Synthesis and Characterization of Magnetically Modified Composites (TiNT/CNT/Fe$_3$O$_4$)

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Abstract. In this study, Titania nanotube (TiNT) had been modified by combining it with carbon nanotube (CNT) and magnetic material, Fe$_3$O$_4$, forming magnetically modified composite (TiNT/CNT/Fe$_3$O$_4$). Magnetic properties were added to the composite to overcome photocatalytic application problem for waste water treatment case, especially the catalyst recovery issue. Prior to the modifications, TiNT was synthesized from TiO$_2$ P25 using hydrothermal process at 130 °C for 6 h. TiNT and CNT were then combined using heteroagglomeration process in acid condition to obtain TiNT/CNT composite. Various amount of Fe$_3$O$_4$ nanoparticles were then composed on the surface of TiNT/CNT using ultrasonic assisted in-situ process, producing TiNT/CNT/Fe$_3$O$_4$ magnetic composites. The samples were analyzed with various characterizations: zeta potential, FT-IR, FE-SEM/EDX, XRD, and VSM. Experimental results show that TiNT/CNT/Fe$_3$O$_4$ composite with good crystallinity and morphology had been successfully synthesized. The optimal amount of Fe$_3$O$_4$ in TiNT/CNT/Fe$_3$O$_4$ magnetic composite was 0.3 times the amount of TiNT to minimize the photodissolution effect, while the composite was still categorized as superparamagnetic materials (with the saturation magnetization value of 21.1 emu/g and coercivity of 84.4 oe). The magnetic separation test also confirmed that prepared magnetic composites could be effectively separated from the test solution.

1. Introduction

Recently, nanosized semiconductor photocatalyst titania (TiO$_2$) has attracted the attention of many scientists, due to its wide range of applications (solar panel, super hydrophilic materials, degradation pollutant, hydrogen production, etc). On the further research, titania nanoparticles morphology has been successfully modified into nanotube form [1, 2]. Titania nanotube has been widely developed, because of its good electronic and mechanic characteristic, large surface area, ion-exchangeable ability, remarkable rapid and long-distance electron-transport capability, and enhanced light absorption [3]. Titania nanotube might also be able to interact with other materials relatively better than titania nanoparticles.

In environmental technology sector, photocatalyst material, peculiarly TiO$_2$ is generally accepted as one of the most effective photo-induced catalysts and is frequently used to oxidize organic and inorganic compounds in air and water due to its strong oxidative ability and long-term photo-stability [4]. Furthermore, to enhance its performance, TiO$_2$ is usually modified by combining it with other
materials, such as carbon nanotube (CNT) which will increase its adsorption ability and photocatalytic efficiency. However, for the field application that demands repeatable usage, nanosized photocatalyst still has a major problem that greatly limits the performance of the catalyst itself: the difficulty to separate catalyst suspension after use for the waste water treatment due to the small dimension of titania that it needs a very complex filtration technology. Many techniques have been applied for solving this problem, for instance by immobilizing TiO\textsubscript{2} catalysts unto a suitable support. Even though this method can solve the catalyst recovery problem, the activity of the photocatalyst would be lower because the catalyst must be attached on the support, limiting the movement of the catalyst and the contact between the photocatalyst, light, and pollutant. The other disadvantage of this method is the difficulty to maintain the catalyst to strongly attach on certain support. Therefore, a long-term usage of immobilized TiO\textsubscript{2}, one of the important parameters for industrial application is difficult to achieve, because a significant decrease of photocatalytic efficiency might occur.

Another way to solve the problem is by combining the photocatalyst with magnetic materials, so the photocatalyst can be magnetically separated from waste water. This method is quite effective and simple, where the after-used photocatalyst can be recovered from the solution and used repeatedly. Compared to the immobilization technique, the advantage in using magnetic composite is that the reaction condition is still slurry, so that photocatalyst particles can move freely into all of the liquid body, making the interaction between particles, light, and pollutant more efficient. Related to the usage of magnetic material, it is better to use superparamagnetic iron oxide-based material, like Fe\textsubscript{3}O\textsubscript{4} and γ-Fe\textsubscript{2}O\textsubscript{3}, because these materials are not toxic, and their presences in nature are abundant with relatively low price.

