Indones. J. Chem., 2017, 17 (1), 37 - 42

Synthesis of TiO_2/Carbon Nanoparticle (C-dot) Composites as Active Catalysts for Photodegradation of Persistent Organic Pollutant

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Received April 29, 2016; Accepted January 24, 2017

ABSTRACT

Perchloroethylene (PCE) is a persistent organic pollutant that can pollute soil and water due to its toxic nature. Photodegradation technologies are being suggested to degrade waste into harmless final products. The TiO_2 was used as the photocatalyst and composited with carbon nanoparticles (C-dot) to increase its photocatalytic activity under visible light. C-dots absorb light in the visible region and emit shorter wavelength light which can potentially be used by TiO_2 to activate its photocatalytic property. The TiO_2/C-dot composites were synthesized by sol-gel method. The photoluminescence properties of C-dots and the composites were observed by visual analysis and fluorescence spectrophotometer analysis. Synthesized composites were characterized by XRD, FTIR, and UV-Vis spectrophotometer. UV-Vis spectrophotometer analysis showed a decrease in the band gap of TiO_2/C-dot composites. Photocatalytic degradation of PCE 0.1% (v/v) in the aqueous phase was investigated under sunlight irradiation for 2 h. The results of the gas chromatography analysis showed that composites of TiO_2/C-dot 2.5% (w/w) successfully degraded PCE under sunlight irradiation with photodegradation ability of up to 89.45%.

***Keywords**: perchloroethylene; photocatalytic; photodegradation; TiO_2/C-dot composites*

ABSTRAK

Perkloroetilen (PCE) merupakan senyawa percemar organik persisten yang dapat mencemari tanah dan air karena bersifat racun. Teknologi fotodegradasi dapat diusulkan untuk mendegradasi limbah menjadi produk akhir yang tidak berbahaya. TiO_2 digunakan sebagai fotokatalis, dan dikompositkan dengan carbon nanopartikel (C-dot) untuk meningkatkan aktivitas fotokatalitiknya di daerah sinar tampak. C-dot menyerap sinar di daerah sinar tampak, dan melepaskan cahaya dengan panjang gelombang lebih pendek yang berpotensi sebagai sumber cahaya untuk mengaktivasi sifat fotokatalitik TiO2. Komposit TiO2/C-dot disintesis menggunakan metode sol-gel. Sifat fotoluminesens ditunjukkan dari analisis visual dan spektrofotometer fluoresens. Komposit hasil sintesis dikarakterisasi menggunakan XRD, FTIR, dan spektrofotometer UV-Vis. Analisis spektrofotometer UV-Vis menunjukkan terjadi penurunan nilai energi celah pada komposit TiO_2/C-dot. Degradasi PCE 0.1% (v/v) dalam fasa air telah diselidiki di bawah sinar matahari selama 2 jam. Formulasi hasil analisis kromatografi gas menunjukkan komposit TiO_2/C-dot 2.5 (b/b) berhasil mendegradasi PCE di bawah sinar matahari dan kemampuan fotodegradasi mencapai 89,45%.

***Kata Kunci**: fotodegradasi; fotokatalitik; komposit TiO_2/C-dot; perkloroetilen*

INTRODUCTION

Persistent organic pollutants (POPs) are chemical substances that persist in the environment and pose a risk of causing adverse effects to human health and the environment. Perchloroethylene (PCE) is a persistent organic pollutant of soil and water because it is toxic, carcinogenic, and extremely long-lasting in the environment [1]. PCE is widely used as an industrial solvent for degreasing metals and for dry cleaning [2]. Sonochemical degradation [3] and photocatalytic degradation [4] have been considered as methods to reduce the amount of POPs in the environment. Photodegradation by photocatalysts such as TiO_2, ZnO, CdS is a more attracting method as the catalysts are highly available, easier to handle, and usually, produce harmless final products [5].

