

Preparation of Green-Emissive Zinc Oxide Composites Using Natural Betacyanin Pigment Isolated from Red Dragon Fruit

Yehezkiel Steven Kurniawan¹, Hendrik Oktendy Lintang^{1,2}, and Leny Yuliati^{1,2,*}

¹Ma Chung Research Center for Photosynthetic Pigments, Universitas Ma Chung, Villa Puncak Tidar N-01, Malang 65151, East Java, Indonesia

²Department of Chemistry, Faculty of Science and Technology, Universitas Ma Chung, Villa Puncak Tidar N-01, Malang 65151, East Java, Indonesia

* **Corresponding author:**

tel: +62-341-550171

email: leny.yuliati@machung.ac.id

Received: December 9, 2019

Accepted: August 25, 2020

DOI: 10.22146/ijc.52351

Abstract: In this work, we reported the synthesis of green-emissive composite materials of zinc oxide (ZnO) and isolated betacyanin pigment from red dragon fruit (RDF) extract utilizing organic linkers, i.e. (3-chloropropyl)trimethoxysilane (CPTMS) and (3-aminopropyl)trimethoxysilane (APTMS). Betacyanin was extracted using a maceration technique, while CPTMS-ZnO and APTMS-ZnO were prepared by mixing ZnO and the respective organic linker in ethanol. The obtained ZnO/CPTMS and APTMS-ZnO composites were separately added into the RDF extract, followed by stirring at room temperature for 24 h. As high as 80 and 90% of betacyanin was successfully impregnated onto CPTMS-ZnO and APTMS-ZnO, respectively. A comparison study was made by preparing RDF-CPTMS and RDF-APTMS first and then introducing them onto ZnO. In this case, as high as 81 and 100% of betacyanin in RDF-CPTMS and RDF-APTMS, respectively, were impregnated onto ZnO. These results revealed that APTMS was a better organic linker than CPTMS and the order of the steps to introduce APTMS was important. The presence of betacyanin on the composite materials was confirmed by FTIR and fluorescence spectroscopy. All the composite materials had an excitation signal at 426–428 nm and emission signals at 459 and 517–518 nm, demonstrating their promising application as green-emissive materials.

Keywords: betacyanin; composite; green-emissive; red dragon fruit; ZnO

■ INTRODUCTION

In recent years, there has been a high demand for research related to photonic materials due to its wide application for human appliances [1-5]. Regarding this topic, many researches are still focused on enhancing and optimizing the efficiency of the materials. Zinc oxide (ZnO), a material with a direct bandgap of 3.3 eV, has been used over the past several years as photocatalysts, semiconductors, electronic material, etc. [6-7]. With such a large bandgap, pure ZnO can only be applied in the UV region [8]. Therefore, enhancing the efficiency of ZnO material in the visible region leaves a challenge for material scientists. Sensitizing ZnO material with either synthetic dye or natural pigment is a well-known procedure to enhance the light absorption region of this

material [9-10]. However, synthetic dye generates serious environmental problems in their application to produce dye-sensitized materials [11].

Red dragon fruit (RDF) is an abundantly available tropical fruit in Indonesia, which contains several unique secondary metabolites, such as betacyanin, flavonoid, and carotenoid [12-14]. It has been reported that betacyanin pigment could be isolated from the flesh of RDF using a maceration method for 24 h [15]. Incorporation of natural pigments may overcome the limitation of the ZnO material as a photocatalyst to be utilized in the visible region, especially in the red color region as the main part of the visible region in the solar spectrum. Betacyanin is recognized as one of the major red natural pigments, and therefore, very potential to be

used to widen the light absorption of ZnO. Owing to the alcohol and carboxylic acid functional groups, it is possible to immobilize the betacyanin pigment onto the surface of ZnO materials using a suitable linker agent. Even though the visible light emissive material is promising, the method to prepare the ZnO composites consisting of the betacyanin pigment from RDF has not been developed yet. We demonstrated that the use of a suitable organic linker would be a great method to prepare the composite. This research opens the possibility to utilize natural pigments to improve the properties of the photonic materials such as ZnO.

In the present work, we also reported that the prepared betacyanin-modified ZnO exhibited strong green emission, which would be very interesting for photonic material application. We prepared green emissive ZnO based composite materials utilizing isolated betacyanin pigment from RDF and either (3-chloropropyl)trimethoxysilane (CPTMS) or (3-aminopropyl)trimethoxysilane (APTMS) as the organic linker agent. By a stirring method for 24 h, four (4) types of ZnO based materials, named as RDF/CPTMS-ZnO, RDF/APTMS-ZnO, RDF-CPTMS/ZnO and RDF-APTMS/ZnO have been successfully obtained based on the use of different linkers and the order to introduce the betacyanin pigment on the ZnO. These materials were thoroughly characterized by spectroscopy instruments to investigate the physicochemical properties as green emissive composite materials.

