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Abstract. A composite $SrTiO_3/TiO_2$ heterojunction photocatalyst was prepared by sonication methods. The heterojunction material $SrTiO_3/TiO_2$ was synthesized using an ultrasonic cleaning bath for 4 hours, by mixing $SrTiO_3$ and TiO_2 with variations in the comparison of mol 1:1, 1:2, 1:4 and 1:6. Characterization using XRD shows heterojunction material consisting of $SrTiO_3$ and TiO_2 anatase without any impurities, with the morphological surface observed using SEM indicating the agglomerated small particles. The bandgap of heterojunction material with a variation in mol $SrTiO_3$: TiO_2 of 1:1, 1:2, 1:4 and 1:6 are 3.11; 3.09; 3.07; and 3.07 eV respectively. The all of bandgap is lower than the $SrTiO_3$ and TiO_2 bandgap, i.e. 3.2 eV.

1. Introduction

Today, pollution from dyes has become one of the environmental problem [1,2]. Various handling methods have been developed, among others is adsorption, ozonation, flocculation, membrane filtration, etc which can create new problems. The photocatalytic is a greener technique that attracts many researchers [2–4]. Photocatalyst technology in Indonesia is very promising because Indonesia has a tropical climate and crossed by the equator, therefore it has abundant sunlight. The average per day of solar radiation received by most of the Indonesian area is around 4 kWh/m^2 [5].

Strontium titanate has reported as a potential photocatalyst with the bandgap of 3.2 eV, so it can only be used in the UV region [2,6], whereas UV light only contributes 5% of the sunlight. Furthermore, the effective utilization of electron-hole pairs is a major factor for the degradation of organic pollutants but the main problem is the recombination of electron pairs and holes which limit photocatalytic activity [7]. Hence, there is a great need to develop means and ways to widen the light absorption region and slow down the rate of recombination [3].

During past decades, numerous new techniques or materials have been created to improve the response of $SrTiO_3$ to visible light. The researchers had previously synthesized $SrTiO_3$-BiOBr heterojunction and concluded that the higher activity of heterojunction photocatalysts than BiOBr is ascribed to lower recombination rate [3]. Coupling $SrTiO_3$ with TiO_2 to form $SrTiO_3/TiO_2$ heterojunction is promoting separation of photogenerated charges [8,9]. According to the matching band principle, $SrTiO_3$ and TiO_2 are appropriate to form the heterojunction structure to promote the separation of carriers [10]. The coupling of $SrTiO_3$ and TiO_2 into a heterojunction can effectively ease the separation of photogenerated electrons and holes between $SrTiO_3$ and TiO_2, and their performances can be enormously enhanced [4].

Photocatalyst performance is also influenced by the size and particle distribution. The smaller and uniform the particle size, the better photocatalytic activity. Sonochemical is one of the simple methods

to produces a very small particle [11]. The advantages of the sonication method are that the time used is relatively fast, simple equipment, low temperatures, and produces uniform particles. Yue, et.al. [6] have studied the photocatalytic activities of the $SrTiO_3/TiO_2$ composites nanosheets and concluded that the performance of $SrTiO_3/TiO_2$ composite nanosheets increased due to the presence of nano-heterojunction. In this work, we synthesis the heterojunction photocatalyst of $SrTiO_3/TiO_2$ using a sonochemical method, followed by calcination. The material was characterized using XRD, SEM and Uv-Vis DRS spectrophotometer.

2. Methods

2.1. Synthesis of materials

$SrTiO_3$ was prepared by the solid-state reaction. In a typical procedure for the synthesis of $SrTiO_3$, $SrCO_3$ (sigma-Aldrich) and TiO_2 (sigma-Aldrich) were a mixture in stoichiometric proportion to form $SrTiO_3$ (STO). They were mixed in an agate mortar for 3.5 hours using acetone up to dryness. The mixed powder was calcined at 700 ℃ for 24 h and then milled again with a calcination temperature increase of 100 ℃ to reach 1000 ℃.