To date, many researchers have conducted studies to produce magnetically recoverable photocatalyst nanoparticles, especially for the application of waste water treatment. However, a study to produce magnetic photocatalyst, using titania with nanotube morphology has not been extensively investigated until now. More than that, many kinds of photocatalyst modifications were done separately. Based on those things, a study to modify photocatalyst TiNT, by combining it with supportive material (CNT) and magnetic materials (Fe\textsubscript{3}O\textsubscript{4}) simultaneously in an integrated process, producing magnetically modified composite TiNT/CNT/Fe\textsubscript{3}O\textsubscript{4} becomes an interesting and strategic topic. This study was aimed to investigate the character of magnetic composite and its potential application to be used for the long term usage in larger scale of waste water treatment application.

A magnetic separation test was also conducted to prove the ability of the magnetic composites to be magnetically recovered.

2. Material and Methods

2.1. Material

TiO\textsubscript{2} P25 with a crystallographic mode of 79% anatase and 21% rutile, a 53.6 m\textsuperscript{2} g\textsuperscript{-1} BET surface area, and an average particle size of 21 nm, used as raw materials, was bought from Evonic Industries. Commercial multi-wall carbon nanotube (MWCNT) was used on this study and purchased from Dong Yang (HK) Int’l Group Limited. Chemical such as sodium hydroxide pellet, concentrated nitric acid (HNO\textsubscript{3}, 65 %), iron (III) chloride hexahydrate (FeCl\textsubscript{3}, 6H\textsubscript{2}O), iron (II) chloride tetrahydrate (FeCl\textsubscript{2}, 4H\textsubscript{2}O), and ammonia solution (NH\textsubscript{3}, 25%) were purchased from Merck, and fuming hydrochloric acid (HCl, 37%) was bought from Mallinckrodt.

2.2. Preparation of Titania Nanotube (TiNT)

The preparation of titania nanotube (TiNT) was similar to the previous study. TiNT was synthesized by dissolving 6 g of titania P25 powder into 300 mL of 10 M NaOH and put into ultrasonic bed TELSONIC for 30 min prior to hydrothermal treatment at 130 °C for 6 h. The sample was then stirred at 600 rpm using a teflon-lined autoclave equipped with adjustable rotating speed mixer. Thereafter, the sample was washed with acid (0.2 NH\textsubscript{3}) repeatedly for a certain time until it
reached pH 2-3 and then with aquadest until the pH of approximately 5 was reached. TiNT powder was then obtained after drying at 80 °C for several hours and calcined at 500 °C for 2 hours.

2.3. Pre-treatment of CNT

CNT, used in this study was firstly pre-treated through acid treatment to generate negative surface charge of CNT. Firstly, 1 g of MWCNT was mixed with 100 mL HNO3 65% and put into ultrasonic bath processor for 1 h. The pre-treatment was continued with reflux process of the mixture for 6 h at temperature 120 °C. After the mixture was cooled enough, it was filtered to obtain the suspension, which was named by pre-treated CNT with negative surface charge. The suspension was washed overnight at 60 °C and the dried product was crushed to obtain modified CNT.

2.4. Synthesis of TiNT/CNT and TiNT/CNT/Fe3O4 Composite

TiNT with weight of 1 g and 0.015 g of pre-treated CNT were mixed in 100 mL aquadest. Then, pH of the mixture was adjusted to 3, using HNO3 solution (0.1 M). The mixture was subsequently put into ultrasonic bath processor for 5 minutes. After that, evaporation of the mixture was conducted at 80 °C to dry off the water. The dried product was crushed to obtain TiNT/CNT composite in powder form.

Synthesis of TiNT/CNT/Fe3O4 was done using ultrasonic assisted in-situ method. Firstly, 2.6 g of FeCl3.6H2O and 1 g of FeCl2.4H2O (mol ratio of Fe3+:Fe2+ = 2:1) were dissolved in 5.15 mL of HCl 0.1 N and stirred till all of the solid fully dissolved. Afterwards, the iron salt solution was diluted by adding 7.5 mL of aquadest, followed by stirring for 15 minutes. Then, the TiNT/CNT composite was mixed with 100 mL of aquadest. Various amount of the iron salt solutions (to vary the composition of Fe3O4 in composite), prepared beforehand were added to the mixture, followed by stirring for 1 h, in order to disperse the iron ions (Fe3+ and Fe2+) in the mixture. Certain amount of NH4OH 1.5 N solution (9 mL/mL of iron salt solution) were added drop by drop to the mixture, while put into ultrasonic bath processor at 65 °C. Ultrasonication treatment was continued for 5 minutes. The mixture was then washed using aquadest and magnetically separated until it reached pH 7. The obtained solid suspension was dried at 60 °C overnight and 80 °C for 2 h. The dried solid was crushed to obtain magnetic composite TiNT/CNT/Fe3O4.