■ EXPERIMENTAL SECTION

Materials

Fresh RDFs were obtained commercially from a supermarket in Malang, East Java. Meanwhile, the ZnO materials were prepared in a similar manner to the procedure which has been reported previously [16]. The organic linkers (3-chloropropyl)trimethoxysilane (CPTMS) and (3-aminopropyl)trimethoxysilane (APTMS) were purchased from Sigma Aldrich. Ethanol was purchased from E-Merck in pro analysis grade and used without any further purifications.

The optical properties of the composite materials were measured by diffuse reflectance ultraviolet-visible

(DR UV-Vis) spectrophotometer (JASCO V-760), while the bandgap energy of the composite materials was calculated from Tauc plot using the data. The infrared and fluorescence spectra of the composite materials were recorded by Fourier transform infrared spectrophotometer (JASCO FTIR-6800) and spectrofluorometer (JASCO FP-8500), respectively.

Procedure

Isolation of betacyanin pigment from the RDF

The isolation of betacyanin pigment from RDF was carried out according to the previously described method [15,17]. In short, the flesh of RDF (5.0 g) was dried at room temperature overnight and macerated with distilled water (50 mL) for 24 h. Afterward, the mixture was filtered. The clear filtrate was finally characterized by FTIR spectrophotometer and spectrofluorometer.

Preparation of composite materials

In this work, there were two types of composite materials, namely RDF/linker-ZnO and RDF-linker/ZnO materials. The term RDF/linker-ZnO material showed that the organic linker was reacted first with ZnO and then further reacted with RDF extract, while the term RDF-linker/ZnO material indicated that the organic linker was first reacted with RDF extract and then further reacted with ZnO.

The RDF/linker-ZnO materials, i.e., RDF/CPTMS-ZnO and RDF/APTMS-ZnO, were prepared through a simple stirring method. First, the organic linker (0.25 mL) and ZnO (0.25 g) were added stepwise into ethanol (12.5 mL), and then the mixture was stirred at 500 rpm at room temperature for 24 h. After that, the residue was filtered and added to 5% v/v RDF extract in ethanol (12.5 mL). The mixture was stirred for another 24 h. The mixture was then filtered and the residue was dried to obtain the RDF/linker-ZnO composite materials.

The RDF-linker/ZnO materials, i.e. RDF-CPTMS/ZnO and RDF-APTMS/ZnO were also simply obtained by a stirring method. First, the organic linker (0.25 mL) was added dropwise to 5% v/v RDF extract in ethanol (12.5 mL) and the mixture was stirred at 500 rpm for 24 h. Afterward, ZnO (0.25 g) was added

and the mixture was stirred for 24 h. The mixture was filtered and the residue was dried to obtain the RDF-linker/ZnO composite materials.

■ RESULTS AND DISCUSSION

Preparation of Composite Materials

In this work, ZnO-based composite materials were prepared and evaluated for their potential application as emissive materials. At first, the betacyanin pigment was isolated from RDF extract through a maceration method with distilled water. As has been reported, betacyanin pigment was confirmed to be successfully isolated from RDF extract using the maceration method [15,18-19]. On the other hand, the prepared ZnO has been reported to give a bandgap energy value of 3.29 eV [16].

The isolated betacyanin pigment was used to prepare the composites in two different procedures. In the first procedure, the organic linker was attached first on the surface of the ZnO material and then the isolated betacyanin pigment was immobilized onto it. Meanwhile, the other way involved the reaction between the isolated betacyanin pigment and organic linker, followed by its immobilization onto the surface of the ZnO material.

The color appearances of the prepared ZnO based materials can be seen in their photographs as shown in Fig. 1. From Fig. 1(a), it can clearly be observed that ZnO has a white color. In contrast, both RDF/CPTMS-ZnO and RDF-CPTMS/ZnO were obtained as bright purplish

solids as shown in Fig. 1(b) and (c), respectively. On the other hand, Fig. 1(d) and (e) showed that RDF/APTMS-ZnO appeared as a pale yellow solid while RDF-APTMS/ZnO appeared as a bright yellow solid. The difference of the color appearance showed the different forms of immobilized betacyanin on the composite material. It was previously reported by Strack et al. (2003) that the color of betacyanin would depend on the pH of the solution [20]. Below pH 10, the color of betacyanin solution is red, while its color turns to yellow when the pH is higher than 10. Since the CPTMS organic linker is acidic, the pH of the filtrate during the reaction was 4.53. Therefore, the color of RDF/CPTMS-ZnO and RDF-CPTMS/ZnO was purplish. On the other hand, the use of APTMS caused the mixture to be alkaline (pH = 10.8), hence the color of betacyanin pigment changed from red to bright yellow. Therefore, it is reasonable for both RDF/APTMS-ZnO and RDF-APTMS/ZnO to be obtained as yellow solids. The formation of such color in the composites showed that the light absorption of ZnO had been expanded successfully to the visible light region.

