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

by Ratnawati .

Photocatalytic Performance of CdS/(Pt-TiO_2)-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-TiO_2) nanocomposite was produced by depositing Pt/CdS on TiO_2 nanoparticles with chemical reduction and hydrothermal method. On the other hand, CdS/(Pt-TiO_2)-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 TiO_2 occurred. Furthermore, decorating Pt/CdS on TiO_2 can reduce bandgap energy compare to the bare TiO_2 according to the UV-Vis DRS analysis. The treatment of E. coli inactivation with CdS/(Pt-TiO_2), CdS/(Pt-TiO_2)-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-TiO_2), *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 overcame. 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.

Revised Manuscript Received on January 15, 2020.
* Correspondence Author
Ratnawati*, Chemical Engineering Department, Institut Teknologi Indonesia, Tangerang Selatan, Indonesia. Email: mwt63@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. TiO_2 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, TiO_2 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-TiO_2) 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 TiO_2 nanotube arrays (TNTA) and TiO_2 nanoparticles/TNP has been performed for the solar H_2 production [8], degradation of pollutant rhodamine B [3] and methylene blue [10]. Some studies also executed by decorating Pt on: TNTA for H_2 reduction [11], TiO_2 nanotube/TNT for fuel cell and H_2 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-TiO_2)-pumice for *E. coli* disinfection in drinking water is still rarely studied.

In this study, we fabricate CdS/(Pt-TiO_2) nanoparticles using H_2PtCl_6 with reducing agent $NaBH_4$ and $CH4N_2S/CdCl_2$ 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 $CdS/Pt\text{-}TiO_2$ and $CdS/Pt\text{-}TiO_2$-pumice were tested.

II. MATERIALS AND METHOD

A. *Materials*

TiO_2 (79% anatase, 21% rutile) with the crystalline size of 20 and 23 nm was purchases from Evonic Industry. Chloroplatinic acid (H_2PtCl_6 $6H_2O$), sodium borohydride ($NaBH_4$), thiourea (CH_4N_2S, 98%), cadmium chloride ($CdCl_2$, 99%), ethanol (96%) and Tetra Ethyl Ortho Silicate (TEOS) with chemical formula: $Si(OC_2H_5)_4$, 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 $CdS/(Pt\text{-}TiO_2)$ and $CdS/(Pt\text{-}TiO_2)$-pumice*

Solution containing CH_4N_2S and $CdCl_2$ were used as S and Cd precursor respectively. After reaction, precipitate of CdS formed was then washed and dried. The sol of 1 g TiO_2 with 1w% of CdS were mixed ultrasonically to produce $CdS\text{-}TiO_2$ via hydrothermal method until the paste of $CdS\text{-}TiO_2$ was obtained, and followed by calcination at 550 ^oC in the muffle furnace.

$Pt\text{-}TiO_2$ was made by added $NaBH_4$ in excess to the suspension of 2 g TiO_2 in 400 ml aqueous solution that contained precursor H_2PtCl_6 (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 ^oC and heated for 1 h at 130 ^oC. Finally, the sample underwent calcination for 1 h at 500 ^oC.

To prepare photocatalyst $CdS/Pt\text{-}TiO_2$, CdS (1 %w) was mixed ultrasonically with the solution of $Pt\text{-}TiO_2$ for 30 min and followed by drying at 110 ^oC. The sample was then experienced calcination process for 1 h at 500 ^oC. 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 $CdS/(Pt\text{-}TiO_2)$ 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 ^oC in the furnace for 1 h. Subsequently, dip coating of pumice in sol of photocatalysts (1% and 2.5% w/w of $CdS/(Pt\text{-}TiO_2)$ 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. coly* in drinking water.

C. *Characterization of $CdS/Pt\text{-}TiO_2$*

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 $CdS/(Pt\text{-}TiO_2)$-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^oC 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 $CdS/(Pt\text{-}TiO_2)$, pumice and $CdS/(Pt\text{-}TiO_2)$-pumice are depicted in Fig. 1. Fig. 1C pointed out that pumice has covered on $CdS/(Pt\text{-}TiO_2)$. It shows that pumice could be impregnated by $CdS/(Pt\text{-}TiO_2)$. 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 $CdS/(Pt\text{-}TiO_2)$, 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 TiO_2. 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 TiO_2 respectively [15]. This result further give evidence that Pt and CdS are decorated on TiO_2.