2.5. Composite Characterization

Prior to the synthesis of the composite, zeta-potential characterization for the raw material (titania and pre-treated CNT) was conducted to investigate the surface charge character of raw materials in various conditions (of pH). Zeta potential of the particles in their aqueous suspensions (with various pH) were measured using Zatsizernano-Zs, Malvern. The magnetic composites were further characterized by several analysis methods. FT-IR characterization was conducted using Fourier Transformation Infra-Red (FT-IR) Spectrophotometer type Shimadzu Prestige 21 to investigate the bond characteristics in samples. The analysis was carried out using IR light with wave number range of 400 – 4000 cm⁻¹. The surface morphology and the material composition of samples were analyzed using a field emission-scanning electron microscope FE-SEM FEI INSPECT F50 equipped with energy dispersive X-ray spectroscopy (EDX) AMETEK which was conducted at 20 kV. The crystalline phase of the composites were determined using powder X-ray diffraction (XRD). The XRD patterns were obtained using a PHILIPS PW1710 with Cu anode tube (λ = 0.154184 nm). XRD tatars at voltage of 40 kV and current of 30 mA, with scanning rate of 2°/min (with sampling pitch : 0.02°) in the range of 2θ=10 – 80°. Magnetic characteristic of samples were measured using Vibrating Sample Magnetometer (VSM) type 1.2 T Oxford. The samples were given magnetic field from -1 to +1 Tesla, with rate of 0.25 Tesla/minute and the magnetic response or mass magnetization of samples were measured and presented in form of hysteresis curve.

2.6. Magnetic Separation Test

Magnetic separation test was conducted to prove the ability of magnetic composite to be separated magnetically. 0.1 g of magnetic composites were mixed with 100 mL of aquadest and stirred
sufficiently. The vessel containing the mixture of composite sol was placed on a rather weak magnetic bar (to make the difference in magnetic strength visually significant). Images of the composite sol condition in the vessel were taken from time to time and the time until all composites particles were fully separated from the liquid phase.

3. Results and Discussion

3.1. Zeta Potential (ζ-potential) Characterization
Figure 1 shows the effect of pH on ζ-potential of TiO$_2$P25 [9], pure MWCNT [10], and CNT which had been given acid treatment (CNT-AT). In this case, TiO$_2$ P25 was considered to have same surface charge characteristic with TiNT. It can be seen that TiO$_2$ and CNT have similar profile of ζ-potential, which means they have similar surface charge characteristic. Associated to that phenomenon, particles with same surface charge (either positive or negative), like TiO$_2$(or TiNT) and CNT would repel and couldn’t attach to each other. Therefore, certain treatment, such as acid treatment, was needed to modify the surface charge of CNT, making it possible to attach with TiNT. It can be seen at figure 1 that ζ-potential of CNT-AT were negative (-10 up to -29 mV) for pH range of 2-11, indicating the negative surface charge of CNT-AT. This phenomenon is strongly related with the formation of hydroxyl, carbonyl, and carboxylic acid at the wall of CNT, which occurred because of the oxidation process by strong acid [11]. The negative surface charge of CNT-AT would enable the heteroagglomeration process between TiNT and CNT at acid condition, where TiNT would have positive surface charge. Hence, they would attach each other making electrostatic attraction force between them. For further sections, the term CNT would refer to pre-treated CNT (CNT-AT).