Characterization of Composite Materials

DR UV-vis spectra of ZnO and the composite materials are shown in Fig. 2. As expected, the white ZnO sample only showed absorption in the UV region up to 380 nm. On the other hand, the composite materials gave extra absorption at the background level in

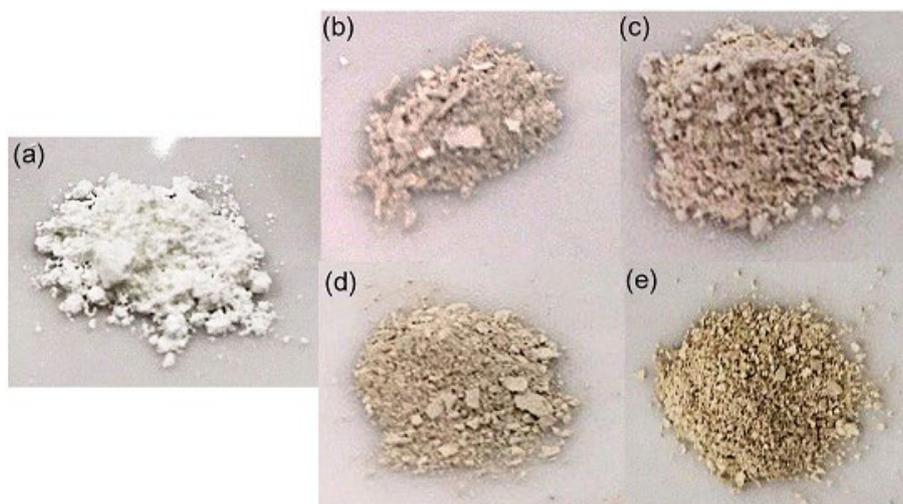


Fig 1. Photographs of (a) ZnO and ZnO based composite materials, including (b) RDF/CPTMS-ZnO, (c) RDF-CPTMS/ZnO, (d) RDF/APTMS-ZnO, and (e) RDF-APTMS/ZnO

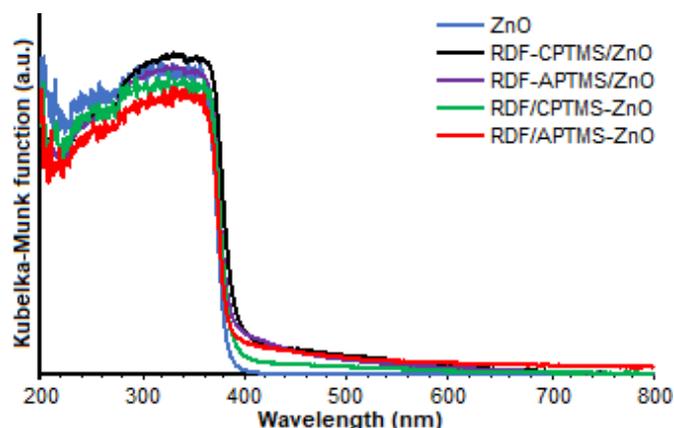


Fig 2. DR UV-vis spectra of ZnO and ZnO based composite materials

the visible region due to the presence of betacyanin from the RDF extract, which is in good agreement to the color appearances of the composites. From the DR UV-vis spectra of the composite materials, the bandgap energy of the composite materials was calculated accordingly and shown in Table 1. The bandgap energy of unmodified ZnO, RDF-CPTMS/ZnO, RDF-APTMS/ZnO, RDF/CPTMS-ZnO and RDF/APTMS-ZnO composite materials were 3.29, 3.22, 3.23, 3.26 and 3.26 eV, respectively. The bandgap energy of the composite materials was not significantly different from the unmodified ZnO because the betacyanin pigment was only immobilized on the surface of the ZnO materials. In this case, the betacyanin pigment would act as the sensitizer. The values of the bandgap energy in this work were close to other reported ZnO dye-sensitized solar cells

[21] and natural pigment-modified ZnO materials prepared from laali [22].

The bandgap energy of the composite materials seemed to be independent on the organic linker, but dependent on the order of betacyanin introduction. For example, when the organic linker was immobilized first onto the ZnO surface, the bandgap energy was 3.26 eV for both CPTMS and APTMS. However, when the organic linker-betacyanin was immobilized onto the ZnO surface, the bandgap energy was slightly lower, which were 3.22 and 3.23 eV for CPTMS and APTMS, respectively. When betacyanin was reacted first with the organic linker, the betacyanin-linker might have created new energy states that were more positive than the conduction band of ZnO and the linker or betacyanin itself, which in turn gave a slightly lower bandgap energy than ZnO and RDF/linker-ZnO.