Synthesis of $SrTiO_3/TiO_2$ heterojunction by mixing $SrTiO_3$ and TiO_2 with various molar ratios 1/1, 1/2, 1/4, and 1/6. Then 20 mL aqua DM and 40 mL ethanol were added (p. a). This mixture was subjected to ultrasonic radiation using an ultrasonic cleaning bath for 2 hours, then evaporated in the oven for 2 hours at 105 ℃. The evaporation results were calcined for 6 hours at 600 ℃.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded using a Panalytical E'xpert pro XRD diffractometer using Cu Kα-radiation, in the 2θ range of 10°– 90°, to identify the phase of the powder. The morphology of the samples was observed using a Scanning Electron Microscopy (SEM) (HITACHI FLEXSEM 1000). The UV–Vis diffuse reflectance spectrum of the heterojunction photocatalysts was measured using a UV–Vis spectrometer (Thermo Scientific Evolution 220) and a Tauc plot [(F(R)hν)n vs hν] profile were used to determine the semiconductor bandgap.

3. Result and Discussion

3.1. XRD analysis

Figure 1 shows the XRD pattern of $SrTiO_3$ prepared by the solid-state reaction method. All of the diffraction peaks in the XRD pattern indicating that cubic $SrTiO_3$ was successfully synthesized (ICSD no. 94-573) without any impurities. The XRD patterns of the heterojunction samples (Figure 2) had both $SrTiO_3$ (ICSD no. 94-573) and TiO_2 (ICSD no. 44882) signatures, and no displacement of $SrTiO_3$ peak is observed in the heterojunction confirm that $SrTiO_3/TiO_2$ heterojunction was successfully synthesized. Furthermore, it can be seen that with increasing the molar of TiO_2, the peak intensity of TiO_2 (011), (004) and (020) is gradually getting stronger, and the peak intensity of $SrTiO_3$ (111), becomes weaker.

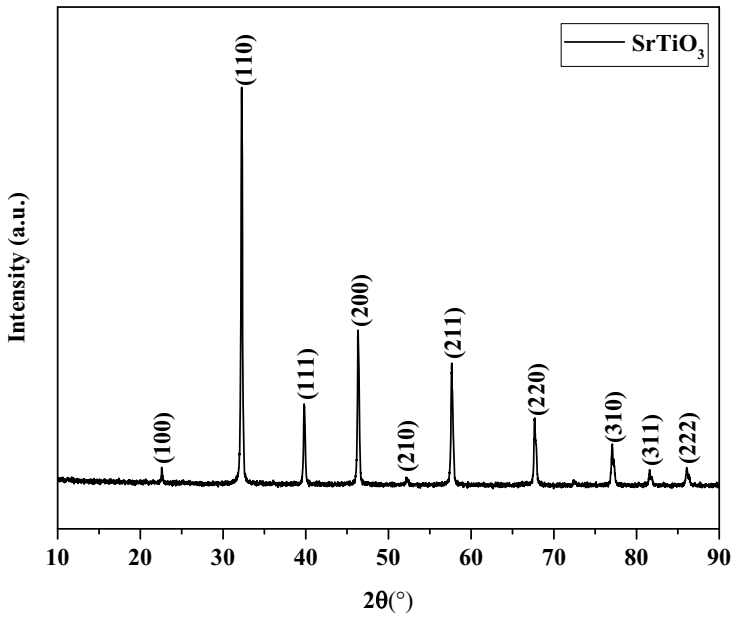

Figure 1. XRD Pattern of $SrTiO_3$.