3.2. FT-IR Characterization
Figure 2 contains the FT-IR spectra of samples TiNT/CNT and TiNT/CNT/Fe$_3$O$_4$ composites. Both samples contain peak at 3400 cm$^{-1}$, 1630 cm$^{-1}$, and 400 – 850 cm$^{-1}$. The peak around 1630 cm$^{-1}$ is due to the bending vibration of the O–H bond of chemisorbed water, and the peak around 3400 cm$^{-1}$ is due to the stretching mode of the O–H bond of free water [12]. The broad band at 400 – 850 cm$^{-1}$ corresponds to the Ti–O–Ti stretching vibration mode in crystal TiO$_2$[12]. TiNT/CNT composite specifically has the quite broad peak around 1080 cm$^{-1}$, indicating the formation of Ti-O-C bond between TiNT and CNT [13]. The strong peak at 1400 cm$^{-1}$ of TiNT/CNT composites signifies the presence of carboxylic acid, C-O-H bond which is deduced to be coming from pre-treated CNT [13]. The last two peaks cannot be found at the FT-IR spectra of TiNT/CNT/Fe$_3$O$_4$, because the amount of CNT in the composite was very small which the CNT could be cloistered by Fe$_3$O$_4$ nanoparticles, making the bonds which involved CNT could not be detected. Ye, Cai, Zheng, Xiao, Hua and Huang [14] obtain similar result, where almost all strong peaks of SiO$_2$/TiO$_2$ sample are covered up after Ag is coated onto the SiO$_2$/TiO$_2$ substrate. For the TiNT/CNT/Fe$_3$O$_4$ composite, the Fe-O-Fe bond is supposed to produce peak at 580 cm$^{-1}$[15]. However, the peaks of Fe-O-Fe bond are overlapping with the broad band of Ti-O-Ti which lies from 400-850 cm$^{-1}$. This phenomenon makes the FT-IR characterization is not enough to determine the presence of Fe$_3$O$_4$ nanoparticles in the magnetic composite (TiNT/CNT/Fe$_3$O$_4$).
Figure 1. Effect of pH on ζ-potential of TiO$_2$ P25[9], pure MWCNT [10], and pre-treated CNT (CNT-AT).

Figure 2. FT-IR spectra of TiNT/CNT and TiNT/CNT/Fe$_3$O$_4$ composite.

3.3. FE-SEM/EDX Characterization
Figure 3 illustrates the FE-SEM image of TiNT, CNT, Fe$_3$O$_4$, TiNT/CNT, and TiNT/CNT/Fe$_3$O$_4$. As-prepared TiNT (figure 3 (a)) has morphology of straight tubes with outer diameter of 24-42 nm. The tubes of TiNT are relatively small but long and separated perfectly from each other. CNT (figure 3 (b)) which had been pre-treated beforehand has the form of curly tube, with outer diameter of 45-70 nm.
The magnetic material, Fe₃O₄ (figure 3 (c)) forms the clustered structure, which each particle of Fe₃O₄ sizes of less than 25 nm. The cluster structure would be giving advantage for the separation process of magnetic particles from the solution, because of its relatively big volume, making the magnetic response stronger. Therefore, the superparamagnetic characteristic of each nanoparticle could be maintained [16]. CNT is found to attach on several tubes of TiNT in TiNT/CNT composite (figure 3 (d)). This phenomenon could occur because of electrostatic attraction force between different surface charges of TiNT and CNT as explained before at ζ-potential characterization section. However, CNT is hardly found in TiNT/CNT/Fe₃O₄ (figure 3 (e)), possibly because of the small composition of CNT which make it could be easily covered by Fe₃O₄, similar to FT-IR result of the composite. In the other hand, TiNT can be easily found in form of long straight tubes which are covered by Fe₃O₄ nanoparticles. The cluster structure of Fe₃O₄ is still there, which would make the composite to have quite strong magnetic response so that the magnetic separation process could be done properly [16]. However, related to the closure of TiNT by the particles of Fe₃O₄, there would be

### Table 1. Energy dispersive X-ray spectroscopy analysis of samples.

| Elements | TiNT (%) | CNT (pre-treated) (%) | TiNT/CNT(1:0.015) (%) | TiNT/CNT/Fe₃O₄(1:0.015:0.3) (%) |
|----------|----------|-----------------------|-----------------------|---------------------------------|
| Ti       | 47.48    | -                     | 50.76                 | 37.77                           |
| O        | 52.52    | 5.79                  | 36.59                 | 50.82                           |
| C        | -        | 94.21                 | -                     | 4.78                            |
| Fe       | -        | -                     | 63.41                 | -                               |

Figure 3. FE-SEM image of: (a) TiNT; (b) pre-treated CNT; (c) Fe₃O₄ nanoparticles; (d) TiNT/CNT(1:0.015) composite; (e) TiNT/CNT/Fe₃O₄ (1:0.015: 0.3) composite.
negative drawbacks for the photocatalytic process including the strong light absorption by iron oxide or photodissolution effect which could interfere the contact between photocatalyst and the light. As a result, it might decrease the photocatalytic activity. Therefore, it is important to determine the optimal amount or composition of the magnetic materials to minimize the photodissolution effect and maintain the good magnetic characteristic.

