Preparation of ZnO/SiO_2 Composite using Silica isolated from Rice Husk

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Abstract
Rice husk is available in abundance in Indonesia since it is one of the by product in rice processing. It contains high amount of silica (SiO_2) and therefore effort towards its utilization has been carried out. Another material that has advantageous properties is zinc oxide (ZnO). These two materials can be fabricated to produce ZnO/SiO_2 composite having wide applications. The present study is directed to synthesize ZnO/SiO_2 composite and determine its properties.

Silica was prepared by alkaline extraction from rice husk char, followed by preparation of sililic acid by formation of sodium metasilicate followed by acidification using hydrochloric acid in a cation exchange resin. The composite was prepared by reacting zinc acetate and sililic acid. The result indicates that the composite material is formed as shown by XRD data. SEM-EDS results indicate that higher ratio of ZnO in the composite will lead to tighter and uniformly spread granules.

Keywords: Rice husk, Composite, Silica, ZnO.

Introduction

As an agrarian country, Indonesia has high rice production. When processed, rice can produce various products. Rice husk, as one of by product in rice processing is abundantly available. Therefore, there is a concern on how to utilize this by product. Rice husk char, or also known as silica char, is incomplete burning product of rice husk. It contains 55-97% silica. Therefore, in our present study, we used this material as starting material for silica-based material.

Silica has good biocompatibility, non-toxic, anti-cracking and emollient agents properties[1]. Due to these properties, silica is often used in cosmetics formulation. Preparation of silica from rice husk can be performed by simple means i.e. alkaline extraction[2]. Separation of silica and carbon from rice husk ash by potassium carbonate can achieve 96.84% recovery[3].

Other than silica, zinc oxide is also commonly found in cosmetics formulation. Zinc oxide has good antibacterial property and can filter UV radiation[4]. In a cosmetics formulation, silica and zinc oxide have their individual role. Their role can be optimized when the two materials are combined to form a composite material. The composite will have higher rigidity and power compared to their individual material[5].

Therefore, the present study is directed to synthesize ZnO/SiO_2 composite with varying ZnO composition.

Material and Methods

Materials: The material used in the present study were rice husk, zinc acetate, formaldehyde, distilled water, sodium hydroxide, Whatmann filter paper no. 40.

Separation of Silica from rice husk ash: Rice husk char was grinded and filtered through a 50-mesh filter. To a 2 L Beaker glass, 50 g of the char was inserted and added by potassium carbonate and distilled water to give ratio of 1:3:150 (char : potassium carbonate: distilled water) and boiled for 150 minutes. The mixture was then filtered using Buchner funnel through a Whatmann no. 40 filter paper while it is still hot. The filtrate was then cooled at room temperature until silica was precipitated. The precipitate was separated by decantation followed by washing using distilled water until reaching neutral pH.

Preparation of sililic acid: As much as 0.172 g sodium hydroxide was dissolved in 14.25 mL distilled water. To the solution, 0.4 g of silica was added gradually while heated and stirred. The formed sodium metasilicate (Na_2SiO_3) was cooled at room temperature followed by dilution to give final volume of 20 mL. As much as 2 mL was drawn and diluted to 100 mL, pass through a cation exchange resin that has been activated by 2 N hydrochloric acid.

Synthesis and Characterization of ZnO/SiO_2 composite: Zinc acetate dihydrate [$Zn(CH_3COO)_2.\ 2H_2O$] was dissolved in 100 mL distilled water, heated and added by 25% ammonium hydroxide solution dropwise until the solution becomes cloudy. The ammonium hydroxide addition was continued until the solution becomes clear again. The solution was then ultrasonicated at 70°C for 45 minutes and sililic acid solution was then added dropwise followed by ultrasonication for another 15 minutes. The product was centrifuged at 4000 rpm for 45 minutes. The precipitate was dried in an oven at 130°C for 12 hours. The dried product was then grinded on mortar and pestle followed by characterization using XRD and SEM-EDS.

Results and Discussion

Preparation and Separation of Silica from Rice Husk Char: Table 1 present moisture and ash content of the rice husk. Moisture content was varied due to humidity and

different storage time which can affect water adsorption to the rice husk. Ash content of the rice husk was 65.85%. The ash content was used to determine the amount of potassium carbonate used for extractor in the extraction process. The ash content was considered equal to silica that will be extracted.

Fine grinded rice husk char was suspended in potassium carbonate with ratio 1:3:150 (char: potassium carbonate: water) and heated for 150 minutes. In the present study, 50.6 g char, 230.3 g potassium carbonate and 1500 mL distilled water were used. The calculation was based on ash content assumed equal to silica content that will be extracted.

The mixture of extraction results was filtered while it is still hot so that silica does not precipitate readily in potassium carbonate when cooled. The filtrate is potassium carbonate solution which contains silica and with residual carbon. The filtrate was then cooled while the precipitate was washed using hot water to eliminate residual potassium carbonate. The silica was then heated in on oven at 100°C to remove excess water. The silica purity used for the next step was 71.24%.