TiO_2 is a catalyst that has gained popularity for use in the photocatalytic process because of its biologically and chemically inert character, resistance to corrosion due to photons, and non-toxicity [6]. TiO_2 can degrade organic pollutants into environmentally safe products, such H_2O and CO_2 [7]. However, TiO_2 is an active photocatalyst in the UV light region due to its large intrinsic band gap [8], limiting its usage in large scale, as UV light sources are relatively small. Sunlight,

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DOI: 10.22146/ijc.23615

an abundant light source, is composed of less than 5% of UV light, with the largest composition in visible light. Therefore, manipulation is needed so that TiO_2 can be activated under visible light. One way to do so is by introducing a substance into the TiO_2 crystal system to reduce its band gap energy. Many doped TiO_2 composites have been reported to be photocatalysts in the visible light region. However, the results still need further improvement. Here, we are reporting a new material with improved TiO_2 photocatalytic activity under UV light, by using a light absorber material, carbon nanoparticles (C-dots), to form TiO_2 composites. The synthesized composite is a natural progression from the results reported by Li et al. [8] who mixed carbon quantum dots (CQDs) with TiO_2 and used it to photodegrade methylene blue with efficiency close to 100%.

C-dots are the analog of CQDs which has a similar structure with graphite and have various properties, such as their good solubility in water, cheap starting materials, efficient synthesis process, low toxicity, good photostability, and strong photoluminescence [9-10]. C-dots have strong luminescence property in the UV-to-near-infrared range [8]. In this study, C-dots were combined with TiO_2 and used as a catalyst in the photodegradation of PCE. The C-dots are believed to act as a source of light for the electron excitation in TiO_2, as C-dots absorb light at a higher wavelength and emit light at a shorter wavelength due to upconversion of its photoluminescence, similar work was previously reported by Zhang et al. [11] by applying Fe_2O_3/C-dots composite photocatalyst. A hole (h^+) will be formed when an electron on TiO_2 exits from the valence band to the conduction band, which will then react with a water or hydroxyl ion (-OH) to form a hydroxyl radical ($^{\bullet}OH$). This radical is very active in attacking organic molecules such as PCE and degrade it into more friendly substances such as CO_2 and H_2O. However, the C-dots might act as a dopant. Determination of band-gap energy is needed to give an insight on the role of C-dots in the composites.

EXPERIMENTAL SECTION

Materials

All chemicals used were an analytical grade, i.e. citric acid, urea, ethanol, and ammonia from Merck, tetrabutyl titanate from Sigma-Aldrich, n-heptane, and perchloroethylene from BDH, and deionized water.

Instrumentation

The instruments used in the synthesis of C-dots, TiO_2, and TiO_2/C-dot composites were a Sharp R-249IN 800 W microwave oven, laboratory oven, and Hermle Labnet Z206A centrifuge. The products were characterized using 365 nm UV light source, X-Ray Diffraction (Shimadzu XRD-7000), Fourier Transform Infrared (Bruker Tensor 3) fluorescence spectrophotometer, UV-Vis spectrophotometer (Ocean Optics). Photocatalytic activity was evaluated by analyzing the residual PCE using Gas Chromatography (Shimadzu 17-A).

Procedure

Catalysts preparation

The C-dots were synthesized by the microwave method [12]. Typically, citric acid (0.5 g) and increasing amounts of urea (0, 20, 60 and 80% (w/w) were transferred into 10 mL deionized water. The solution was then heated by microwave oven for 4 min until the color of the solution changed from a colorless to brown liquid and finally formed a dark-brown precipitate. This solid material was then heated in an oven at 60 °C for 1 h to remove the residual water. An aqueous solution of C-dots was purified by centrifuging at 5000 rpm for 20 min to remove large agglomerated particles. The liquid phase of C-dot underwent a solidification process on a hot plate.

In this study, TiO_2 was synthesized from tetrabutyl titanate by a sol-gel method. In this method, inorganic compounds are formed by a chemical reaction in a solution at low temperatures, where the colloidal suspension (sol) phase gradually changes into a gel-like diphasic system. Various concentrations of C-dot solutions from citric acid-urea 80% was used in the synthesis of TiO_2/C-dot composites. Composites of TiO_2/C-dot were synthesized by the sol-gel method [8]. Firstly, tetrabutyl titanate (0.5 mL) was dissolved in ethanol (20 mL) and then water (9 mL) and ammonia (5 mL, ammonia 25%) were added with stirring. The mixture was left to stand for 12 h, and then the samples were collected by centrifugation and dried in an oven at 80 °C for 6 h. TiO_2 nanoparticles were prepared by calcining the above sample at 500 °C for 1 h. Secondly, TiO_2 nanoparticles were combined with the C-dots synthesized from citric acid and 80% urea (w/w). Seven combinations of composites were made by mixing 0.1 g of TiO_2 and various quantities of C-dots (0, 0.5, 1, 1.5, 2, 2.5 and 100% (w/w)). Each of the mixtures was added to 5 mL deionized water with stirring for 10 min and then dried in an oven at 80 °C for 12 h. The luminescence of C-dots, TiO_2, and the TiO_2/C-dot composites was observed under the 365 nm UV light source. They were characterized and analyzed using XRD, FTIR, fluorescence spectrophotometer, and UV-Vis spectrophotometer.

