Research Article

8

INDONESIAN SCHOLAR SOCIETY

Indones. J. Chem. Stud.
2022, 1(1), 8–12
Available online at journal.solusiriset.com
e-ISSN: 2830-7658; p-ISSN: 2830-778X

Indonesian Journal of Chemical Studies

Synthesis of Modified TiO_2 Nanocomposite using Fe_3O_4 and Nickel as Photocatalyst in Reduction of Silver

Adya Rizky Pradipta[1*], Aslan Irunsah[2]

[1]*Department of Chemical Analysis, Politeknik AKA Bogor, Jl. Pangeran Sogiri No.283, Kota Bogor 16154, Indonesia*

[2]*Department of Biotechnology, Buton Institute of Marine Technology, Jl. Balai Kota No. 1, Pasarwajo, Buton 93754, Indonesia*

Received: 24 May 2022; Revised: 2 Jun 2022; Accepted: 2 Jun 2022;
Available online: 10 Jun 2022; Published regularly: 30 Jun 2022

Abstract— The use of TiO_2 nanocomposite modified with Fe_3O_4 dan Ni dopping for silver ion photoreduction has been successfully performed. In this study, nanocomposites were fabricated through the sol-gel technique. Structure, optical, and magnetic properties were analyzed using XRD, DRUV-Vis, FTIR, and VSM analysis. The XRD pattern revealed the anatase phase of TiO_2 and the iron oxide formed was Fe_3O_4. UV-Vis spectroscopy showed the formation of absorption in the visible region in the presence of Ni doping. The nanocomposite had magnetic properties of 12.6 emu/g with paramagnetic type. TiO_2 nanoparticles presented the percentage reductions of Ag ions with UV and Visible light of 82.65% and 21.43%, respectively, while Fe_3O_4/ TiO_2-Ni with UV and Visible light were 80.93% and 90.72%, respectively. Ni-dopped nanocomposites showed high photocatalytic activity under both UV and Visible irradiation.

Keywords— Photocatalyst; TiO_2-Nickel; Nanocomposite; Fe_3O_4; Ag Ions.

1. INTRODUCTION

During the last decade, numerous studies on catalysts have been developed as a solution to the environmental pollution issue, especially metal waste, which continues to increase. Silver metal is one of the dangerous metals that is often found in wastewater. Silver metal (Ag) is one of the precious metals that is very commonly used by humans. The use of silver metal on a large scale can result in the accumulation of large amounts of waste. The disposal of waste containing silver ions directly into the environment can cause environmental pollution and various health problems such as agyria (pigmental), brain damage, and central nervous system poisoning [1]. Ag(I) metal ions bound by nitrate ions (NO_3^-) to form $AgNO_3$ can cause skin irritation, are corrosive and can even cause death [2]. Heterogeneous photocatalysis is a widely developed method and is considered to have profound potential to control contaminants, especially in water. Titanium dioxide has caught the attention of numerous researchers in recent decades due to its simple application and ability to be applied to organic, inorganic, and microbiological pollutants. Titanium dioxide has been shown to be the most efficient photocatalyst owing to its strong oxidizing capacity, long-term stability against light and chemical corrosion, suitable band gap energy, and electrical and optical properties. Moreover, titanium dioxide is photocatalytically stable, relatively easy to produce, and an effective catalyst for chemical reactions [3].

When TiO_2 is utilized as a photocatalyst, many issues arise, such as its wide band gap (3.2 eV), which causes only a tiny portion (5 percent) of the solar spectrum to be absorbed [4,5]. TiO_2 is stimulated only by ultraviolet light; it is inactive when exposed to visible light. In addition, the short distance between the conduction band and the valence band, as well as the rapid e/h+ recombination speed, diminish the performance of TiO_2. Numerous studies have been conducted to manufacture TiO_2-semiconductor composites with decreased band gap energies. Many researchers have synthesized a TiO_2 composites with a modification in which CdS nanoparticles are immobilized in the TiO_2 system. [6-10]. There is also a method of increasing activity by doping cobalt on TiO_2 [11]. Some researchers have succeeded in preparing TiO_2 photocatalyst doped with a luminescence agent. Thus, it can work in visible light [11-13].