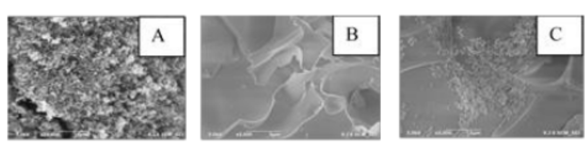

Fig 1. FESEM images of (A) $CdS/(Pt\text{-}TiO_2)$, (B) Pumice (C) $CdS/(Pt\text{-}TiO_2)$-pumice

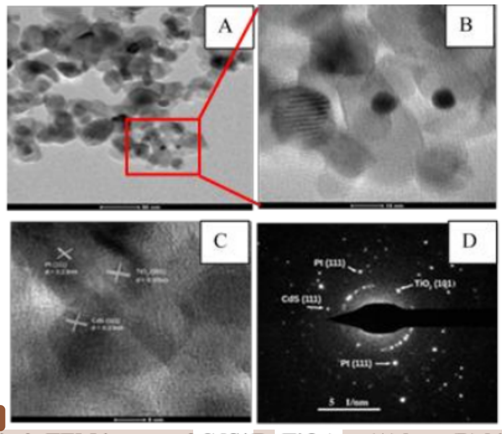

Fig 2. TEM images of CdS/(Pt-TiO$_2$) at (A) low, (B) high magnification, (C) high resolution and (D) SAED pattern

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 TiO_2 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 TiO_2 could present strong absorptions in redshift region. As a result, lowering band gap energy of Pt-TiO_2, CdS-TiO_2, and CdS/(Pt-TiO_2) were occurred compare to the based material (TiO_2). It is most likely due to deposition of CdS and Pt on TiO_2 and could come from the electronic interaction among TiO_2, Pt and CdS as reported by previous authors [15]. The lowering band gap of Pt-TiO_2, CdS-TiO_2 and CdS/Pt-TiO_2 suggests that decoration of Pt and CdS on TiO_2 can promote a red shift of photon absorption.

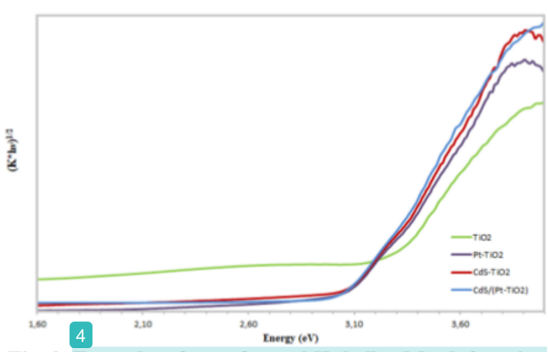

Fig. 3. Tauc plot of transformed Kubelka-Munk function vs energy (*hv*) for various photocatalysts, where F(R) = (1-R)^2/2R, R = reflectance, *hv* = photon energy

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]:

$$TiO_2 + hv \rightarrow TiO_2 + e^-_{cb} + h^+_{vb} \quad (1)$$

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

$$h^+_{vb} + H_2O \rightarrow {}^{\bullet}OH + H^+$$
$$h^+_{vb} + OH^- \rightarrow {}^{\bullet}OH \quad (2)$$

Meanwhile O_2 can react with electrons in the conduction band to become superoxide anion. The superoxide anion reacts with water to produces the •OH as follows [16]:

$$e^-_{cb} + O_2 \rightarrow O_2^{\bullet-}$$
$$2O_2^{\bullet-} + 2H_2O \rightarrow 2{}^{\bullet}OH + 2OH^- + O_2 \quad (3)$$

Microorganisms + ·OH → corrupt the cell wall (4)

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 •OH can corrupt cell wall, cell membrane and finally damage the nucleus. For the CdS/(Pt-TiO_2) that uncoated on pumice (pure CdS/Pt-TiO_2 as photocatalyst), the photodegradation of *E. coli* was faster compare to the CdS/(Pt-TiO_2)-pumice. This phenomenon is caused by CdS/(Pt-TiO_2) in the suspension have larger surface area that irradiated by photon compare to the CdS/(Pt-TiO_2)-pumice, and therefore more •OH produced and it will attack the *E. coli*. As a consequence, photocatalytic reaction rate on pure CdS/(Pt-TiO_2) in the solution faster than on CdS/(Pt-TiO_2)-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 •OH (hydroxyl radical)