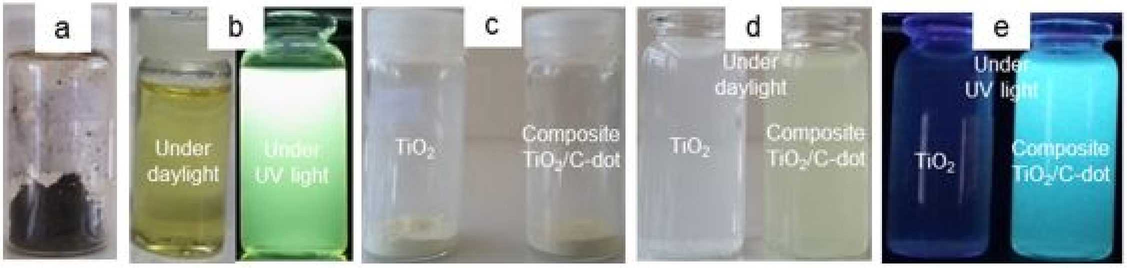

Fig 1. (a) C-dots, (b) C-dot aqueous solution (100 mg/L), (c) TiO_2 and composite TiO_2/C-dot, (d) TiO_2 and composite TiO_2/C-dot solution (100 mg/L) under daylight, (e) under 365 nm UV lamp source

Photocatalytic experiments

TiO_2/C-dot composites, pure TiO_2, and pure C-dots (0.1 g each) as catalysts were added to PCE 0.1% (v/v) (25 mL) and then irradiated under sunlight for 2 h. The solution was then extracted by n-heptane (25 mL). The organic phase was analyzed by GC to measure the residual concentration of PCE to observe photodegradation ability of composites under visible light.

RESULT AND DISCUSSION

Catalyst Preparation Results

The synthesized C-dots appeared to have dark brown color (Fig. 1a) and were found to have a lower yield as the urea concentration increased. The yield of synthesized C-dot without the addition of urea was obtained at 99.06%. The addition of 20, 40, 60 and 80% urea gave the yield of C-dot at 91.29, 85.53, 75.87, and 37.87%, respectively. It was also found that the higher the amounts of urea in the synthesis of C-dots, the higher the agglomeration of formed C-dots. However, similar to that reported by Sugiarti [10], emission intensity increased with the increased concentration of urea as a passivation agent in the reaction process. The photoluminescence from C-dots that have surface passivation is attributed to the presence of surface energy traps that become emissive upon stabilization [13]. The intensity of luminescent emission from C-dot solutions was determined by a visual analysis under UV light (365 nm). C-dots synthesized with 80% of urea had greater luminescent intensity compared with the other C-dots. The increased intensity of luminescent shows the effect of urea as a passivation agent on the C-dot surface. Therefore, C-dots from citric acid-urea 80% were chosen to be combined with TiO_2.

The TiO_2/C-dot composites had a darker color than the TiO_2 and were close to the dark brown color of C-dots (Fig. 1c). This indicated the presence of C-dots in the composites. The intensity of luminescent emission of the TiO_2/C-dot composite solutions was observed under UV light (365 nm) as shown in Fig. 1e. The fluorescence properties of C-dots in the composites were observed even though the photostabilities of the solution decreased due to a decrease in the transparency of the solution in the presence of TiO_2. Photostabilities properties such as strong photoluminescence properties are generated when the C-dots freely dispersed in water with a transparent appearance [8].