With the modifications made (referring to previous research), the TiO_2 material acquires a new energy level formed in the band gap or aids in dealing with ultraviolet light, increasing its photocatalytic activity. Therefore, the photocatalyst can display significant photocatalytic activity even when exposed to sunshine or fluorescent light. However, these advances are

***Corresponding author**.
Email address: adya.rizky.p@gmail.com
DOI: 10.55749/ijcs.v1i1.7

urgently required to enhance the photocatalytic capabilities of TiO_2 photocatalyst [11, 12, 13].

To obtain a TiO_2 photocatalyst that is responsive to a wider range of light, a modification of the band gap energy is required. Furthermore, by applying magnetic behavior to the TiO_2 system, the photocatalyst will have a more significant advantage in the treatment. Magnetic separation means that the material can be used more than once [14,15]. This adds more value to the modification of TiO_2. This work is expected can advance continuous efforts to develop modified TiO_2 photocatalysts to operate efficiently under a wider range of light and work effectively in applications with their separation capabilities.

Recently, numerous studies have focused on expanding the optical absorption of TiO_2 to the visible part of the spectrum in order to substitute UV radiation with sunlight to harness solar energy for practical applications and improve its photocatalytic activity. At present, doping with transition metal elements has been tested to enhance TiO_2 catalysts with visible light response because transition elements have multiple valences and traces of transition metal ions doped in TiO_2 matrix can trap the superficial potential of photogenerated electron-hole pairs, thereby prolonging the lifetime of electrons and holes and enhancing the photocatalytic activity. Furthermore, by applying magnetic behavior to the TiO_2 system, the photocatalyst will be easier to maintain. It can be separated using a magnetic field, so it can be used repeatedly. This adds to the list of advantages of the modified TiO_2. This work is expected to contribute to advancing continuous efforts to develop modified TiO_2 photocatalysts that operate efficiently under visible light, work effectively in Ag ion reduction applications, and improve their separation capabilities.

2. EXPERIMENTAL SECTION

2.1. Materials

The materials used in this research were $Fe_2SO_4{\cdot}7H_2O$ (Merck), $FeCl_3{\cdot}6H_2O$ (Merck), NH_4OH 25% (Merck), ethanol, Titanium tetraisopropoxide (TTIP) 97% (Sigma-Aldrich), NaOH, $NiCl_2{\cdot}6H_2O$, $AgNO_3$ (Merck), and deionized water (Inorganic Laboratory UGM).

2.2. Instrumentation

The instruments used for characterization were FTIR spectrophotometer (Shimadzu Prestige 21), X-Ray Diffractometer (Shimadzu XRD 6000), Transmission Electron Microscope (JEOL JEM-1400), Scanning Electron Microscope with Energy Dispersive X-Ray Spectrometer (EDAX SL AMETEK),Diffuse Reflectance UV-Visible Spectrophotometer (Shimadzu 2450), Vibrating Sample Magnetometer (OXFORD VSM 1.2H), and and Atomic Absorption Spectroscopy (Perkin Elmer 3110)

2.3. Procedure

2.3.1 Synthesis of magnetite (Fe304) nanoparticles

In the presence of nitrogen gas, 100 mL of deionized water was used to dissolve 5.41 g $FeCl_3{\cdot}6H_2O$ and 2.78 g $Fe_2SO_4{\cdot}7H_2O$. The solution was ultrasonicated, and a 25% NH_4OH solution was added drop by drop (30 mL). The precipitate was then collected, rinsed with deionized water, and dried overnight at 80 °C.