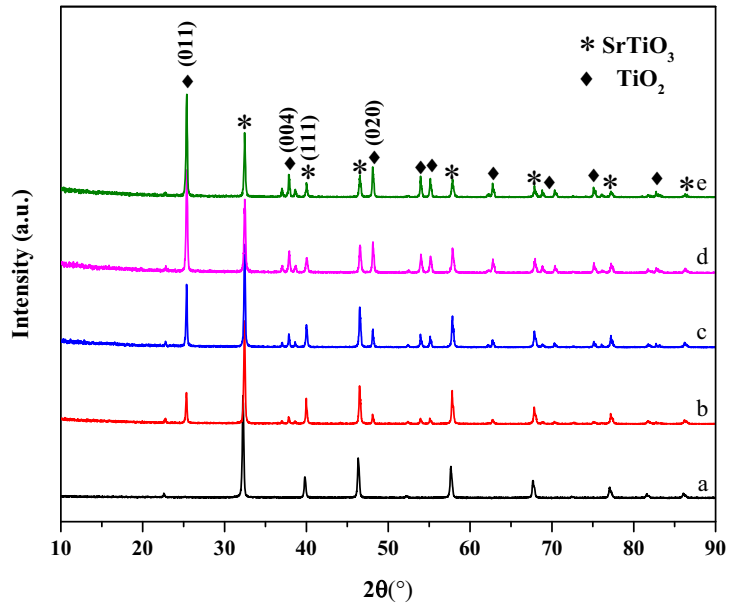

Figure 2. XRD Patterns of heterojunction photocatalyst: (a) $SrTiO_3/TiO_2$ (1:0); (b) $SrTiO_3/TiO_2$ (1:1); (c) $SrTiO_3/TiO_2$ (1:2); (d) $SrTiO_3/TiO_2$ (1:4); (e) $SrTiO_3/TiO_2$ (1:6).

3.2. SEM analysis

Figure 3 shows the image of the particle morphology of samples. In all of the micrographs, the $SrTiO_3/TiO_2$ particles are presented in agglomerated, therefore the particles sizes could not be correctly determined, but it was clear that heterojunction material was composed of small particles. It related to the acoustic cavitation wave during the sonication process which the formation, growth, and implosive collapse of bubbles in a liquid helps in creating nanoparticles [7].

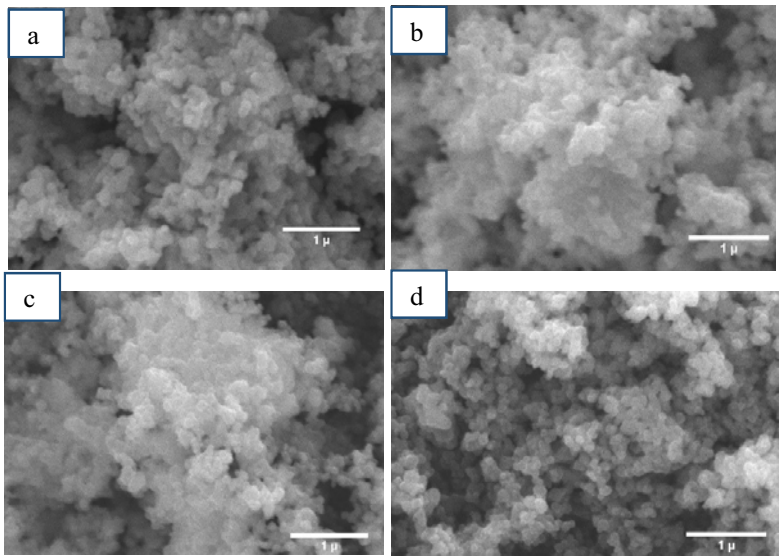

Figure 3. SEM images of heterojunction photocatalyst: (a) $SrTiO_3/TiO_2$ (1:1); (b) $SrTiO_3/TiO_2$ (1:2); (c) $SrTiO_3/TiO_2$ (1:4); (d) $SrTiO_3/TiO_2$ (1:6).

3.3. UV-Vis DRS analysis

The absorption edge of $SrTiO_3$ and TiO_2 (anatase) in previously reported was the same as 387.5 nm correspond to the band-gap is 3.2 eV, which means that $SrTiO_3$ and TiO_2 enable to absorb UV light. The band gaps of the samples were calculated using the Kubelka-Munk equation and the Tauc plot method shown in Figure 3, and the conversion to the wavelength is shown in Table 1. According to Figure 4 and Table 1, the absorption edge of the heterojunction material was slightly increased. It is evident that the formation of $SrTiO_3/TiO_2$ heterojunctions altered the electronic structures of the semiconductors [12]. Furthermore, the heterojunction formation causes a red-shift of the absorption edge, thus narrowing the bandgap of the photocatalyst.

Table 1. Band gap energy and related absorption edges of the photocatalysts.