The FTIR spectra of ZnO, RDF extract, and composite materials are shown in Fig. 3. The FTIR spectrum of unmodified ZnO showed two main absorption peaks at 3394 and 434 cm^{-1} , corresponding to Zn-O-H and Zn-O-Zn moieties, respectively [23].

Table 1. Bandgap energy of the composite materials

Materials	Bandgap (eV)
ZnO	3.29
RDF-CPTMS/ZnO	3.22
RDF-APTMS/ZnO	3.23
RDF/CPTMS-ZnO	3.26
RDF/APTMS-ZnO	3.26

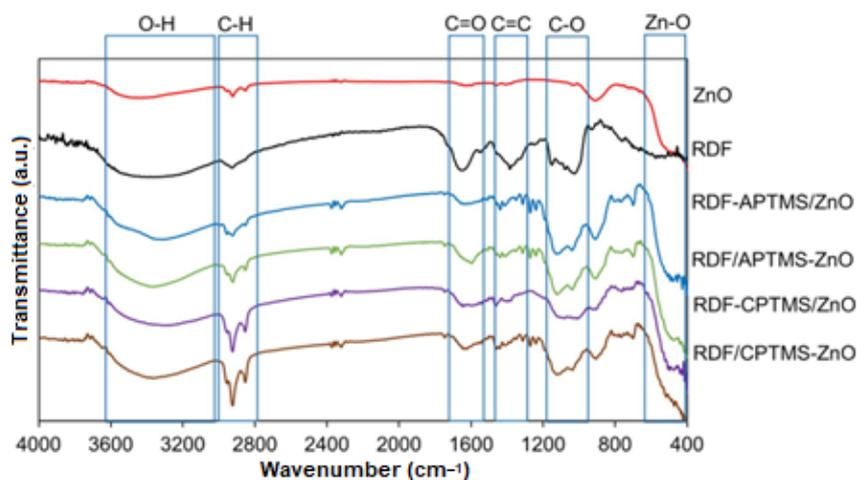


Fig 3. FTIR spectra of ZnO, RDF, and ZnO based composite materials

The FTIR spectrum of isolated betacyanin from the RDF extract showed O-H, C-H sp^3 , C=O, C=C, and C-O functional groups at 3340, 2902–2891, 1628, 1512–1314, and 1024 cm^{-1} , respectively [19]. As depicted in the FTIR spectra of the composite materials, in addition to the ZnO absorption peaks, the peaks of betacyanin functional group also existed, strongly indicating that the

immobilization of betacyanin pigment on the surface of the ZnO material has been successfully carried out.

Further characterization of composite materials was investigated by fluorescence spectroscopy. The three-dimensional fluorescence spectra of unmodified ZnO, RDF extract, and the composite materials are shown in Fig. 4. The unmodified ZnO gave a strong excitation

