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TiO_2 Nanoparticles-Graphene Composite for Photocatalytic Application

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ABSTRACT

Titanium dioxide (TiO_2) nanoparticles, a candidate photocatalyst for organic pollutant treatment is controversially suspected from negative impact by the remaining residues. In this study, TiO_2-graphene composite pellet was proposed as a removable catalyst for wastewater treating. Graphene was selected to enhance photocatalytic activity and promote the adhesion of composite ceramic. TiO_2-graphene composite pellet was successfully fabricated by solvothermal synthesis, mixing, hydraulic compressing and sintering which were characterized by X-ray diffracting (XRD) analysis, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). Preliminary test of photocatalytic activity was evaluated by determining methylene blue (MB) degradation efficiency where 74% of MB was degraded within 2 hrs in the visible region (λ_{max} at 662 nm). Furthermore, nanocomposite pellet can be easily retrieved without degradation in solution after treatment.

INTRODUCTION

Persistent organic pollutants (POPs) is highly concerned among the scientific community through its accumulation in the household and industrial environment. For many years, semiconductor in particular, TiO_2 photocatalysts had shown a great potential for organic waste treatment applications due to its low cost, environmental friendliness and high efficiency as a photocatalyst [1-3]. Their ability to promote photo-oxidation has been used to remove persistent organic compounds and contaminants in water. The reaction was catalyzed by absorption of a photon with sufficient energy equals or higher than the band gap of catalyst particularly 3,2 *e*V for TiO_2. The light wavelength for such photon energy corresponds to $\lambda < 380$ nm [4]. However, the main barriers that prevent it from commercialization are poor efficiency when used under sunlight, difficulty in particle recovery and separation problem. The band gaps of TiO_2 absorb in the UV region where only about 35%- of sunlight comprises UV radiation. To improve the photocatalytic efficiency of TiO_2, many studies have been carried out with the goal to overcome those limitations. Doped TiO_2 with substitute metals, such as Cr, Fe or Ni could shifted the absorption band to the visible light region [5-7]. However, these approaches were not widely accepted and suffered from some serious drawbacks, i.e. thermal/chemical instability and low quantum efficiency of the photo-induced charge carriers [8]. Meanwhile, scaling optical and electronic properties of nanomaterials are more favorable, many researches incorporated variety of nanomaterials in many application including semiconductor devices. TiO_2 nanoparticles provide high surface to volume ratio which benefits in enhancing the photocatalytic activity [9-12]. Nevertheless, nanoparticles in form of powder has a number of drawbacks. Photocatalytic activity can be decrease due to particle agglomeration. In addition, recovery problem will be a great concern on environmental issues. The low-density nanoparticle composites were proposed as floating photocatalyst to solve such problems; besides enhancing absorption efficiency as it can remain on the surface of water [13,14]. The nanoparticle composites with low-density polyethylene (LDPE) or expanded polystyrene beads (EPS) were utilized as a support for TiO_2-nanoparticles (TiO_2-NP); however, the efficiency is not considerable with volume [15, 16]. In this study, we proposed a porous TiO_2-Graphene composite material as photocatalyst for organic waste degradation. Graphene is extremely light and possesses excellent electronic properties, was selected as a composite material with TiO_2 nanoparticles. The carbon in two-dimension structure of graphene together with TiO_2 nanoparticles were combined to create nanomaterials composites that help extend the solar absorption into the visible region. The composite would promote the photocatalytic performance by merely exploiting sunlight. Moreover, graphene will be utilized as a binding agent for TiO_2 nanoparticles assembly. The promising photocatalyst material would be realized with high photocatalytic efficiency, better stability and ease of recovery.