Photocatalyst	Band gap energy	
	Eg (eV)	λ (nm)
TiO2 (anatase)	3.20	387.50
SrTiO3	3.20	387.50
SrTiO3/TiO2 (1/1)	3.11	398.71
SrTiO3/TiO2 (1/2)	3.09	401.29
SrTiO3/TiO2 (1/4)	3.07	403.91
SrTiO3/TiO2 (1/6)	3.07	403.91

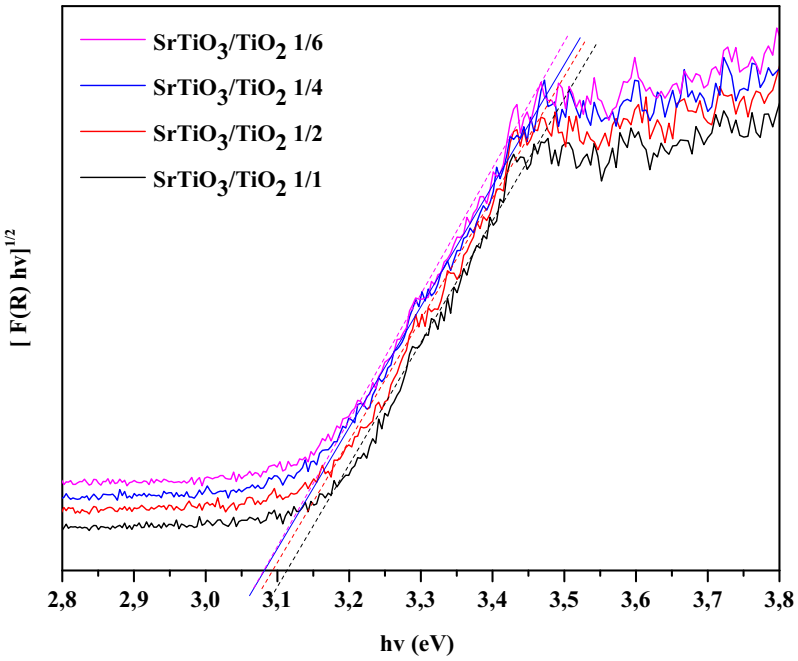

Figure 4. The plot of $[F(R)hv]^{1/2}$ vs hv.

4. Conclusions

Various molar ratios of $SrTiO_3/TiO_2$ heterojunction material were successfully synthesized by sonochemical method. The particle of $SrTiO_3/TiO_2$ heterojunction material was composed of agglomerated small particles. The bandgap energy of heterojunction material is lower than TiO_2 as well as $SrTiO_3$. It indicated that heterojunction material can work in visible light.

Acknowledgments

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References

[1] Lu H, Hao Q, Chen T, Zhang L, Chen D, Ma C, Yao W and Zhu Y 2018 *Appl. Catal. B-Environ.* **237** 59–67
[2] Ruzimuradov O, Nurmanov S, Hojamberdiev M, Prasad R M, Gurlo A, Broetz J, Nakanishi K and Riedel R 2014 *Mater. Lett.* **116** 353–5
[3] Kanagaraj T and Thiripuranthagan S 2017 *Appl. Catal. B-Environ.* **207** 218–32
[4] Khemakhem O, Bennaceur J, Cheikhrouhou-Koubaa W, Koubaa M, Chtourou R and Cheikhrouhou A 2017 *J. Alloy. Compd.* **696** 682–7
[5] Handayani N A and Ariyanti D 2012 *Int. J. Renew. Energy Dev.* **1** 33
[6] Yue X, Zhang J, Yan F, Wang X and Huang F 2014 *Appl. Surf. Sci.* **319** 68–74
[7] Anandan S, Sivasankar T and Lana-Villarreal T 2014 *Ultrason. Sonochem.* **21** 1964–8
[8] Marchelek M, Grabowska E, Klimczuk T, Lisowski W, Mazierski P and Zaleska-Medynska A 2018 *Mol. Catal.* **452** 154–66
[9] Zhou J, Yin L, Li H, Liu Z, Wang J, Duan K, Qu S, Weng J and Feng B 2015 *Mat. Sci. Semicon.*

Proc. **40** 107–16
[10] Wang L, Wang Z, Wang D, Shi X, Song H and Gao X 2014 *Solid State Sci.* **31** 85–90
[11] Suslick K S, Casadonte D J, Green M L H and Thompson M E 1987 *Ultrasonics* **25** 56–9
[12] Ng J, Xu S, Zhang X, Yang H Y and Sun D D 2010 *Adv. Funct. Mater.* **20** 4287–94