Preparation of Sililic Acid: pure silica was extracted from rice husk and added with sodium hydroxide and distilled water. Addition of sodium hydroxide will convert silica to sodium silicate and conducted while the solution is still hot while stirring to prevent gel formation.

Sodium silicate solution was set to give 20% when immersed in cation exchange resin which was then activated using 2 N hydrochloric acid to reduce pH of the basic solution.

Sodium silicate solution was then stirred on hot plate with magnetic stirrer and the pH was monitored. When pH of the solution reaches constant value (pH $\geq$2.87), the solution was then filtered using funnel with glass wool to separate formed sililic acid.

Synthesis of ZnO/SiO_2 composite: zinc acetate was used as precursor for zinc oxide. Zinc acetate was dissolved in distilled water and ammonium hydroxide was added into it to form zinc hydroxide. Addition of ammonium hydroxide makes the solution become cloudy and when excess ammonium hydroxide was added, the solution becomes clear again.

Characterization of ZnO/SiO_2 composite with SEM-EDS: The SEM-EDS results of ZnO/SiO_2 composite with ratio of 3:1, 4:1 and 5:1 is presented in figure 1. The values of percentage ratio of the zinc are found to be increased in line with increasing mole ratio of the zinc oxide which are 37.32, 52.15 and 71.57% for mole ratio zinc oxide to silica 3:1, 4:1 and 5:1 respectively. Theoretical calculation of the mass percentage of each ratio should be 51.78, 54.48 and 56.16% respectively. The results showed different results due to several factors such as error in weighing and missing zinc oxide.

A

ZAF Method Standard less Quantitative Analysis
Fitting Coefficient: 0.3175

Element	(keV)	Mass%	Error%	Atom%
O	0.525	48.91	0.31	70.81
Si	1.739	13.76	0.26	13.48
Zn	8.630	37.32	3.79	15.71
Total		100.00		100.00

B

ZAF Method Standard less Quantitative Analysis
Fitting Coefficient: 0.3295

Element	(keV)	Mass%	Error%	Atom%
O	0.525	38.37	0.31	69.86
Si	1.739	9.49	0.30	9.56
Zn	8.630	52.15	4.03	22.58
Total		100.00		100.00

C

ZAF Method Standard less Quantitative Analysis
Fitting Coefficient: 0.3504

Element	(keV)	Mass%	Error%	Atom%
O K	0.525	23.78	0.31	54.11
Si K	1.739	4.65	0.30	6.03
Zn K	8.630	71.57	3.65	39.86
Total		100.00		100.00

Figure 1: SEM-EDS results of ZnO/SiO_2 composite and their composition. The above data are for composite with ratio of ZnO/SiO_2 of (A) 3:1 (B) 4:1 and (C) 5:1.