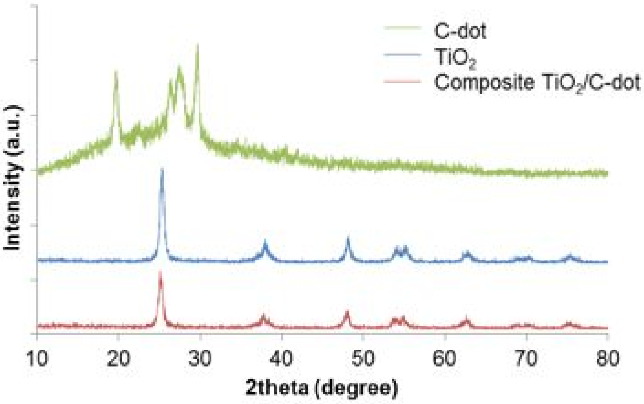

Fig 2. X-ray diffraction of C-dots, TiO_2/C-dot composite, and TiO_2

X-Ray Diffraction Analysis Results

X-ray diffraction (XRD) analysis was done on C-dots from citric acid-urea 80%, on the composite TiO_2/C-dot 2.5%, and on TiO_2. The resulting analysis is illustrated in Fig. 2. X-ray diffraction patterns of the C-dots exhibited intense peaks at 2θ (intensity) = 19.73° (77); 27.52° (79); and 29.60° (98). These peaks were attributed to highly disordered carbon atoms [12]. The crystallinity of the C-dots was 30.4564%. XRD patterns of the TiO_2/C-dot composites exhibited intense peaks at 2θ (intensity) = 25.19° (59); 37.77° (18); and 47.96° (12). The crystallinity of the TiO_2/C-dot composites was 78.2537%. For TiO_2, the XRD pattern exhibited intense peaks at 2θ (intensity) = 25.36° (101); 37.95° (24); and 48.10° (18). The crystallinity of TiO_2 was 84.2055%. Match analysis was done on a TiO_2 and the result shows that the TiO_2 presence in the form of anatase phase (JCPDS card no. 21-1272). The TiO_2 with anatase crystal system was reported to have a better photocatalytic activity under UV light, compare to other crystal systems such as rutile [14].

The C-dot influence in the composite can be known from the XRD diffractogram. The intensity and crystallinity of the TiO_2/C-dot composites were less than that of TiO_2. This decrease was due to the addition of a relatively amorphous C-dot in the composite. However, there were no significant changes in the XRD pattern of the composites compared to the XRD pattern of TiO_2. All peaks on TiO_2/C-dot were similar with the diffraction angle of TiO_2, indicating that there was no new compound formed from mixing C-dot with TiO_2.

Functional Group Analysis Results

Functional group analysis by FTIR was done on the C-dots from citric acid-urea 80%, on the TiO_2/C-dot 2.5% composite, and on TiO_2. Fig. 3 shows the FTIR spectra of the samples. The FTIR results for the C-dots were similar to those reported by Qu et al. [8], with an absorption band at 1600-1770 cm^{-1} for C=O and for the CH_2 vibration occurred in the region of 1350-1460 cm^{-1}. These absorption bands did not appear in the FTIR results for the TiO_2/C-dot composite. The TiO_2/C-dot composite spectra were similar to the spectra of TiO_2 with an absorption band for Ti-O-Ti in the region of 400-800 cm^{-1} [15]. An absorption band at 1054 cm^{-1} was due to stretch vibration of O-O. Absorption bands at 1631 and 3420 cm^{-1} were due to H-O-H (water) vibration and O-H (hydroxyl) vibration [14]. So, based on the FTIR analysis we conclude there was no chemical bond between TiO_2 and C-dot because there were no other absorption bands formed in the TiO_2/C-dot composite such as C=O and CH_2 vibration bands.

Spectrum of Fluorescence Intensity

Fluorescence intensity measurement was performed on C-dots from citric acid-urea 80%, TiO_2/C-dot 2.5% composite and TiO_2 to determined maximum fluorescence emission of the samples. Fig. 4 shows the analysis results. The maximum fluorescence emission of C-dot was at the wavelength of 536.33 nm when it was excited at a wavelength of 405 nm ± 10. The recorded maximum emission spectrum was higher than reported by Sugiarti [10], where C-dot synthesized from ascorbic acid-urea 75% has a maximum emission at wavelength 500 nm when excited at a wavelength of 400 nm. This difference may be due to the influence of passivation agent concentration on C-dots in the reaction process. The C-dots did not lose their fluorescence properties in the composite with TiO_2. The maximum fluorescence emission of TiO_2/C-dot composite was at the wavelength of 537.96 nm and the intensity decreased due to the TiO_2 presence in the solution. However, similar to the observations made under UV light (365 nm) the TiO_2 solution had no detectable fluorescence.

Band Gap Analysis Results

Early determination of the band gap energy for the C-dot, TiO_2/C-dot composite, and the TiO_2 was done by measuring their absorption using UV-Vis spectrophotometer [16]. Fig. 5a shows the UV-Vis spectra of the C-dots from citric acid-urea 80%, TiO_2/C-dot 2.5% composite, and TiO_2. The absorption coefficient value (α) is obtained from –lnT/d. The film thickness (d) was measured using Teclock 0.01 mm, to obtain the thicknesses of the C-dots, TiO_2/C-dot composite, and TiO_2 of 0.025; 0.005; and 0.01 mm, respectively.