2.3.2 *Synthesis of Fe_3O_4 / TiO_2-Ni nacomposite*

A 1:10 mixture of TTIP and distilled water was stirred for at least 60 min using the stirring method. Before adding aged $NiCl_2{\cdot}6H_2O$ to the TiO_2 sol-gel, 10% of the weight of TiO_2 determined from TTIP was dissolved in ethanol. The combination was then subjected to thirty minutes of ultrasonic irradiation. This procedure produced a combination of Ni-doped TiO_2 sol-gel. Fe_3O_4 powder mixed in a 1:5 ethanol and water solution was ultrasonically irradiated for 15 min. The Ni-doped TiO_2 sol-gel was then added to the magnetite mixture and ultrasonically irradiated for one hour. The resultant sol-gel composite was dried in an oven before being calcined for four hours at 450 °C.

2.3.3 *Photocatalytic activity*

The photoreduction procedure was carried out in a batch system in a closed reactor fitted with ultraviolet and visible lamps. The study of the effect of pH on the photoreduction of Ag(I) ions was performed using the following procedure. 25 mL of a solution of 12.5 mg L^{-1} $AgNO_3$ was prepared into a beaker containing a magnetic stirrer. Then, 25 mg of TiO_2 and Fe_3O_4 /TiO_2-Ni were added to the solution. The solution added to the catalyst was placed into the photocatalytic reactor. The solution was stirred and irradiated with UV and visible light for 60 min. The photocatalyst was separated using an external magnet. The absorbance of the filtrate before and after the addition of photocatalyst was analyzed using AAS.

3. RESULT AND DISCUSSION

3.1. Crystal Analysis using X-ray Diffraction

XRD analysis indicates the crystallinity and phase of the synthesized sample formation. **Fig. 1** displays the XRD patterns of Fe_3O_4, TiO_2, and Fe_3O_4/TiO_2–Ni nanoparticles. Fe_3O_4 diffraction peaks appeared at 2θ: 30°, 35°, 43°, 54°, 57°, and 63° were assigned to the planes (220), (311), (400), (422), (511), and (440) according to ICDD no: 00-019-0629. The XRD results of the synthesized TiO_2 showed peaks at 25°, 38°, 48°, 54°, 55°, 63°, 75°, and 82° referred to (101), (112), (200), (105), (211), (204), (215), and (224) according to ICDD no: 00-021-1272. The XRD results showed that the synthesized TiO_2 was in the anatase phase. The crystal phase of TiO_2 anatase does not change despite the presence of Ni ions in the TiO_2 lattice. TiO_2 nanoparticles doped with Ni showed peaks with an angular shift of 2θ. This indicates that the Ni dopant has been successfully added in TiO_2

nanoparticles. No significant peaks appeared indicating Ni in the nanocomposite. When Ni ions are doped into the TiO_2 matrix, they will substitute for the TIO_2 matrix. Ni ions will replace Ti in the crystal structure and will produce slightly amorphous properties [18].

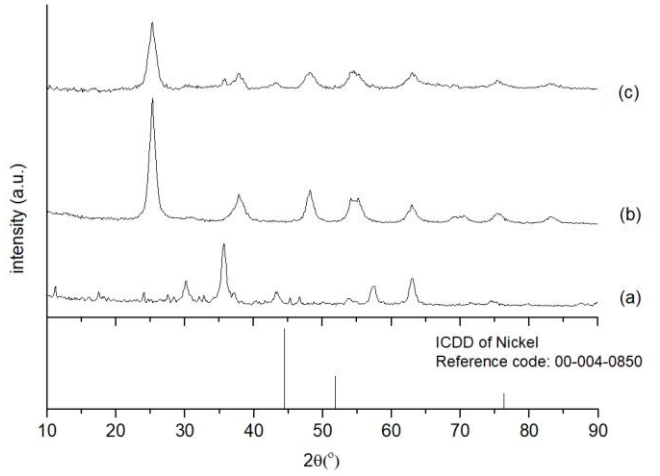

Fig. 1. XRD patterns of (a) Fe_3O_4, (b) TiO_2, and (c) Fe_3O_4/TiO_2-Ni nanoparticles

