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Colorimetric Oxygen Indicator from Titanium Dioxide Nanocomposite by Mechanical Milling Process

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Abstract

This research aims to develop the efficiency of colorimetric oxygen indicator by titanium dioxide/methylene blue nanocomposite. The indicator was composed of titanium dioxide (TiO_2) nanoparticles as a semiconductor photocatalyst, methylene blue (MB) as a redox dye, and citric acid as a sacrificial electron donor. TiO_2/MB nanocomposite was synthesized via a mechanical milling process based on crucial parameters of rotation speed and milling time. Rotation speed in the milling process was studied at 200, 250, and 300 rpm with different milling times in the wet process at 15, 30, and 45 min. After that, all conditions of TiO_2/MB nanocomposite in blue ink suspension were pasted on glass slide substrate by screen printing technique and baked at 100°C for 30 min. TiO_2/MB indicators were exposed under UVA irradiation (λ_{max} at 360 nm) for 3 min until bleaching state. The bleached indicators were placed in an air environment and recovered in a blue state. Switching time at activated TiO_2/MB nanocomposite layer was monitored by the timer that indicated on the colorimetric switching color responsibility recovery with oxygen gas in the environment. Functional groups of TiO_2/MB nanocomposite before/after colorimetric state were analyzed by fourier transform-infrared (FT-IR) spectrometer. Meanwhile, the absorption and diffuse reflection properties of the indicators were monitored by a UV-VIS-NIR spectrophotometer. The mechanism of color switching in the TiO_2/MB indicator depends on the structural changing of methylene blue with the cooperation with TiO_2 photocatalyst in the nanocomposite.

Keywords: Colorimetric, Milling, Nanocomposite, Oxygen indicator, TiO_2/methylene blue

1. Introduction

Nowadays, the modified atmosphere packaging (MAP) process is one of the effective methods to extending the shelf life of fresh food in the food package. The advantage of the MAP process is the preservation of food quality during storage and transportation to consumers. However, if the packaging is leaked on the product without any traces, the food inside the container can be oxidized by oxygen gas in the atmosphere relating to low quality and rotten food. Therefore, the indicator on food packaging is important to monitor food quality. Oxygen indicator is an interesting device for monitoring some leaks inside food packaging by the detection of oxygen gas. There are three types of oxygen indicators as electrochemical oxygen indicator, optical oxygen indicator, and colorimetric oxygen indicator [1]. The first indicator type as electrochemical oxygen indicator is the earliest oxygen sensor with Clark electrode and designed for the measurement of oxygen pressure in arterial blood samples. This kind of oxygen indicator provides the determination of oxygen gases and gives information on food quality and package integrity. However, this indicator is high-cost, destroys the packaging, and requires a specialized person to operate. For the second indicator type, the optical oxygen indicator is widely used in chemical, clinical, and environmental applications. The mechanism of the optical oxygen indicator is operated by the reduction of fluorescence intensity with an excited fluorescent indicator as a

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result of the quenching effect induced by the oxygen environment. The active component of the optical oxygen indicator is usually fabricated by a long-delay fluorescent or phosphorescent dye encapsulated in a solid polymer matrix with thin-film formation. Nevertheless, the materials of fluorescent complexes are composed of ruthenium, palladium(II)- and platinum(II)-porphyrin complexes and related structures on the oxygen indicator layer. Therefore, this indicator is not compatible with oxygen detection in food packaging. The last indicator type is the colorimetric oxygen indicator which an inexpensive cost, easy to read and store, irreversible O_2 indicator corresponding to the assurance of package integrity and direct application in the MAP process. Dye properties in colorimetric oxygen must be required as a redox-dye that shown a strong reducing agent and easily re-oxidized by oxygen. The examples of common redox-dye for colorimetric oxygen indicator are methylene blue, indigo (blue), and thioindigo (red), respectively that related to its chemically reduced color and colorless form.

In this work, the colorimetric oxygen indicator is focused on metal oxide nanocomposite with redox dye. Titanium dioxide (TiO_2) and methylene blue (MB) were chosen as semiconductor photocatalyst and redox dye. Meanwhile, citric acid was added to the nanocomposite for a sacrificial electron donor to promote color switching in the indicator. TiO_2/MB nanocomposite was synthesized via mechanical high energy milling process assisted with a dry and wet method to produce homogenous suspension for the active layer in the indicator. The ball milling process is one of the simple mechanical techniques and cost-effective green technology that widely used in grind powders into fine particles and blend material. Meanwhile, the milling process is a common technique used in the industry due to its low operating cost, high flexibility, and suitability for large-scale production [2]. The crucial parameters on homogenous TiO_2/MB nanocomposite suspension were concentrated on operation speed and milling time. After that, TiO_2/MB nanocomposite active layer in blue color (colored state) was coated by printing technique owing to a suitable label in food packaging [3]. Then, TiO_2/MB indicators were exposed under UVA irradiation (λ_{max} at 360 nm) for 3 min until bleached state to activate in an initial state of the indicator. The bleached indicators were placed in an air environment and recovered in a colored state after oxygen detection on TiO_2/MB nanocomposite active layer. Switching time at activated TiO_2/MB nanocomposite layer was monitored on colorimetric switching color responsibility recovery with oxygen gas in the environment.