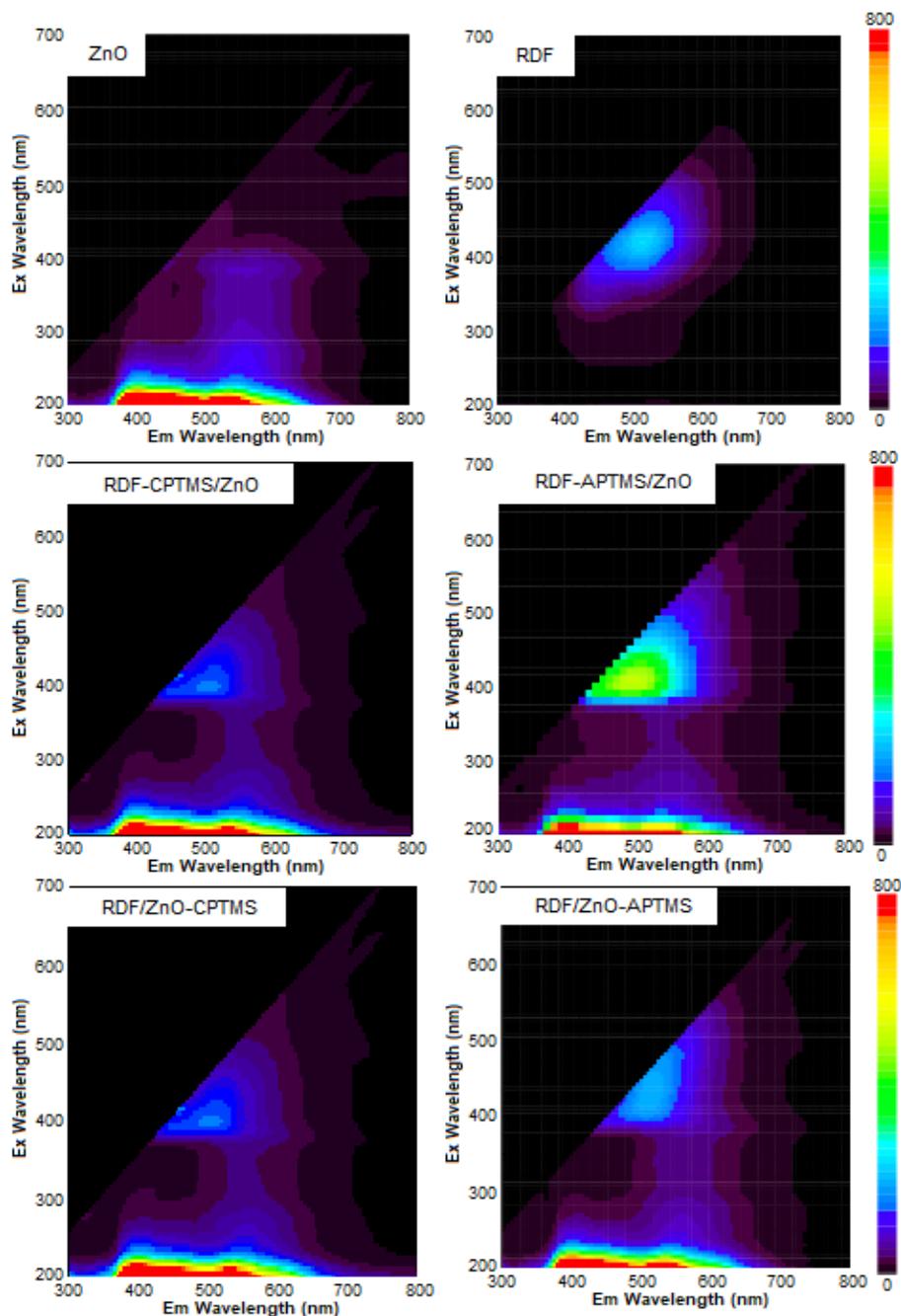


Fig 4. Three-dimensional fluorescence spectra of ZnO, RDF, and ZnO based composite materials

peak around 200 nm in good agreement with the strong light absorption of ZnO in the UV region and the weak excitation peak could be observed around 428 nm. The emission region of ZnO was wide and in the range of 350–650 nm. On the other hand, the RDF extract gave a weak excitation peak around 405 nm and the emission region was in the range of 430–680 nm. It was obvious that the three-dimensional fluorescence spectrum of composite materials was indeed a combination of the

three-dimensional fluorescence spectrum of ZnO and RDF extract. This result again clearly indicated the successful immobilization of the RDF extract onto ZnO.

From the fluorescence spectrum in the visible region of ZnO (Fig. 5), it was confirmed that the wavelengths of the excitation and emission were at 428 and 459 nm, respectively. These wavelengths were different from those of the RDF extract, where the maximum wavelengths of the excitation and emission