3.2. Optical Studies: Diffuse Reflectance UV-Vis

Measurement of the UV-visible absorption of the sample was performed in the wavelength range of 200-800 nm (**Fig. 2**.). The result of the analysis showed maximum absorption in the UV region and a red shift occurred in the presence of Ni dopant. Because of its band gap energy of 3.2-3.4 eV, TiO_2 has the propensity to exclusively absorb UV light. The band gap energy of the sample was computed using the Tauc plot based on its crystalline phase, as seen in **Fig. 2.**

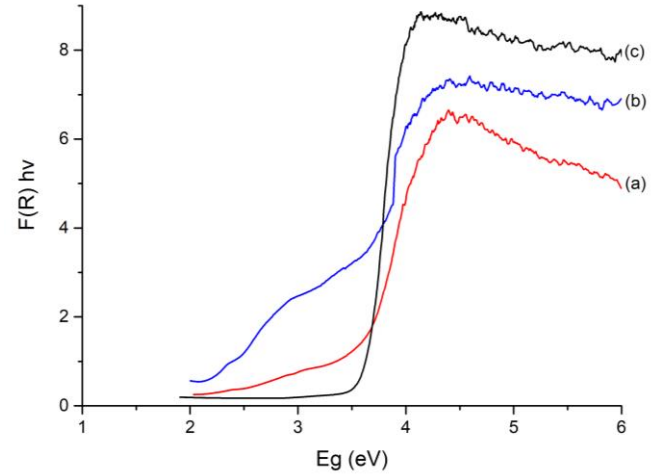

Fig. 2. Band gap estimation-Tauc plot of (a) Fe_3O_4/TiO_2, (b) Fe_3O_4/TiO_2-Ni, and (c) TiO_2

The nanoparticles' band gap energy was calculated by constructing a straight line from the Tauc plot [hγ vs. $(\alpha h\gamma)^2$]. The band gap energies for TiO_2 and Fe_3O_4 were, respectively, 3.5 eV and 3.4 eV. Ni-doped Fe_3O_4/TiO_2 specimens have two band gap energies, 3.5 eV and 2.1 eV. The results showed that the band gap energy decreased with the addition of dopants up to Ni. Ni-doped Fe_3O_4/TiO_2 nanocomposite can capture visible light at a wavelength of 588 nm.

3.3. Chemical Bonding Analysis: FTIR

Fig. 3. shows the FTIR spectrum of Fe_3O_4, TiO_2, and Fe_3O_4/TiO_2-Ni nanoparticles after being calcined at 450 °C for 2 h. Fe_3O_4 FTIR results showed an absorption band at around 580 cm^{-1}. This indicates Fe-O stretching vibrations. Wavenumbers 3278 and 3448 cm^{-1} indicate stretching vibration of the hydroxide (-OH) group that is possible from Fe-OH and H_2O. The FTIR analysis of TiO_2 revealed a wide band centered at 500-650 cm^{-1}. This verifies the existence of metal oxide linkages (Ti-O-Ti) [17]. Sharp peaks also emerged at 3440 and 1630 cm^{-1} corresponding to the O-H stretching vibration and the H-O-H bending vibration mode of physically adsorbed water in the synthesized samples. Fe_3O_4/TiO_2-Ni FTIR results reveal an absorption band that is a combination of Fe_3O_4 and TiO_2. However, the effect of the addition of Ni does not show a new absorption band.

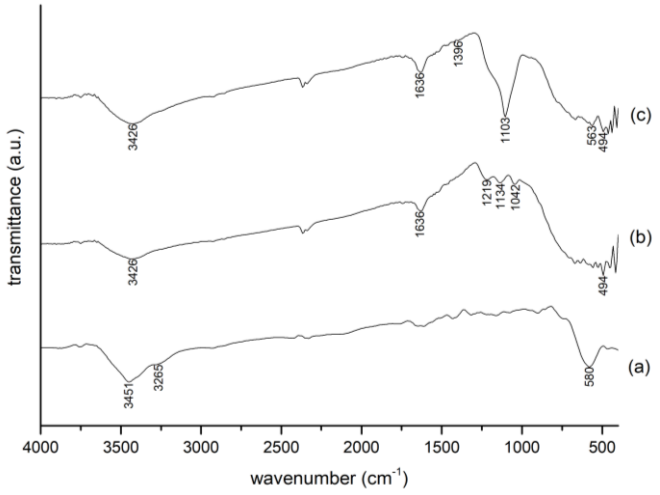

Fig. 3. FTIR Spectra of (a) Fe_3O_4, (b) TiO_2 and (c) Fe_3O_4/TiO_2-Ni nanoparticles