METHODOLOGY

TiO_2 nanoparticles and graphene were separately prepared into a powder form by hydrothermal process. TiO_2-NP, namely commercial P25, from Loudwolf limited company was prepared by sonicating for 30 minutes in deionized water, filtering through 2٫5 µm pore size and freezing-dry. Synthesized dry powder nanoparticles are shown in Figure 1a. Graphene oxide was initially synthesized using standard Hummer's method [17]. Graphite powder was mixed with sodium nitrate, sulfuric acid, potassium permanganate, distilled water, hydrogen peroxide and hydrochloric acid under controlled temperatures. The solution of mixture was centrifuged and sonicates to separate graphene out from other compounds. Graphene solution was then filtered and purified by polyvinylidene difluoride (PVDF) and freeze-drying. Black powder of graphene presents in Figure 1b.

Composite solution was prepared by mixing TiO_2 nanoparticle powder and 3 wt٪ graphene in 75 mL of distilled water. Figure 1c shows the TiO_2-graphene composite solution after went through hydrothermal process with 170°C for 6 hours. Powder composite was obtained after freeze-drying the TiO_2-graphene solution with the same method that being used. TiO_2-graphene powder with the net weight of 0٫4 grams was compressed using force pressure of 7٫5 tons by hydraulic press machine into previously designed tablet-shape metal mold. The composite tablet has approximately 1 cm diameters and 0٫3 cm thickness as depicted in Figure 1d. Pellet was sintered to modify the porous structure of ceramics into nano-porous and coalesce the particles with heating rate of 6°C/minute in inert environment. It was heated up to 700 °C for 180 minutes and cool down overnight in the chamber. TiO_2 pellet was also prepared with the same methods for comparison in the following test.

Samples' characteristics and properties were evaluated by X-ray diffraction (XRD) to identify the phase and crystal structure, Fourier transform infrared spectroscopy (FT-IR) to check the trace of graphene functional group, Scanning electron microscopy (SEM) to observe the morphology and geometry of composite. XRD was carried out using Bruker D8 Advance X-ray diffractionwith scanning angles from 20 to 80°. FT-IR absorption spectrum was recorded using the Perkin Elmer Spectrum One (FT-IR Spectrometer) in the spectral region of 400–4000 cm^{-1}. SEM image was obtained from SEM-Inspect S50, FEI. Eventually, photocatalytic activity was determined using methylene blue (MB) degradation as an indicator utilizing UV-visible absorption spectroscopy. Stock solutions of methylene blue (9٫38 x 10^{5-} mol/L) were prepared as a representative of organic pollutant because methylene blue degradation is easily monitored through decolorization. All test solutions were prepared with total volume of 100 mL of methylene blue.

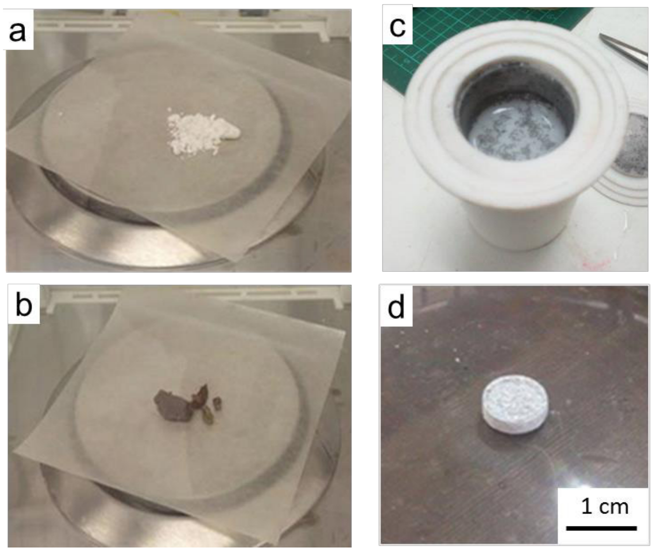

Figure 1. Images of synthesis samples (a) TiO_2 nanoparticles powder. (b) Graphene powder. (c) Mixture solution of composite. (d) TiO_2-graphene composite tablet.