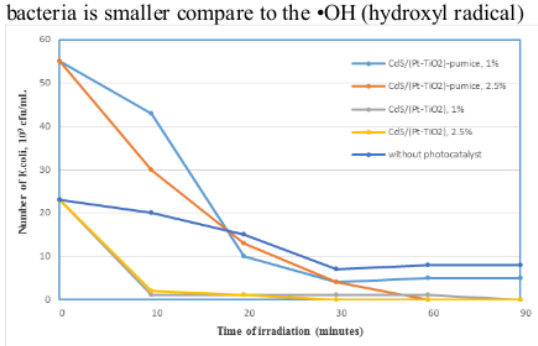

Fig. 4. The effect of various photocatalyst on *E. coli* disinfection

IV. CONCLUSION

Decorating of Pt and CdS on TiO_2 has been successfully performed evidenced by TEM analysis and therefore it could enhance its photocatalytic performance. Although pure dS/(Pt-TiO_2) gave better performance compare to CdS/(Pt-TiO_2)-pumice, dip coating photocatalyst on pumice gave benefit since it doesn't need additional equipment for separating pure CdS/(Pt-TiO_2) from the solution.

ACKNOWLEDGMENT

The authors would like to thank Ministry of Research, Technology and Higher Education, for financial support of this study (Riset Dasar grant no.4/AKM/PNT/2019) and LPKT Institut Teknologi Indonesia. Thank also to Novita Lestari NT and Abrar Fadhilah in collecting data.

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 TiO_2 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 TiO_2 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 TiO_2: 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/TiO_2 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 TiO_2 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 TiO_2 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/TiO_2 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 TiO_2 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 TiO_2 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

Singgih 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.

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

ORIGINALITY REPORT

14%	9%	11%	5%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Submitted to Universitas Indonesia Student Paper	3%
2	ejournal2.undip.ac.id Internet Source	2%
3	eprints.umm.ac.id Internet Source	2%
4	Ratnawati, , Jarnuzi Gunlazuardi, and Slamet. "Development of titania nanotube arrays: The roles of water content and annealing atmosphere", Materials Chemistry and Physics, 2015. Publication	1%
5	Jianjun Chen, Huilan Su, Yujia Liu, Yiwei Zeng, Wang Zhang, Jiajun Gu, Woon Ming Lau, Di Zhang. "Efficient photochemical hydrogen production under visible-light over artificial photosynthetic systems", International Journal of Hydrogen Energy, 2013 Publication	1%

6	Ratnawati, , Jarnuzi Gunlazuardi, Eniya Listiani Dewi, and Slamet. "Effect of NaBF4 addition on the anodic synthesis of TiO2 nanotube arrays photocatalyst for production of hydrogen from glycerol–water solution", International Journal of Hydrogen Energy, 2014. Publication	1%
7	Zhu, Yuxiang, Zhi Chen, Tong Gao, Qiaoli Huang, Feng Niu, Laishun Qin, Peng Tang, Yuexiang Huang, Zuoliang Sha, and Yanfei Wang. "Construction of hybrid Z-scheme Pt/CdS–TNTAs with enhanced visible-light photocatalytic performance", Applied Catalysis B Environmental, 2015. Publication	1%
8	academic.hep.com.cn Internet Source	1%
9	Xiaobo Chen, Shaohua Shen, Liejin Guo, Samuel S. Mao. "Semiconductor-based Photocatalytic Hydrogen Generation", Chemical Reviews, 2010 Publication	1%
10	www.mdpi.com Internet Source	<1%
11	ir.lib.uwo.ca Internet Source	<1%

12	www.ijrte.org Internet Source	<1%
13	Ratnawati, Jarnuzi Gunlazuardi, Slamet. "Development of titania nanotube arrays: The roles of water content and annealing atmosphere", Materials Chemistry and Physics, 2015 Publication	<1%
14	fr.scribd.com Internet Source	<1%
15	www.mrs.org Internet Source	<1%
16	worldwidescience.org Internet Source	<1%
17	Anna Kubacka, Marcos Fernández-García, Gerardo Colón. "Advanced Nanoarchitectures for Solar Photocatalytic Applications", Chemical Reviews, 2011 Publication	<1%

Exclude quotes	Off	Exclude matches	Off
Exclude bibliography	On		