3.4. Morphological Analysis

The surface morphology of Fe_3O_4/TiO_2 was analyzed using SEM and TEM images. **Fig. 4**. exhibits typical SEM and TEM images of Fe_3O_4/TiO_2-Ni nanoparticles showing a spherical shape with agglomeration. Most particles are almost spherical and have a consistent size distribution, as seen in **Fig. 4**.

The pores detected on the nanocomposite's surface exhibited a mesoporous nature. This may occur because of the nanocrystalline composites aggregating. EDS examination verified the presence of Fe, Ti, Ni, and O in the produced samples, as shown in **Fig. 4**. The presence of Cl element in the EDS analysis probably comes from the remains of the $FeCl_3$ precursor. The results of TEM measurements displayed that the nanocomposite had a size of 23.59 nm with a standard deviation of 2.19 and a dispersity index (DI) value of 0.65.

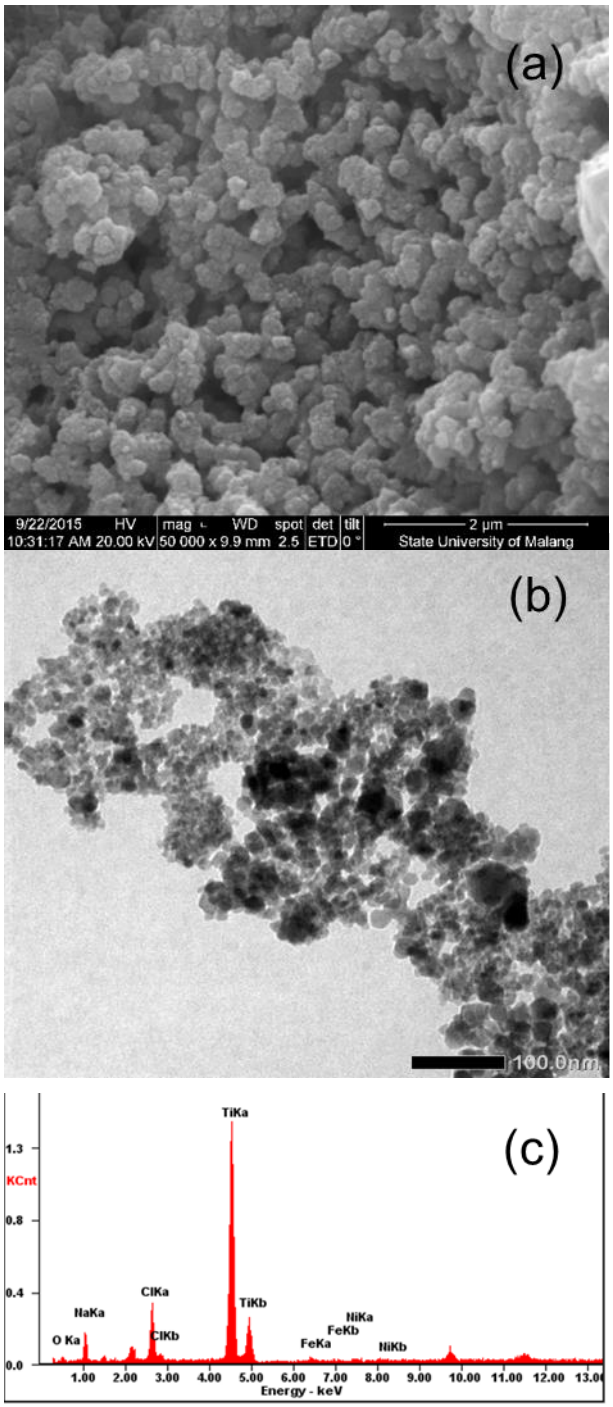

Fig. 4. SEM Image with 50,000x magnification (a), TEM Image with 100,000x magnification (b), and EDS (c) of Fe_3O_4/TiO_2-Ni