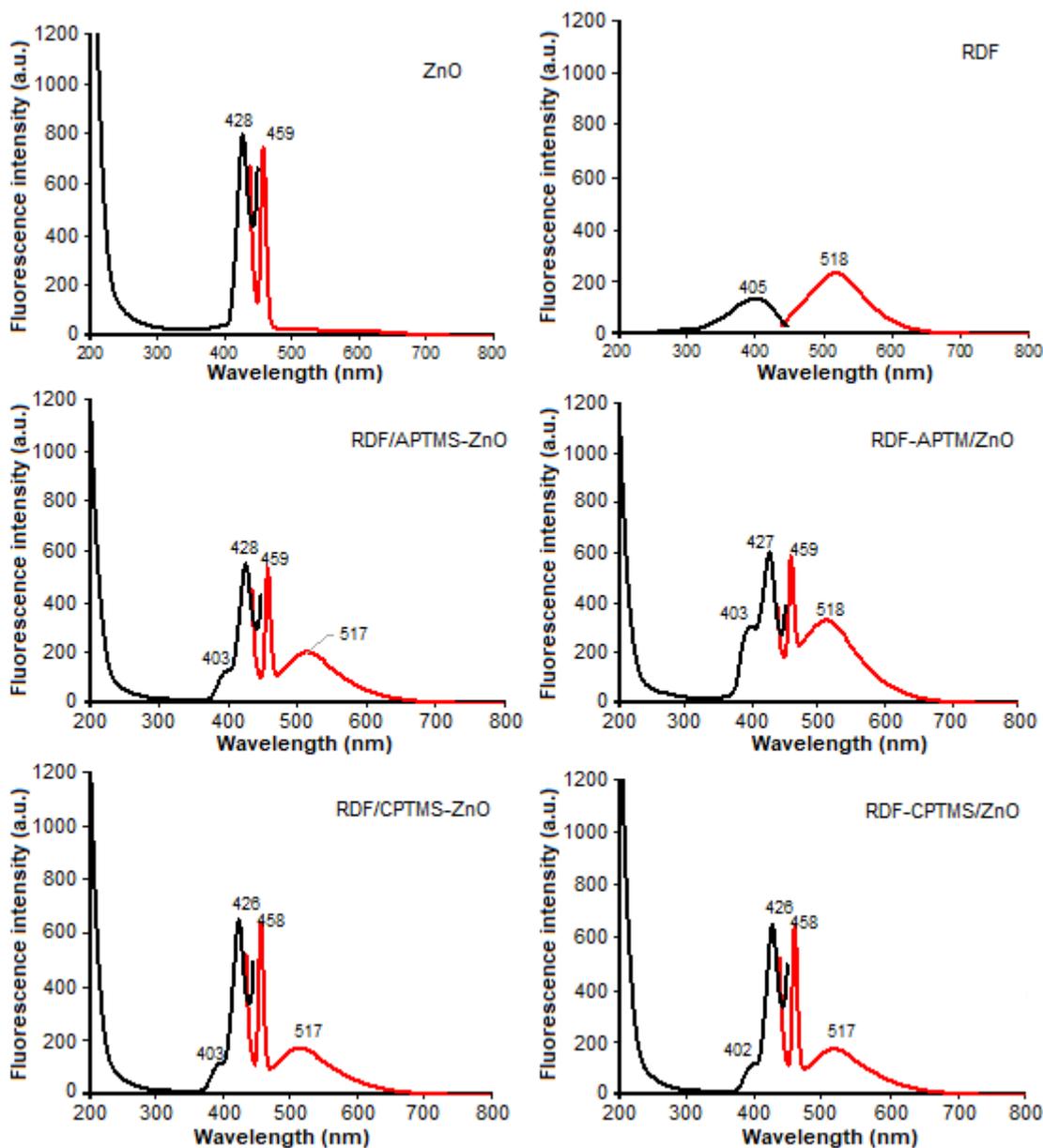


Fig 5. Fluorescence spectra of ZnO, RDF, and ZnO based composite materials. Black and red lines represent excitation and emission spectrum, respectively

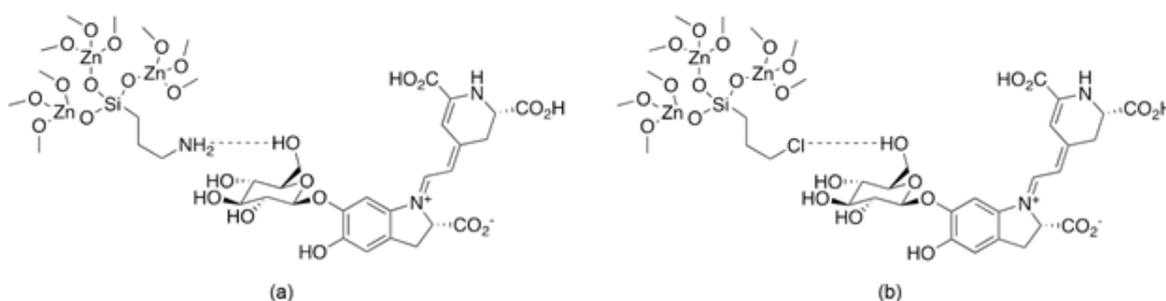


Fig 6. Proposed interactions between betacyanin pigment with (a) APTMS and (b) CPTMS on the ZnO surface

spectrum were found at 405 and 518 nm, respectively. As shown in Fig. 4, all the excitation and emission peaks of ZnO and RDF extract also existed on the composite materials. This work demonstrated that the immobilization of betacyanin pigment onto the ZnO surface has successfully enhanced the absorption region of the composite materials. Since the emission signals were found in 458–518 nm region, the prepared composite materials are promising to be used as green-emissive materials.

From the fluorescence intensity of the emission peak at 518 nm, the immobilization percentage of betacyanin pigment on the composite materials was calculated and shown in Table 2. The immobilized betacyanin amounts on the RDF-CPTMS/ZnO and the RDF-APTMS/ZnO were found to be 81% and 100%, respectively. This result showed that APTMS was a better organic linker than CPTMS in obtaining the ZnO composite. As betacyanin pigment has alcohol and carboxylic acid groups, betacyanin pigment would interact well with the amino substituent of APTMS through the hydrogen bondings rather than with the chloro substituent of CPTMS. This would be the reason why the immobilization percentages of betacyanin pigment were higher on the APTMS-based composite than the CPTMS-based one. The proposed interactions between the betacyanin pigment and the organic linker on the ZnO surface are shown in Fig. 6. Similar to our previous work [24], the interactions would mainly happen between either amino or chloro substituent of the organic linker and the primary alcohol substituent on the tetrahydropyran ring of the betacyanin due to less steric hindrance. Therefore, it was reasonable that flavonoid and carotenoid pigments were not immobilized

Table 2. Immobilized betacyanin percentages on the ZnO based composite materials

Materials	Immobilized betacyanin (%)
ZnO	0
RDF-CPTMS/ZnO	81
RDF-APTMS/ZnO	100
RDF/CPTMS-ZnO	80
RDF/APTMS-ZnO	90

on the ZnO materials because these pigments are non-polar [25], and thus, could not interact through hydrogen bondings with the linker agents.

