.5% w/w of photocatalyst toward pumice performed the best photocatalyst performance since it gave higher *E. coli* reduction compare to 1% w/w. This is because, more $\bullet OH$ can corrupt cell wall, cell membrane and finally damage the nucleus. For the CdS/(Pt-TiO₂) that uncoated on pumice (pure CdS/Pt-TiO₂ as photocatalyst), the photodegradation of *E. coli* was faster compare to the CdS/(Pt-TiO₂)-pumice. This phenomenon is caused by CdS/(Pt-TiO₂) in the suspension have larger surface area that irradiated by photon compare to the CdS/(Pt-TiO₂)-pumice, and therefore more $\bullet OH$ produced and it will attack the *E. coli*. As a consequence, photocatalytic reaction rate on pure CdS/(Pt-TiO₂) in the solution faster than on CdS/(Pt-TiO₂)-pumice. If the removal of the bacteria performed without photocatalyst (only irradiation by mercury light), the efficiency of *E. coli* photocatalytic disinfection is slower than if it used it. This can be ascribed that the ability of UV light in the working against the DNA of bacteria is smaller compare to the $\bullet OH$ (hydroxyl radical)

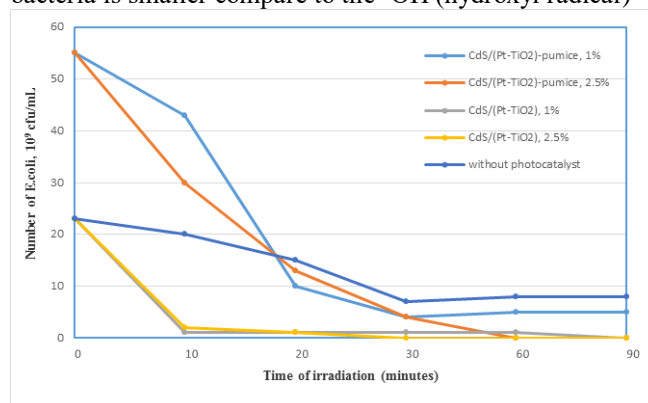


Fig. 4. The effect of various photocatalyst on *E. coli* disinfection

IV. CONCLUSION

Decorating of Pt and CdS on TiO₂ has been successfully performed evidenced by TEM analysis and therefore it could enhance its photocatalytic performance. Although pure dS/(Pt-TiO₂) gave better performance compare to CdS/(Pt-TiO₂)-pumice, dip coating photocatalyst on pumice gave benefit since it doesn't need additional equipment for separating pure CdS/(Pt-TiO₂) from the solution.



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REFERENCES

1. W. Wang, G. Huang, J. C. Yu, P. K. Wong, "Advances in photocatalytic disinfection of bacteria: Development of photocatalysis and mechanisms," *Journal of Environmental Science*, Vol 34, pp. 232-247, 2015
2. Abu S. P, A. Ghicov, S. Aldabergenova, P. Drechsel, D. LeClere. "Formation of double-walled TiO₂ nanotubes and robust anatase membranes," *Advance Material*, Vol 20, pp. 4135-4139, 2008
3. X. Cheng, G. Pan, X. Yu, T. Zheng, "Preparation of CdS NCs decorated TiO₂ nano-tubes arrays photoelectrode and its enhanced photoelectrocatalytic performance and mechanism," *Electrochemical Acta*, Vol 105, pp. 535-541, 2013
4. M. Subrahmanyam, P. Boule, V. D. Kamari, D. N. Kumar, M. Sancelme, A. Rachel, "Pumice stone supported titanium dioxide for removal of pathogen in drinking water and recalcitrant in wastewater," *Solar Energy*, Vol 82, pp. 1099-1106, 2008
5. Y. Wang, Y. He, Q. Lai, M. Fan, "Review of the progress in preparing nano TiO₂: An important environmental engineering material," *Journal of Environmental Sciences*, Vol 26, pp. 2139-2177, 2014
6. Slamet, Ratnawati, J. Gunlazuardi, E. L Dewi., "Enhanced photocatalytic activity of Pt deposited on titania nanotube arrays for the hydrogen production with glycerol as a sacrificial agent," *International Journal of Hydrogen Energy*, Vol 42, pp. 24014-24025, 2014
7. M. Van, W. Li, P. Sheng, H. Van, Q. Cai, "Photoelectrochemical label-free immunoassay of octachlorostyrene based on heterogeneous CdSe/CdS/Pt/TiO₂ nanotube array," *Journal Electroanalytical Chemistry*, Vol 736, pp. 69-75, 2015
8. Y. Zhu, Y. Wang, Z. Chen, L. Qin, L. Yang, "Visible light induced photocatalysis on CdS quantum dots decorated TiO₂ nanotube arrays," *Applied Catalysis. A: Environmental*, Vol 498, pp. 159-166, 2016
9. K.V.S Rao, A. Rachel, M. Subrahmanyam, P. Boule, "Immobilization of TiO₂ on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants," *Applied. Catalysis. B: Environmental*, Vol 46, pp. 77-85, 2003
10. A. Makama, A. Salmiaton, E. Saion, T. Chong, N. Abdullah, "Synthesis of CdS sensitized TiO₂ photocatalysts: methylene blue adsorption and enhanced photocatalytic activities," *International Journal of Photoenergy*, pp. 1-14, 2016
11. C. Zhang, H. Yu, Y. Li, L. Fu, Y. Gao, "Simple synthesis of Pt/TiO₂ nanotube arrays with high activity and stability," *Journal Electroanalytical Chemistry*, Vol 701, pp. 14-19, 2013
12. R. Antony, T. Mathews, C. Ramesh, N. Murugesan, A. Dasgupta., "Efficient photocatalytic hydrogen generation by Pt modified TiO₂ nanotubes fabricated by rapid breakdown anodization," *International Journal of Hydrogen Energy*, Vol 37, pp. 8268-8276, 2012
13. F. M. Hassan, H. Nanjo, S. Venkatachalam, M. Kanakubo, T. Ebina, "Functionalization of electrochemically prepared titania nanotubes with Pt for application as catalyst for fuel cells," *Journal of Power Sources*, Vol. 195, pp. 5889-5895, 2010
14. V. M. Daskalaki, D. I. Kondarides, "Efficient production of hydrogen by photo-induced reforming of glycerol at ambient conditions", *Catalysis Today*, Vol 144, pp. 75-80, 2009
15. Y. Zhu, Y. Wang, Z. Chen, L. Qin, L. Yang, "Construction of hybrid Z-scheme Pt/CdS-TNTAs with enhanced visible-light photocatalytic performance," *Applied Catalysis B: Environmental*, Vol 163, pp. 16-22, 2015
16. S. Souzanchi, F. Vahabzadeh, S. Fazel, S. N. Hosseini, "Performance of an Annular Sieve -Plate Column photoreactor using immobilized TiO₂ on stainless steel support for phenol degradation," *Chemical Engineering Journal*, Vol 223, pp. 268-276, 2013

AUTHRS PROFILE



Ratnawati, Graduate Doctoral Program at Chemical Engineering Department, Universitas Indonesia. Scopus H Index = 3



Singih Hartanto, Graduate Master Program at Chemistry Department, Universitas Indonesia, Google Scholar Index = 3



Yuli Amalia Husnil, Graduate Ph. D Program at Chemical Engineering, Yeungnam University, South Korea, Scopus H Index = 4



Christin Rina Ratri, Graduate Master Program at Advance Materials Engineering, The University of Manchester, United Kingdom.