RESULTS AND DISCUSSION

Characterization by X-ray diffraction (XRD)

X-ray diffraction measurements were performed to investigate the crystalline structure and phase composition of TiO_2 and TiO_2-graphene samples. The XRD patterns exhibited typical diffraction of anatase phase of both samples shown in Figure 2. Anatase is one form of titania that gives the best combination of photoactivity and photostability reported elsewhere [18]. The spectrums showed strong diffraction peaks of anatase phase of TiO_2, namely (101), (004), (200) planes, at 2θ values approximate to 25°, 38°, 48°, respectively. There are no differences between XRD patterns of TiO_2 and TiO_2-graphene samples. It implied that graphene is not incorporated onto the TiO_2 crystalline lattice. The characteristic (002) peak of sp^2 carbon at approximately 25٫9° of graphene was shielded by the adjacent (101) peak of anatase TiO_2 at 25٫4° possibly due to low quantity of graphene added to TiO_2 (3 wt.٪).

Characterization by Fourier transform infrared (FT-IR) spectroscopy

The infrared spectroscopy was performed to determine the graphene existence and composite bonding traces. The sample was glided into a fine powder and prepared in KBr matrix for the FT-IR analysis. Figure 3 presents FT-IR spectra of TiO_2 and TiO_2-graphene samples. Peaks located at 3434 cm^{-1} and 1630 cm^{-1} represents O-H stretching and O-H bending respectively which originated from the surface-absorbed with water [19]. The broad infrared (IR) band between 500900- cm^{-1} (in particular 695, 531 cm^{-1}) corresponding to TiO_2 stretching mode (Ti-O-Ti) in crystalline titania [20]. Those peaks are the characteristic footprints for TiO_2 and they presented in the FT-IR spectrum of both TiO_2 and TiO_2-graphene samples. The additional peaks located in the range of 9001100- cm^{-1} was only appeared in TiO_2-graphene composite which represented as a trace of graphene [21]. They were C-H bonding, C-H bending and alkoxy C-O stretching located at 974 cm^{-1}, 1024 cm^{-1} and 1047 cm^{-1} respectively shown in magnified panel of Figure 3. At that range, the spectrum of TiO_2 was almost flat. Moreover, peak reduction at 3434 cm^{-1} (O-H bond) of TiO_2-graphene sample explained the removal of terminal hydroxyl group and replacing with graphene molecules on the composite surface. The results agreed well with XRD analysis where there was no peak shift observed between TiO_2 and TiO_2-graphene samples.

Characterization by scanning electron microscopy (SEM)

Scanning electron microscopy was used to investigate particle size and the morphology of the testing catalysts in powder and tablet form. Figure 4a shows the particle sizes of TiO_2-graphene powder before compression and sintering which are ranging from 327 nm to 693 nm and they are well distributed. Important characteristic is the morphology of TiO_2-graphene where graphene merely attached onto TiO_2 surface. The result implied that no graphene was doped into TiO_2's lattice. It was also concordant with XRD and FTIR results. The SEM image of TiO_2-Graphene in tablet form showed in Figure 4b. Its porous sizes are ranging from microscale about 1٫457 µm to 3٫788 µm down to nanoscale about 145 nm to 874 nm. This result demonstrated that with the fabrication process and its controlling condition, we can achieve the TiO_2-Graphene photocatalyst with nano-porous structure.

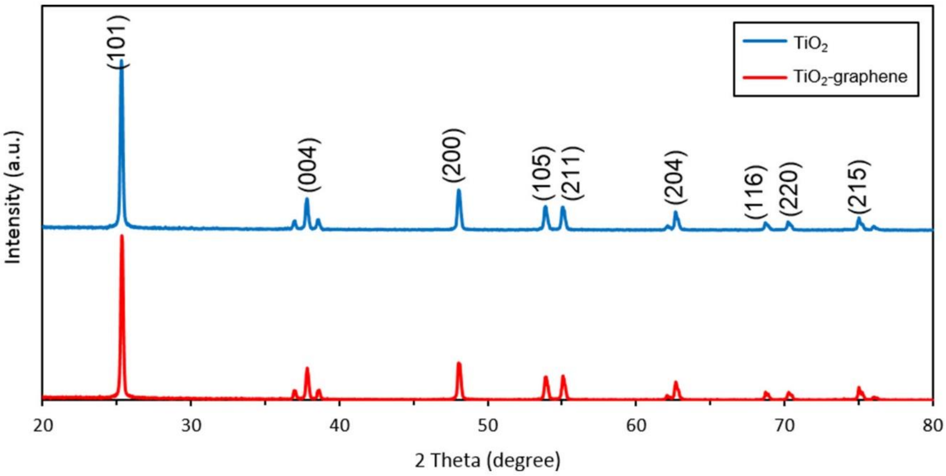

Figure 2. XRD plots of TiO_2 vs TiO_2-graphene composite.