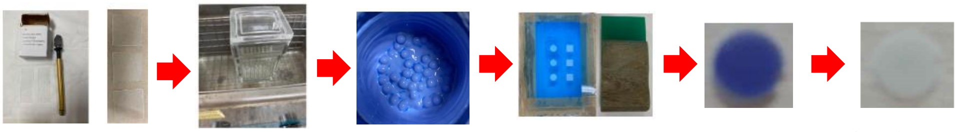
2. Experimental

2.1 Synthesis of TiO_2/MB nanocomposite

As-received TiO_2 P25 nanopowder was used as a metal oxide precursor. Methylene Blue and citric acid in AR grade were purchased from LOBA Chemie and Ajax Finechem company. Homogenous nanocomposite suspension was prepared by adding TiO_2 3 g, MB 12.5 mg, and citric acid 0.15 g in a zirconia container and operated with a high-energy milling process. The ratio weight of precursors and zirconia balls was fixed at 1:10. Firstly, the precursors were milled for 30 min in a dry grinding process with different rotation speed at 200, 250, and 300 rpm. Then, 5 ml of DI water was added in both pots and continuously milled at different milling times at 15, 30, and 45 min. Table 1 showed five samples with different milling time and rotation speed conditions, labeled as samples A, B, C, D, and E. Finally, the homogeneous blue solution of TiO_2/MB nanocomposite was obtained.

Table 1. Conditions of samples with different speed and time

Sample	Rotation speed (rpm)	Milling time in dry grinding (min)	Milling time in wet grinding (min)
A	200	30	30
B	250	30	30
C	300	30	30
D	250	30	15
E	250	30	45



Step 1: Substrate preparation

Step 2: Substrate cleaning process

Step 3: TiO_2/MB nanocomposite suspension

Step 4: Coating process by screen printing technique

Step 5: TiO_2/MB indicator in colored state

Step 6: TiO_2/MB indicator in bleached state

Fig. 1. The schematic of TiO_2/MB nanocomposite indicator preparation

2.2 Preparation of TiO_2/MB nanocomposite layer by a screen printing technique

TiO_2/MB nanocomposite layer was prepared on glass slide substrate by screen printing technique as presented in Fig. 1. Firstly, glass slides were designed with area 2.5×2.5 cm^2 and followed by the cleaning process with alcohol process (Step 1 and 2). The cleaned substrate was fixed under the block screen. Then, TiO_2/MB nanocomposite suspension was put on the block screen design and pressed with squeegees. TiO_2/MB nanocomposite layer was printed onto the glass slides, followed by a dry process at 100°C for 30 min. Before using an indicator, UVA irradiation (λ_{max} at 360 nm) was required for 3 min to activate TiO_2/MB nanocomposite layer for switching between colored state and bleached state.

2.3 Characterizations

The functional group of TiO_2/MB nanocomposite was identified by was measured by Fourier transform infrared spectrometer (FT-IR) in the range of wavelength 400-4,000 cm^{-1}. The optical property of TiO_2/MB nanocomposite layer in reflectance mode was measured by UV-VIS-NIR Spectrophotometer in the range of wavelength 200-800 nm to detect the status of colored state and bleached state before and after UVA irradiation.