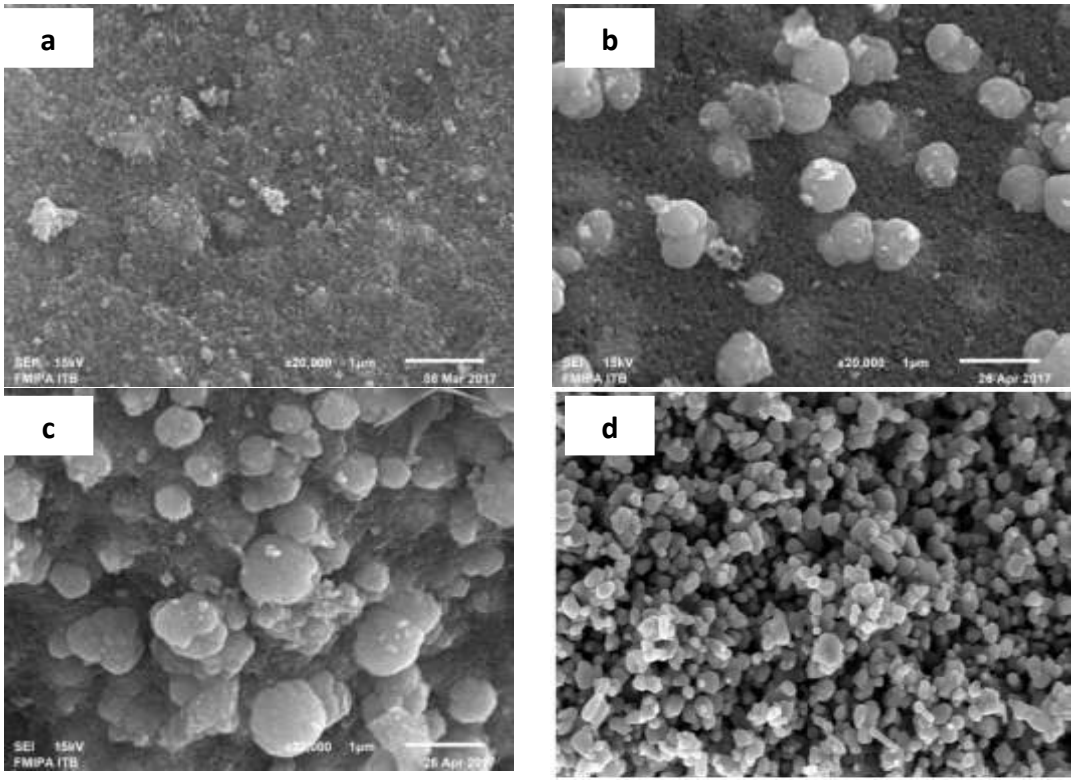

Figure 2: SEM image of ZnO/SiO_2 composite at 20000× magnification. The above images are for composite with ratio of ZnO/SiO_2 of (A) 3:1 (B) 4:1 and (C) 5:1 and (D) ZnO reference[6]

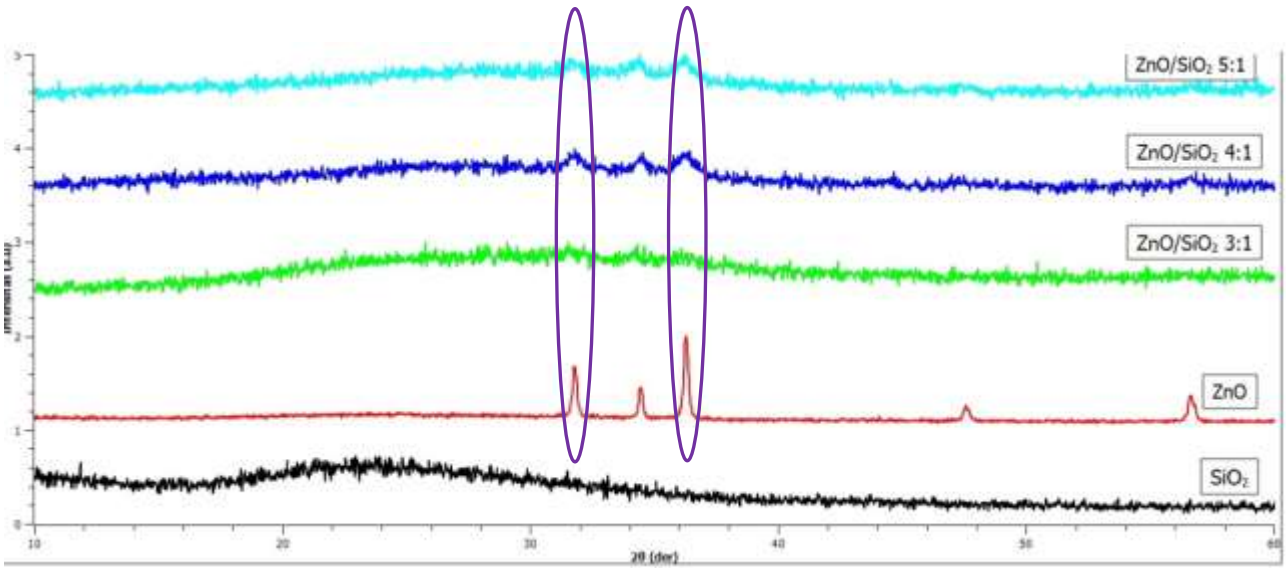

Figure 3: XRD pattern of ZnO/SiO_2 composite compared to ZnO and SiO_2 reference

Table 1
Moisture and ash content of rice husk char

Moisture content (%)	Average ± SD	Ash (%)	Average ± SD
8.63	4.36 ± 2.63	59.64	65.85 ± 5.38
4.58		64.11	
1.51		62.54	
3.56		71.36	
3.53		71.58	

SEM results of the composite are presented in figure 2. Figure 2(a) showed composite with 3:1 = ZnO/SiO_2 ratio and it can be observed that less granule is formed on top of the samples. Figure 2(b) with 4:1 ratio indicates that granules are spread all over the surface. SEM result of composite with 5:1 ratio is presented in figure 2(c) and showed denser and equally spread. Compared to zinc oxide reference (figure 2(d)) published by Sarma et al[6], the morphology of the ZnO/SiO_2 composite highly resembles to the reference.

Characterization of ZnO/SiO_2 composite with XRD: The synthesized composite was XRD was compared to reference ZnO. On the XRD pattern, peaks of ZnO appear and become clearer when higher ratio of ZnO was used. Two peaks were used as reference as indicated in figure 3. The composite XRD pattern indicates the presence of other peak than the ZnO peak while some of them represent SiO_2 peaks. According to Zhai et al[7], when silica used in the fabrication of composite is relatively small, it will give faint peak of amorphous silica on the XRD pattern.

Conclusion

XRD indicates that ZnO/SiO_2 composite has peaks in agreement with ZnO and SiO_2 reference peaks. SEM-EDS results lead us to conclude that higher ratio of ZnO in the composite will lead to tighter and uniformly spreaded granules. This phenomenon may be due to increasing ratio of Zn in the composite.

Acknowledgment

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