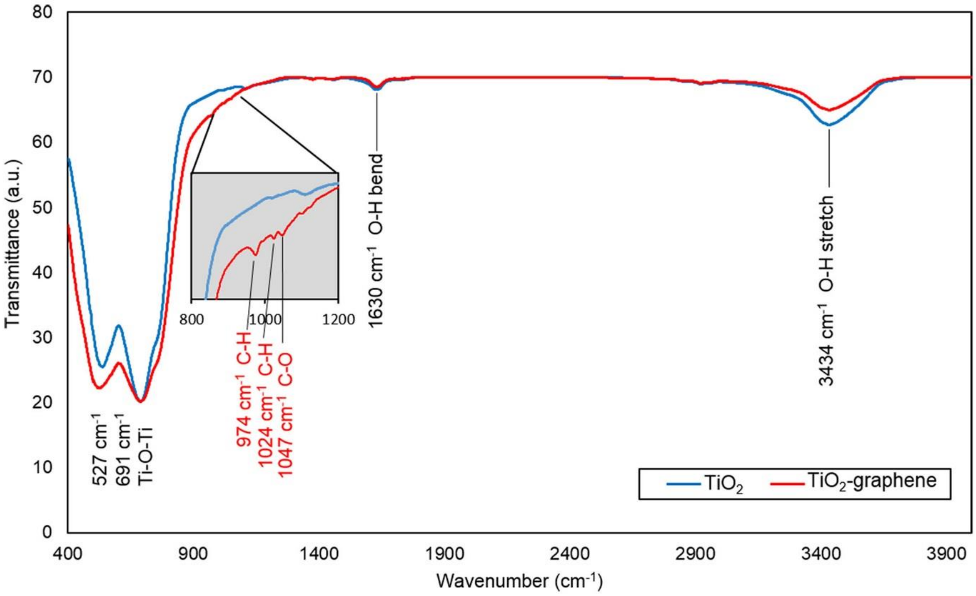

Figure 3. FT-IR spectra of TiO_2 and TiO_2-graphene composite.

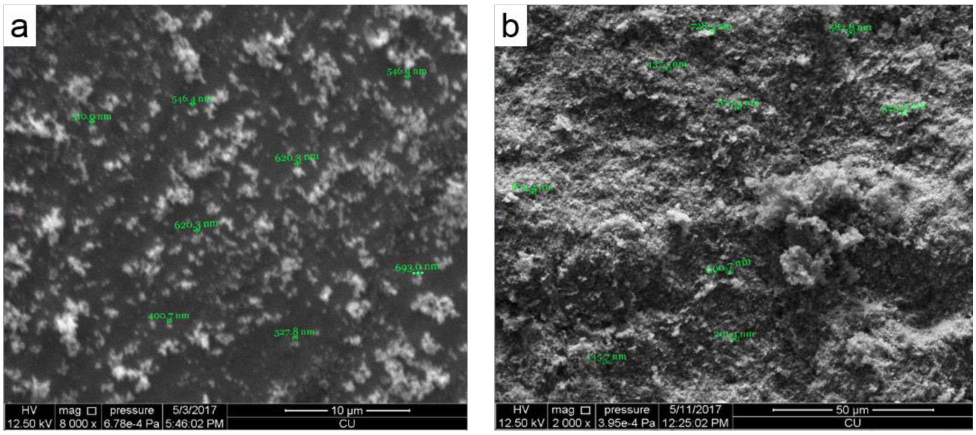

Figure 4. SEM images of TiO_2-graphene powder sample and TiO_2-Graphene composite tablet.