3. Results and discussion

Functional chemical groups of TiO_2/MB nanocomposite in the colorimetric and bleached state were investigated by Fourier transform infrared spectrometer (FT-IR) with different rotation speed and milling time are depicted in Fig. 2. Same patterns of FT-IR spectra with different rotation speed is shown in Fig. 2(a). The intense peak at 690 cm^{-1} is assigned to the Ti-O stretching band which is the TiO_2 characteristic peak [4]. FTIR peaks at 885, 1,220, and 1,249 cm^{-1} are indicated to C-H bond vibrations of methylene blue. Meanwhile, the characteristic C=C band of the aromatic rings detected at 1,179 cm^{-1} in the methylene blue spectra appeared at 1,175 cm^{-1}. In addition, the bands at 3,030 cm^{-1} and 3,370 cm^{-1} are attributed to the stretching vibration of the O-H bond and C-H bond, indicating its adsorption onto the methylene blue [5]. The vibrational modes of citric acid are identified as CH_2 rocking at 779 cm^{-1}, C-OH stretching at 1,106 cm^{-1}, C=O stretching (C(O)-OH) at 1,722 $cm^{-1,}$ and O-H stretching (R-C(O)-OH) at 3,290 cm^{-1} [6]. Moreover, a broad peak at 3,414 cm^{-1} assigned to the stretching vibration of the O-H bond of a hydroxyl group on the sample surface. For rotation speed in the milling process, the same patterns of FTIR spectra have occurred as illustrated in Fig. 2(b). It could be concluded that the chemical structure of precursor materials still the same structure after varying rotation speed in the milling process. In the case of different milling times, the same FTIR spectra are obtained and identical to the spectra of rotation speed. Therefore, FTIR results can be confirmed that the chemical structure of nanocomposite is not changed with different rotation speed and milling time by high energy milling process. Moreover, the comparison of TiO_2/MB nanocomposite in colorimetric and bleached state at rotation speed 250 rpm and milling time 45 min in condition E as depicted in Fig. 2(c). FTIR spectra of the sample before and after UVA irradiation shows the same patterns without disguised peak appearing in the pattern. Thus, the difference of color changing in methylene blue structure is not identified by the functional chemical group.

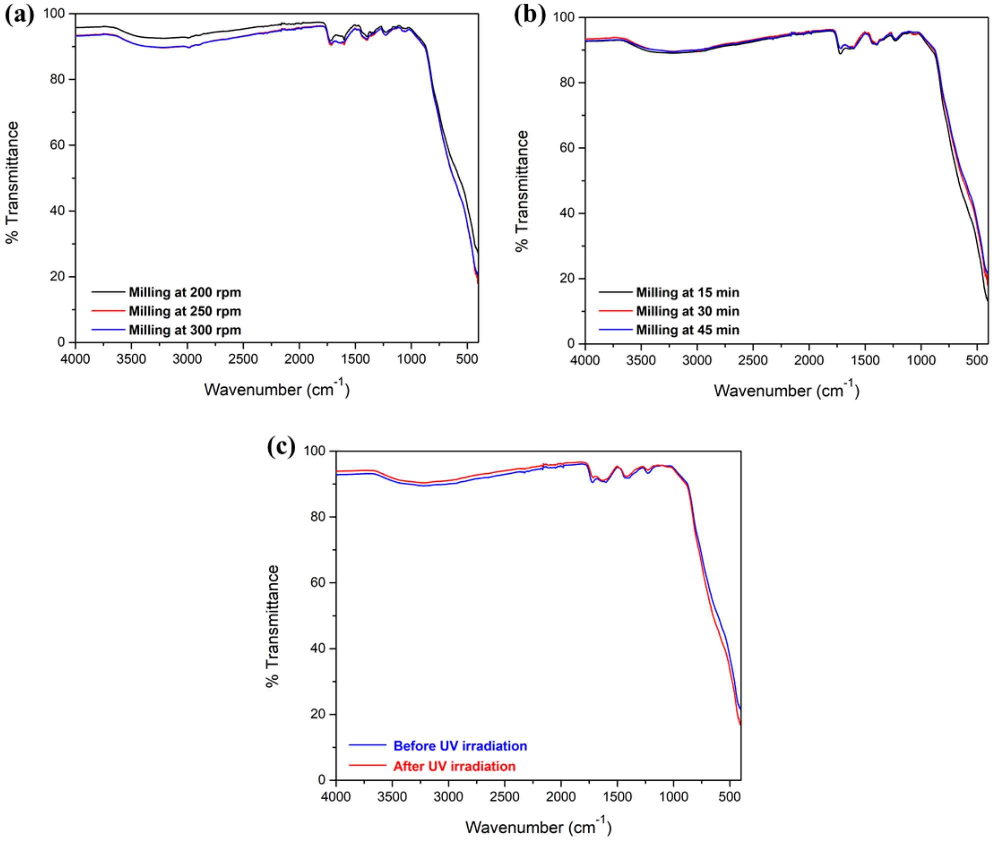


Fig. 2. FT-IR spectra of TiO_2/MB nanocomposite with different parameters in high energy milling process (a) milling at a different rotation speed, (b) milling at different time, and (c) the sample of condition E before and after UVA irradiation