On the other hand, only 80% and 90% of betacyanin was impregnated onto CPTMS-ZnO and APTMS-ZnO, respectively. While this result also showed that APTMS was better than CPTMS to impregnate the betacyanin onto ZnO, the order to introduce APTMS was found to be critical to obtaining larger amounts of immobilized betacyanin. When the betacyanin pigment was reacted with APTMS-ZnO material, it is possible for the betacyanin pigment to interact weakly with the Zn-OH group. Because of that, after filtration the immobilization percentage of betacyanin pigment on the RDF/APTMS-ZnO was lower than that of the RDF-APTMS/ZnO material.

■ CONCLUSION

In the present work, we successfully prepared four types of ZnO based composite materials through immobilization of betacyanin pigment on the surface of ZnO material using either CPTMS or APTMS as the organic linker. Both the RDF/CPTMS-ZnO and RDF-CPTMS/ZnO were obtained as purplish solids, while the RDF/APTMS-ZnO and RDF-APTMS/ZnO materials

appeared as pale yellow and bright yellow solid, respectively. The bandgap energy of the composite materials was not significantly different from the unmodified ZnO because the betacyanin pigment was immobilized on the surface of the ZnO. The FTIR spectra of the composite materials showed the presence of O–H, C–H sp^3 , C=O, C=C, and C–O functional groups. As high as 100% immobilized betacyanin could be achieved when the betacyanin was reacted first with APTMS, followed by impregnation onto ZnO. This result showed the importance of using APTMS and the order to introduce the betacyanin pigment onto ZnO. From the fluorescence spectrum of the composite materials, the emission signals were found at 458–518 nm region, demonstrating that the prepared composite materials are promising to be used as green-emissive materials.

■ ACKNOWLEDGMENTS

Support from the Directorate General of Research Strengthening and Development, Ministry of Research, Technology and Higher Education of the Republic of Indonesia via the Higher Education Excellent Applied Research scheme (PTUPT 2019 and PTUPT 2020, No. 041/SP2H/LT/MULTI/L7/2019 as revised in 041/SP2H/AMD/LT/MULTI/L7/2020, No. 005/MACHUNG/LPPM/SP2H-LIT-MULTI/III/2019, and No. 002/MACHUNG/LPPM/SP2H-LIT-MULTI/AMD/VI/2020) is greatly acknowledged.

■ REFERENCES

- [1] Ramkumar, V., and Kannan, P., 2015, Novel heterocyclic based blue and green emissive materials for opto-electronics, *Opt. Mater.*, 46, 314–323.
- [2] Zhu, C., Liu, X., Ni, Y., Fang, J., Fang, L., Lu, C., and Xu, Z., 2017, Novel fluorescence adjustable photonic crystal materials, *Opt. Mater.*, 73, 415–422.
- [3] Böttner, S., Jorgensen, M.R., and Schmidt, O.G., 2016, Rolled-up nanotechnology: 3D photonic materials by design, *Scr. Mater.*, 122, 119–124.
- [4] Freitag, M., Teuscher, J., Saygili, Y., Zhang, X., Giordano, F., Liska, P., Hua, J., Zakeeruddin, S.M., Moser, J.E., Grätzel, M., and Hagfeldt, A., 2017, Dye-sensitized solar cells for efficient power generation under ambient lighting, *Nat. Photonics*, 11 (6), 372–378.
- [5] Zheng, X., Li, D., Li, X., Chen, J., Cao, C., Fang, J., Wang, J., He, Y., and Zheng, Y., 2015, Construction of ZnO/TiO₂ photonic crystal heterostructures for enhanced photocatalytic properties, *Appl. Catal., B*, 168–169, 408–415.
- [6] Chen, Y., Bagnall, D., and Yao, T., 2000, ZnO as a novel photonic material for the UV region, *Mater. Sci. Eng., B*, 75 (2-3), 190–198.
- [7] Lee, K.M., Lai, C.W., Ngai, K.S., and Juan, J.C., 2016, Recent developments of zinc oxide based photocatalyst in water treatment technology: A review, *Water Res.*, 88, 428–448.
- [8] Xu, L., Zhou, Y., Wu, Z., Zheng, G., He, J., and Zhou, Y., 2017, Improved photocatalytic activity of nanocrystalline ZnO by coupling with CuO, *J. Phys. Chem. Solids*, 106, 29–36.
- [9] Dhafina, W.A., Salleh, H., Daud, M.Z., and Ghazali, M.S.M., 2018, Low cost dye-sensitized solar cells based on zinc oxide and natural anthocyanin dye from *Ardisia elliptica* fruits, *Optik*, 172, 28–34.
- [10] Vittal, R., and Ho, K.C., 2017, Zinc oxide based dye-sensitized solar cells: A review, *Renewable Sustainable Energy Rev.*, 70, 920–935.
- [11] Hassaan, M.A., and Nemr, A.E., 2017, Health and environmental impacts of dyes: Mini review, *Am. J. Environ. Sci. Eng.*, 1 (3), 64–67.
- [12] Liaotrakoon, W., De Clercq, N., Van Hoed, V., Van de Walle, D., Lewille, B., and Dewettinck, K., 2013, Impact of thermal treatment on physicochemical, antioxidative and rheological properties of white-flesh and red-flesh dragon fruit (*Hylocereus* spp.) purees, *Food Bioprocess Technol.*, 6 (2), 416–430.
- [13] Lee, K.H., Wu, T.Y., and Siow, L.F., 2013, Spray drying of red (*Hylocereus polyrhizus*) and white (*Hylocereus undatus*) dragon fruit juices: Physicochemical and antioxidant properties of the powder, *Int. J. Food Sci. Technol.*, 48 (11), 2391–2399.
- [14] Kim, H., Choi, H.K., Moon, J.Y., Kim, Y.S., Mosaddik, A., and Cho, S.K., 2011, Comparative antioxidant and antiproliferative activities of red and white pitayas and their correlation with