The function $(\alpha E)^{1/2} = B(E-E_g)$, which was obtained using the Tauc's Plot method, intersects the hv axis at E_g, and B is the slope. The optical band gap (E_g) was obtained by linear extrapolation of graph hv (or E) and $(\alpha h\nu)^{1/2}$ until it crosses the energy axis (E) [16,17] (Fig. 5b), where h is Planck's constant = 4.136 x 10^{-15} eVs and v is the UV-Vis frequencies which are

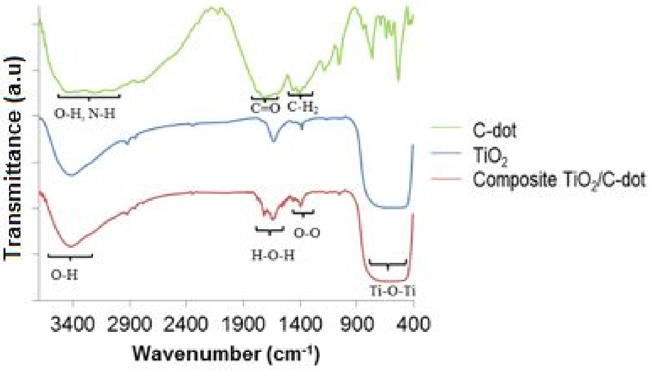

Fig 3. FTIR spectrum of C-dots, TiO_2/C-dot composite, and TiO_2

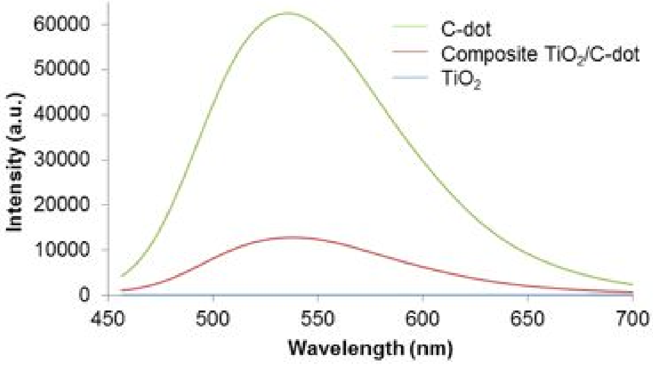

Fig 4. Fluorescence emission spectrum of C-dots, TiO_2/C-dot composite, and TiO_2 (100 mg/L)

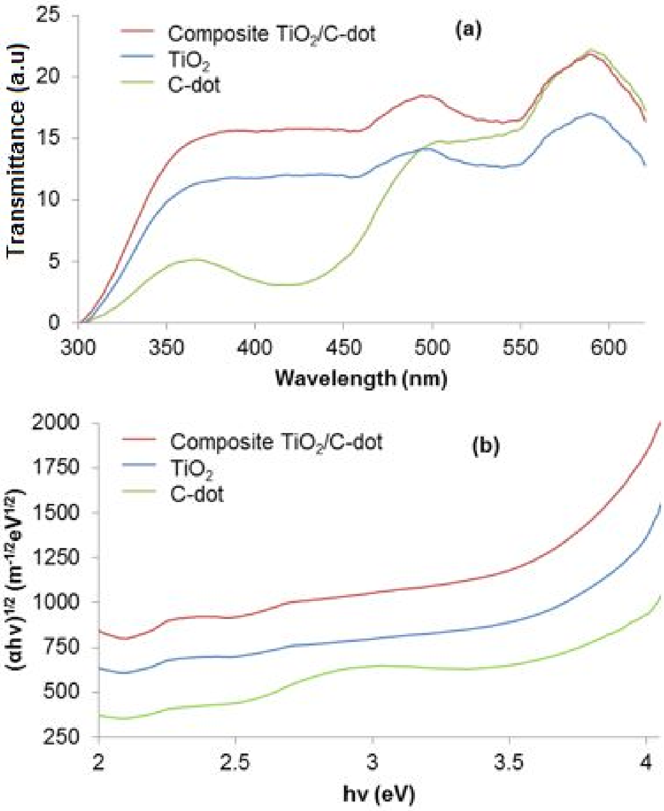

Fig 5. (a) Wavelength versus transmittance spectrum and (b) the optical band gap energy