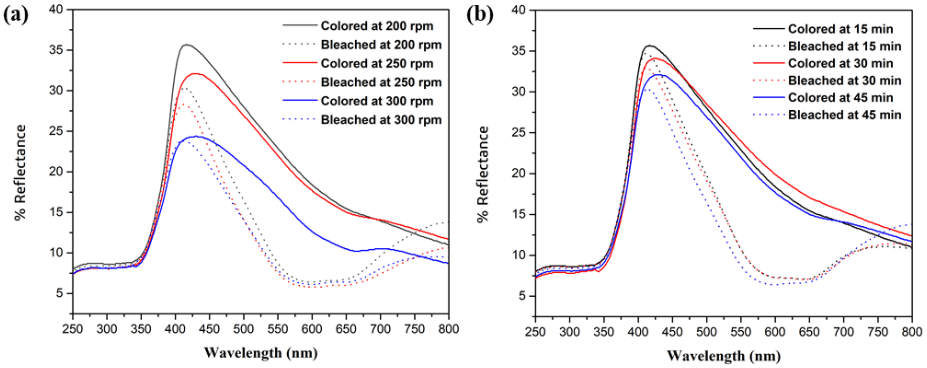
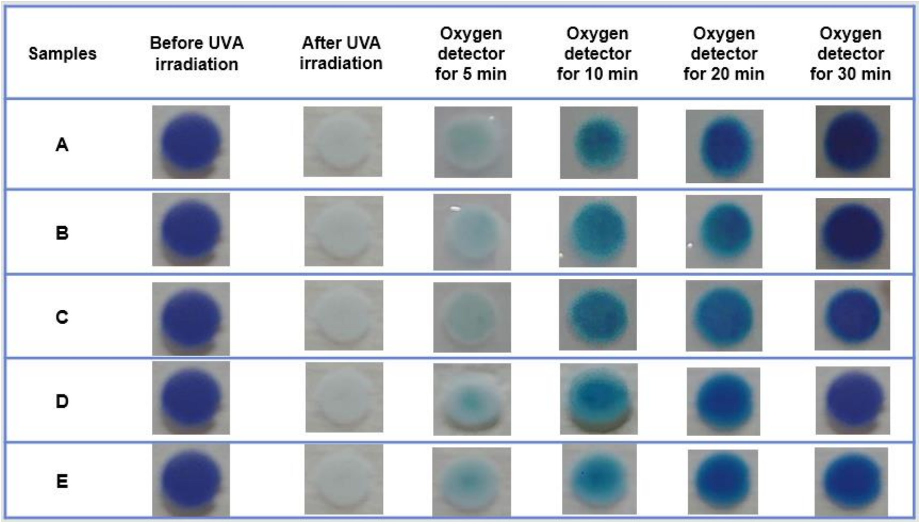


Fig. 3. UV-Vis diffuse reflection spectra of TiO_2/MB nanocomposite with different parameters in high energy ball milling process at different (a) rotation speed and (b) milling time with the colored state (solid line) and bleached stated (dotted line)

Fig. 3 shows diffuse reflection spectra of TiO_2/MB nanocomposite indicators with different rotation speeds and milling time characterized by UV-VIS-NIR spectrophotometer. The colorimetric state in blue color is presented by a solid line, meanwhile, the samples after UVA irradiation with the colorless or bleached state are shown by a dotted line. The diffuse reflection spectra around 250-350 nm are related to TiO_2 nanoparticles with a bandgap of 3.25 eV. Meanwhile, the deteriorate intensity in the range of 500 to 750 nm corresponds to methylene blue as absorption maximum at 665 nm [7]. DRS patterns in the colored state of TiO_2/MB nanocomposite with different rotation speeds were identical as shown in Fig. 3(a). The increase of rotation speed in the milling process was an effect on the decrease of reflectance intensity. This result could be expected that the dispersion of methylene blue was well-defined on the TiO_2 matrix with high rotation speed. However, the suspension at the maximum speed of 300 rpm was in non-sticky and high liquid then it was not suitable to film fabrication by screen printing technique. For the bleached state, DRS patterns were in the same spectra with each condition corresponding to the decrease of MB reflectance intensity in the range of 550 to 650 nm. This result can be indicated by the change of chemical structure from MB to LMB. Meanwhile, Fig. 3(b) illustrated DRS results of the colored state of TiO_2/MB nanocomposite with different milling times. These spectra were identical to the condition of a rotation speed of TiO_2/MB nanocomposite. The decrease of reflectance intensity was obtained by prolonging milling time at 250 rpm. Therefore, the optimized rotation speed of TiO_2/MB nanocomposite suspension was conducted at 250 rpm with milling time in wet grinding for 45 min as condition E. The homogenous suspension of TiO_2/MB nanocomposite is good for film formation by screen printing, meanwhile, the difference of %R in colored and bleached in MB region around 550 to 650 nm was appropriate than other samples.