- flavonoid and polyphenol content, *J. Food Sci.*, 76 (1), C38–45.
- [15] Priatni, S., and Pradita, A., 2015, Stability study of betacyanin extract from red dragon fruit (*Hylocereus polyrhizus*) peels, *Procedia Chem.*, 16, 438–444.
- [16] Nimpoeno, W.A., Lintang, H.O., and Yuliati, L., 2020, Methyl red dye-sensitized zinc oxide as photocatalyst for phenol degradation under visible light, *AIP Conf. Proc.*, 2237, 020048.
- [17] Kurniawan, Y.S., Adhiwibawa, M.A.S., Setiyono, E., Fahmi, M.R.G., and Lintang, H.O., 2019, Statistical analysis for evaluating natural yellow coloring agents from peel of local fruits in Malang: Mangosteen, honey pineapple and red dragon fruits, *Indones. J. Nat. Pigm.*, 1 (2), 49–52.
- [18] Stintzing, F.C., Schieber, A., and Carle, R., 2002, Betacyanins in fruits from red-purple pitaya, *Hylocereus polyrhizus* (Weber) Britton & Rose, *Food Chem.*, 77 (1), 101–106.
- [19] Calogero, G., Yum, J.H., Sinopoli, A., Marco, G.D., Grätzel, M., and Nazeeruddin, M.K., 2012, Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells, *Sol. Energy*, 86 (5), 1536–1575.
- [20] Strack, D., Vogt, T., and Schliemman, W., 2003, Recent advances in betalain research, *Phytochemistry*, 62 (3), 247–269.
- [21] Ayinde, W.B., Dare, E.O., Bada, D.A., Alayande, S.O., Oladoyindo, F.O., Idowu, M.A., Bolaji, B.O., Ezeh, M.I., and Osuji, R.U., 2017, Dye-modified ZnO nanohybrids: Optical properties of the potential solar cell nanocomposites, *Int. Nano Lett.*, 7 (3), 171–179.
- [22] Nunes, V.F., Souza, A.P.S., Lima, F., Oliveira, G., Freire, F.N., and Almeida, A.F., 2018, Effects of potential deposition on the parameters of ZnO dye-sensitized solar cells, *Mat. Res.*, 21 (4), e20170990.
- [23] Zhang, Q., Xu, M., You, B., Zhang, Q., Yuan, H., and Ostrikov, K., 2018, Oxygen vacancy-mediated ZnO nanoparticle photocatalyst for degradation of methylene blue, *Appl. Sci.*, 8 (3), 353.
- [24] Kurniawan, Y.S., Anggraeni, K., Indrawati, R., and Yuliati, L., 2019, Selective betalain impregnation from red amaranth extract onto titanium dioxide nanoparticles, *AIP Conf. Proc.*, 2175, 020049.
- [25] Purnomo, T.A.B., Kurniawan, Y.S., Kesuma, R.F., and Yuliati, L., 2020, Selection of maceration solvent for natural pigment extraction from red fruit (*Pandanus conoideus* Lam), *Indones. J. Nat. Pigm.*, 2 (1), 8–12.