3.5. Magnetic Properties

The qualitative test of magnetic properties conducted with VSM showed that the nanocomposites performed magnetic properties, as shown in **Fig. 5**. Thus, it is easy to recover and reuse in the next photocatalysis process. Fe_3O_4 and Fe_3O_4/TiO_2-Ni nanoparticles have paramagnetic type magnetic properties. Fe_3O_4 material has the largest magnetic moment 33.2 emu/g and Fe_3O_4/TiO_2-Ni has a magnetic moment 12.6 emu/g. The decrease in the magnetic properties of the nanocomposite is caused by the addition of TiO_2 and Ni increasing the weight of the material.

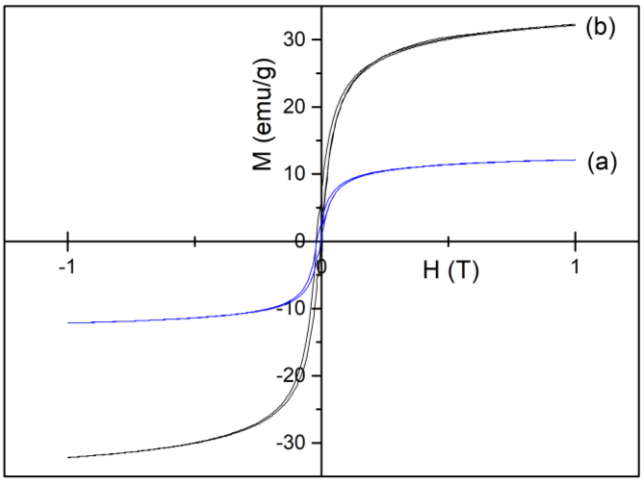

Fig. 5. Magnetization curve of a) Fe_3O_4/TiO_2-Ni and b) Fe_3O_4

3.6. Photoreduction Activity

The photocatalytic activity was tested using UV and visible light, as displayed in **Fig. 6**. The nanocomposite had almost the same photocatalytic activity as TiO_2 with the use of UV light. TiO_2 nanoparticles provided a reduction percentage of Ag ions of 49,24% while Fe_3O_4/TiO_2-Ni 80.93%. However, the later had a much higher activity when using visible light than TiO_2. The nanocomposite provided the percentage of Ag ion reduction of 90.72% while TiO_2 was only 15,43%. This indicates that Ni has been successfully doped on TiO_2, so it can work in visible light. Fe_3O_4 also plays a role in photocatalytic activity where Fe_3O_4 is also a semiconductor with a band gap energy in the visible light region [18]. Even so, the role of Fe_3O_4 is not as significant as the role of Ni in the photocatalytic process. This is due to the position of Fe_3O_4, which is on the inside and is covered by TiO_2, so it is difficult to make contact with the sample.

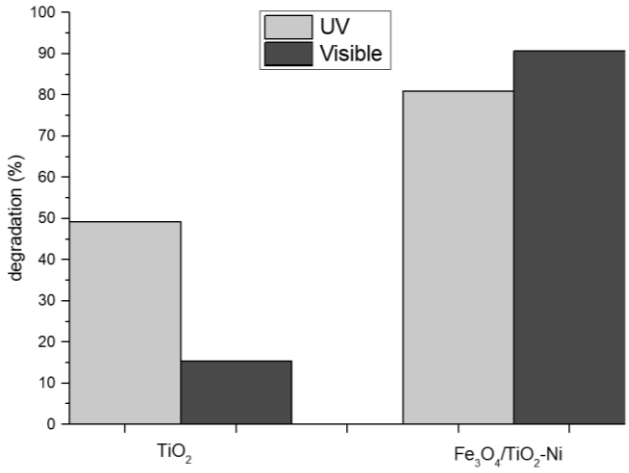

Fig. 6. Photocatalytic activity of the materials in the photoreduction of Ag ions.