Photocatalytic activity testing

Photocatalytic activity was measured using UV-visible spectroscopy on separated 100 mL test solutions which are TiO_2 tablet treated MB, TiO_2-Graphene tablet treated MB and negative control (untreated MB solution). Figure 5a shows the absorption spectrum of test samples after 2 hrs treatment under sunlight. It indicated that methylene blue has highest absorbance value of 0.528 at wavelength of 662 nm, this value was set as standard absorbance value to compare the efficiency of each testing catalysts in degrading methylene blue. The result of photodegradation demonstrated as 72% and 74% of MB degraded in the visible region (λ_{max} at 662 nm) when treated with TiO_2 tablet and TiO_2-graphene composite tablet respectively. In this test, the effective volume of degradation considered to be more than a 100 times comparing with catalyst material. The catalyst tablet volume is about 0.94 mL (without concerning porous volume), while methylene blue test solution is set to be 100 mL for all tests. Degradation efficiency of TiO_2 and TiO_2-graphene composite are comparable where TiO_2-graphene can improve the efficiency merely about 2% in compare with pure TiO_2. Significant improvement was expected in the addition of graphene % composition that would be further investigated in the future. The color of MB is distinctly clear after treating with photocatalyt for 2 hrs illustrated in Figure 5b. Pure TiO_2 pellets were break in the solution and required filters before measuring the absorption; however, TiO_2-graphene composite remain as the initial tablet form without dissolving as shown in Figure 5c. In other words, TiO_2-graphene composite can easily be retrieved without degradation into the solution after treating in the test.

CONCLUSION

TiO_2-graphene composite presents as a promising candidate for photocatalyst that could acheive almost 74% of methylene blue degradation within 2 hrs in the study. The active degradation volume is over 100 times of photocatalyst material which is very attractive for large-scale and industrial usage. In comparing with previous literatures, the degradation efficiency is promising with an outstanding waste-treating throughput and the retrievement is at ease. Further increasing of graphene composition should be investigated to promote the performance of catalyst. The size of nanoporous could be tunable by varying the composition of TiO_2 and graphene together with the fabrication procedure that would determine the enhancement of photocatalytic efficiency as well. Variety of organic wastes will be tested to observe the effect for each types and be able to bring this composite material to use as the universal photocatalyst and other photon harvesting applications.

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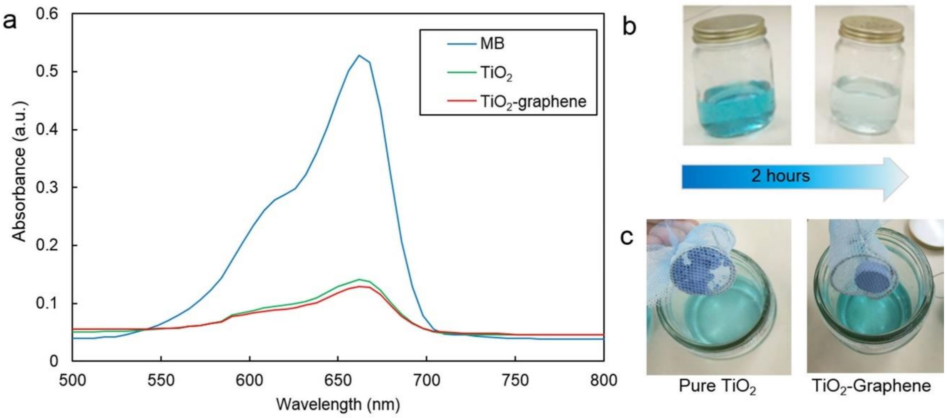

Figure 5. Photo catalytic testing results. (a) UV-absorption spectrum between untreated MB, TiO_2 pellet treated MB and TiO_2-graphene pellet treated MB solution. (b) Methylene blue solution before and after 2 hrs treated by TiO_2-graphene pellet. (c) TiO_2 and TiO_2 graphene pellet after photocatalytic treatment.

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