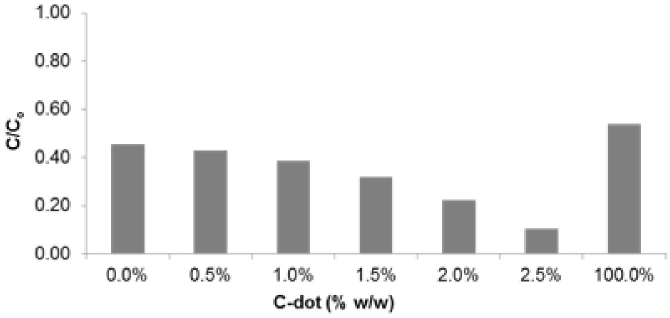

Fig 6. Photocatalytic activity of TiO_2/C-dot composites on PCE 0.1% (v/v) under sunlight

obtained by dividing the speed of light (c) = 2.998×10^8 m/s with the wavelength (λ).

According to the calculation from the Tauc's Plot the optical band gap energy of the C-dots, TiO_2/C-dot composite, and TiO_2 are 2.79; 3.10; and 3.23 eV, respectively. These results show that C-dots can reduce the band gap of TiO_2 in the TiO_2/C-dot composite thereby widening the TiO_2 uptake range.

Photocatalytic Experiment Results

The experiments were done for TiO_2/C-dot composites using 25 mL PCE 0.1% (v/v) under sunlight irradiation for 2 h. Fig. 6 shows the photocatalytic activities of the catalysts. The concentration of PCE was decreased with increasing quantity of C-dots in the TiO_2/C-dot composite compared to pure TiO_2 as a catalyst. This proved that C-dots are effective in improving TiO_2 photocatalytic activities under sunlight. PCE was successfully degraded and its photodegradation ability was up to 89.45% using the TiO_2/C-dot 2.5% composite as a catalyst. Whereas under the same conditions, pure TiO_2 and pure C-dot showed lower degradation ability (54.52 and 46.33%, respectively). According to Ming et al. [18], C-dots have peroxidase-like ability to degrade pollutant compounds. The photocatalytic ability of C-dots are derived from the C-dot properties of being very soluble in water, and of having protons that are easily taken from the C atoms in C-dots, such that H_2O and H_2O_2 can readily be transformed into hydroxyl radicals ($^{\bullet}OH$) during photoreaction.

In this study, the role of C-dots in the PCE photodegradation process by the TiO_2/C-dot composites was seen from the success of C-dots to decrease the optical band gap energy of TiO_2, so that the photocatalytic process can occur over a larger range of wavelengths. However, the lowering value of TiO_2 band gap energy in the composite was not great, suggesting that the C-dots also play another role in the composites. Zhang et al. [11] reported that C-dots play important roles in photocatalytic processes as an electron reservoir to trap electrons thus preventing electron-hole recombination. The oxygen radicals ($^{\bullet}O_2^-$) can be formed by the reduction reaction of oxygen (O_2) by electrons on the surface of C-dots, subsequently, the hydroxyl radicals ($^{\bullet}OH$) is produced by the reaction of $^{\bullet}O_2^-$ with water. The C-dots can absorb light at a longer wavelength and then emit light at a shorter wavelength as a result of their upconversion photoluminescence property which could, in turn, excite TiO_2 electrons from valence band to conduction band, a process that results in the formation of holes (h^+). The $^{\bullet}OH$ is produced by the interaction of h^+ with water or with hydroxyl ions (OH^-). The $^{\bullet}OH$ can also be produced via reduction reaction of oxygen molecules by electrons in the conduction band. Hydroxyl radicals are extremely reactive and attack organic pollutants such as PCE and degraded those pollutants into environmentally benign molecules such as CO_2 and H_2O.

CONCLUSION

TiO_2/C-dot composites were successfully synthesized by the sol-gel method. The C-dots were physically bound on TiO_2 and did not lose their fluorescence properties in the composites and they also reduced the band gap of TiO_2 in the TiO_2/C-dot composite, thereby was widening the TiO_2 uptake range and increasing the TiO_2 photocatalytic activity. The TiO_2/C-dot 2.5% (w/w) composite successfully degraded 89.45% of the PCE tested under sunlight.

ACKNOWLEDGEMENT

The authors would like to thank the Indonesian Ministry of Research, Technology, and Higher Education which sponsored this research.

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