The photographs of the activated TiO_2/MB nanocomposite layer with 5 conditions under UVA irradiation and oxygen detection are depicted in Table 2. TiO_2/MB nanocomposite films after coating by screen printing method (the row of before irradiation) were mostly in blue due to methylene blue structure. After UVA irradiation in 3 minutes, the activated nanocomposite layer was changed to colorless in the bleached state by the influence of bonding change in methylene blue to leuco-methylene blue. These mechanisms could be described by the cooperation of photocatalytic and oxidation processes in TiO_2/MB nanocomposite. Firstly, the colorimetric switching process from a colored state to a bleached state could be occurred by the photocatalytic reaction on activated TiO_2 semiconductor under

Table 2. The comparison of TiO_2/MB nanocomposite indicators with different conditions for the application of oxygen detection under air ambient



Samples	Before UVA irradiation	After UVA irradiation	Oxygen detector for 5 min	Oxygen detector for 10 min	Oxygen detector for 20 min	Oxygen detector for 30 min
A						
B						
C						
D						
E						

UVA irradiation corresponding to photogenerated electron-hole pairs on the surface. Then, citric acid as a sacrificial electron donor reacted with photogenerated holes. The rest of leaving photogenerated electrons on TiO_2 surface to reduce the redox dye in methylene blue structure (blue color) to leuco-methylene blue (colorless) as bleached stage [8]. The colorless indicator with LMB structure was preserved after UVA irradiation indicating the absence of oxygen gas. When the activated layer interacted with oxygen gas under air ambient, LMB structure may be oxidized and switched to MB structure as colored state after the observation with the initial blue color at the middle area of the indicator for 5 min. The TiO_2/MB nanocomposite indicator completely turned to blue color in 30 min. All conditions showed same color-switching from bleach to a blue state. However, slower color changing to blue state was observed at 10 min in condition E. Therefore, this condition was chosen for the study of color shading and the percentage of cyan color on indicator sample under air ambient with time period as shown in Fig. 4 and Table 3. The initial color of the as-obtained TiO_2/MB indicator appeared in blue shade with 100% of cyan color. After UVA irradiation at 0 min, the indicator turned to bleached area as a colorless state with 7.3% of cyan color. Then, the indicator was placed in air ambient to detect oxygen gas. Within 5 min, the sample changed to light blue shading at 71.7% of cyan color. Meanwhile, the indicator regained blue color around 10 to 20 min according to the increase of cyan percentage at 93.0 and 99.7. Finally, the sample completely changed to its original color as blue color after oxygen detection at 30 min. Therefore, the performance of oxygen indicator by TiO_2/MB nanocomposite was affirmed by oxygen responsibility in color-changing mechanism from colorless to colored state. Moreover, the efficiency of oxygen indicator by TiO_2/MB nanocomposite in our work was also effectively related to graphene/TiO_2 composite colorimetric indicator by Shuting Huang and coworker [9]. The result revealed that the indicator remained in its bleached state (0 min) after UV irradiation and removed oxygen gas from the packaging. When the package damaged or detected oxygen on the indicator surface, the color on the indicator changed to a blue state with slight color restoration. The color recovery in the blue state was completely in 30 min. However, the efficiency of the TiO_2/MB nanocomposite indicator should be proposed to improve its fast response under the oxygen atmosphere.

Fig. 4. Color shading with different times of TiO_2/MB nanocomposite oxygen indicator under air ambient.

Table 3. The percentage of cyan color in TiO_2/MB nanocomposite indicators under oxygen detection in air ambient with the time change.

Time (min)	The percentage of cyan color
Before UVA irradiation	100
0	7.3
5	71.7
10	93.0
20	99.7
30	100

4. Conclusion

The production of a colorimetric oxygen indicator based on TiO_2/MB nanocomposite was successfully obtained in this work. Homogenous suspension of TiO_2/MB nanocomposite could be occurred by the optimization of rotation speed at 500 rpm and milling time in wet process for 45 min via mechanical high energy ball milling process. This condition is well defined for film fabrication by the screen printing technique on a glass slide. FTIR spectra of TiO_2/MB nanocomposite were identical patterns with different rotation speeds and milling time by high energy milling process. This result could be confirmed that the chemical structure of nanocomposite was not changed by the influence of the milling process. Meanwhile, color switching of TiO_2/MB nanocomposite by the effect of MB and LMB structure was implicitly proven by UV-VIS-NIR spectrophotometer. The mechanism of TiO_2/MB nanocomposite indicator can be responded with oxygen gas in air ambient by completely color changing from colorless to blue state in 30 min.

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