4. CONCLUSION

In summary, TiO_2 nanoparticles modified with Fe_3O_4 and doped with Ni were synthesized by the sol-gel method. The results of X-ray diffraction exhibited the formation of TiO_2 in the anatase phase. The optical absorption spectrum of Fe_3O_4/TiO_2-Ni showed absorption in the visible region. SEM and TEM images displayed spherical morphology and agglomeration. EDS confirmed the presence of Ni in the synthesized nanocomposite. The synthesized nanocomposite showed magnetic properties confirmed by VSM. The photocatalytic activity of Fe_3O_4/TiO_2-Ni was much higher using visible light than TiO_2 without modification.

ACKNOWLEDGEMENTS

The authors highly acknowledge Prof. Dr. Eko Sri Kunarti, who has guided this research, and the Head of Inorganic Laboratory, Universitas Gadjah Mada, for permitting the use of the research facilities.

CONFLICT OF INTEREST

We declare that there is no conflict of interest among authors.

AUTHOR CONTRIBUTIONS

ARP conducted the experiment and interpretation, ARP and AI wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

REFERENCES

[1] Jung, I., Joo, E.-J., Suh, B.S., Ham, C.-B., Han, J.-M., Kim, Y.-G., Yeom, J.-S., Choi, J.-Y., & Park, J.-H. 2017. A case of generalized argyria presenting with muscle weakness. *Ann. Occup. Environ. Med.* 29(45), 1-5. doi: 10.1186/s40557-017-0201-0.

[2] Kim, J.S., Song, K.S., Sung, J.H., Ryu, H.R., Choi, B.G., Cho, H.S., Lee, J.K., & Yu, I.J. 2013. Genotoxicity, acute oral and dermal toxicity, eye and dermal irritation and corrosion and skin sensitisation evaluation of silver nanoparticles. *Nanotoxicology*. 7(5). 953–960. doi: 10.3109/17435390.2012.676099.

[3] Shirsath, S.R., Pinjari, D.V, Gogate, P.R., Sonawane, S.H., & Pandit, A.B. 2013. Ultrasound assisted synthesis of doped TiO_2 nano-particles: Characterization and comparison of effectiveness for photocatalytic oxidation of dyestuff effluent. *Ultrason. Sonochem.* 20(1). 277–286. doi: https://doi.org/10.1016/j.ultsonch.2012.05.015.

[4] Sun, S., Zhang, J., Gao, P., Wang, Y., Li, X., Wu, T., Wang, Y., Chen, Y., & Yang, P. 2017. Full visible-light absorption of TiO_2 nanotubes induced by anionic S_2^{2-} doping and their greatly enhanced photocatalytic hydrogen production abilities. *Appl. Catal. B Environ.* 206. 168–174. doi: 10.1016/j.apcatb.2017.01.027.

[5] Zubair, M., Kim, H., Razzaq, A., Grimes, C.A., & In, S.-I. 2018. Solar spectrum photocatalytic conversion of CO_2 to CH_4 utilizing TiO_2 nanotube arrays embedded with graphene quantum dots. *J. CO_2 Util.* 26. 70–79. doi: 10.1016/j.jcou.2018.04.004.

[6] Hirai, T., Suzuki, K., & Komasawa, I. 2001. Preparation and Photocatalytic Properties of Composite CdS Nanoparticles–Titanium Dioxide Particles. *J. Colloid Interface Sci.* 244(2). 262–265. doi: 10.1006/jcis.2001.7982.

[7] Kaur, A., Umar, A., Anderson, W.A., & Kansal, S.K. 2018. Facile synthesis of CdS/TiO_2 nanocomposite and their catalytic activity for ofloxacin degradation under visible illumination. *J. Photochem. Photobiol. A Chem.* 360. 34–43. doi: 10.1016/j.jphotochem.2018.04.021.

[8] Du, Y.-E., Niu, X., He, X., Hou, K., Liu, H., & Zhang, C. 2021. Synthesis and Photocatalytic Activity of TiO(2)/CdS Nanocomposites with Co-Exposed Anatase Highly Reactive *Facets. Molecules.* 26(19). 6031. doi: 10.3390/molecules26196031.

[9] Song, J., Zeng, D., Xie, Y., Zhang, F., Rao, S., Wang, F., Zhao, J., Zhang, J., & Wang, L. 2020. Preparation of CdS nanoparticles-TiO_2 nanorod hererojunction and their high-performance photocatalytic activity. *Catalysts.* 10(441). 1-14. doi: 10.3390/catal10040441.

[10] Kudhier, M.A., ALKareem, R.A.S.A., & Sabry, R.S. 2021. Enhanced photocatalytic activity of TiO_2-CdS composite nanofibers under sunlight irradiation**. *J. Mech. Behav. Mater.* 30(1). 213–219. doi: 10.1515/jmbm-2021-0022.

[11] Ramadhan, M., Pradipta, A.R., & Kunarti, E.S. 2017. Synthesis of Fe_3O_4/TiO_2-Co nanocomposite as model of photocatalyst with magnetic properties, *Mater. Sci. Forum,* 901, 14-19 doi: 10.4028/www.scientific.net/MSF.901.14.

[12] Gao, J., Jiang, R., Wang, J., Wang, B., Li, K., Kang, P., Li, Y., & Zhang, X. 2011. Sonocatalytic performance of Er^{3+}:$YAlO_3/TiO_2$–Fe_2O_3 in organic dye degradation. *Chem. Eng. J.* 168(3). 1041–1048. doi: https://doi.org/10.1016/j.cej.2011.01.079.

[13] Trabelsi, F., Mercier, F., Blanquet, E., Crisci, A., & Salhi, R. 2020. Synthesis of upconversion TiO_2:Er^{3+}-Yb^{3+} nanoparticles and deposition of thin films by spin coating technique. *Ceram. Int.* 46(18, Part A). 28183–28192. doi: 10.1016/j.ceramint.2020.07.317.

[14] Jarosz-Duda, A., O'Callaghan, P., Kuncewicz, J., Łabuz, P., & Macyk, W. 2020. Enhanced UV Light Emission by Core-Shell Upconverting Particles Powering up TiO_2 Photocatalysis in Near-Infrared Light, *Catalysis* , 10(232). 1-10 doi: 10.3390/catal10020232.

[15] Pradipta, A.R., Mauludi, K., Kartini, I., & Kunarti, E.S. 2020. Synthesis of Fe_3O_4/TiO_2 Nanocomposite as Photocatalyst in Photoreduction Reaction of CO_2 Conversion to Methanol, *Key Eng. Mater.* 840. 454-458 doi: 10.4028/www.scientific.net/KEM.840.454.

[16] Sakthivel, T., Kumar, K.A., Senthilselvan, J., & Jagannathan, K. 2018. Effect of Ni dopant in TiO_2 matrix on its interfacial charge transportation and efficiency of DSSCs. *J. Mater. Sci. Mater. Electron.* 29(3). 2228–2235. doi: 10.1007/s10854-017-8137-2.

[17] Kunarti, E., Syoufian, A., Budi, I., & Pradipta, A. 2016. Preparation and Properties of $Fe_3O_4/SiO_2/TiO_2$ Core-Shell Nanocomposite as Recoverable Photocatalyst. *Asian J. Chem.* 28. 1343–1346. doi: 10.14233/ajchem.2016.19697.

[18] Pradipta, A.R., Enriyani, R., Rahmatia, L., & Utami, A. 2021. Sintesis Nanokomposit Fe_3O_4/TiO_2 Sebagai Fotokatalis yang Dapat Diambil Kembali Dalam Fotoreduksi Limbah Ion Perak(I). *War. Akab.* 44(2). 32–39. doi: 10.55075/wa.v45i1.6.