Energy dispersive X-ray spectroscopy result of TiNT, CNT, Fe₃O₄, TiNT/CNT, and TiNT/CNT/Fe₂O₃ could be seen in Table 1. TiNT contains only Ti and O elements only, while Fe₂O₃ contains only Fe and O elements, as they should be. For acid treated CNT, besides C element, there is O element which derives from carboxylic acid (as the outcome of the acid treatment). As the result of the combination between TiNT and CNT, TiNT/CNT composite contains the constituent elements of each material, which are Ti, O, and C. Table 1 also shows that TiNT/CNT/Fe₃O₄ composite contains the elements of Ti, O, C, and Fe, which proves the presence of each material: TiNT, CNT, and Fe₂O₄. C element of CNT is found in minor amount which supports the result of FE-SEM and FT-IR analysis.

### 3.4. XRD Characterization

Figure 4 shows the XRD pattern of TiNT, TiNT/CNT, and TiNT/CNT/Fe₂O₃ with varied compositions of Fe₂O₃. All samples give out the dominant peaks at 2θ of 25.6°, 37.6°, 47.9°, 53.7°, and 55.1°, which are conforming to crystalline structure of anatase TiO₂ (according to JCPDS file no. 21-1272). Each of the magnetic composites (TiNT/CNT/Fe₂O₃) contains magnetite, Fe₂O₄ which produces XRD peaks at 30.2°, 35.5°, 43.3°, 56.8° (JCPDS file no. 03-0863), similar to the magnetite phase for pure Fe₂O₃ (figure 3(f)). As the amount of Fe₂O₃ goes higher in the composite, the peaks of TiO₂ anatase become shorter and the peaks of magnetite grow higher. However, calculation by Scherrer equation shows that the size of anatase crystallite sizes of pure TiNT, TiNT/CNT composite, and TiNT/CNT/Fe₂O₃ composites are not significantly different (see table 2), which means that the addition of Fe₂O₃ and CNT did not affect the crystal of TiNT.

It is noticeable that there is no significant difference between the peaks of TiNT/CNT/Fe₂O₃ (1: 0.015: 0.5) composite and the peaks of TiNT/CNT/Fe₂O₃ (1: 0.015: 0.3) composite, which means their magnetic properties would be similar. This phenomenon might happen due to the instability of Fe₂O₃ in open air, which make it could easily be oxidized to Fe₂O₃ along the preparation and storing process. For TiNT/CNT/Fe₂O₃ (1: 0.015: 0.5) composite, the preparation process is relatively longer, especially for the step of adding ammonia (NH₄OH) solution drop by drop, where the composite needs more ammonia due to larger amount of Fe₂O₃. The oxidation process might also be accelerated by the ultrasonication process.

| Samples                        | Anatase crystallite size (nm)* | Saturation magnetization (emu/g) | Coercivity (oe) |
|--------------------------------|-------------------------------|---------------------------------|-----------------|
| TiNT                           | 11.0                          | -                               | -               |
| TiNT/CNT (1 : 0.015)           | 10.5                          | -                               | -               |
| TiNT/CNT/Fe₂O₃ (1 : 0.015 : 0.1) | 9.02                          | 4.12                            | 110.4           |
| TiNT/CNT/Fe₂O₃ (1 : 0.015 : 0.3) | 9.79                          | 21.1                            | 84.4            |
| TiNT/CNT/Fe₂O₃ (1 : 0.015 : 0.5) | 10.4                          | 26.8                            | 72.9            |
| Fe₂O₄                          | -                             | 79.7                            | 59.5            |

* calculated by Scherrer equation
Figure 4. XRD patterns of: (a) TiNT; (b) TiNT/CNT (1:0.015); (c) TiNT/CNT/Fe$_3$O$_4$ (1:0.015:0.1); (d)TiNT/CNT/Fe$_3$O$_4$ (1:0.015:0.3); (e)TiNT/CNT/Fe$_3$O$_4$ (1:0.015:0.5); (f) pure Fe$_3$O$_4$.

3.5. Evaluation of Magnetic Properties

The magnetic response of prepared Fe$_3$O$_4$ and TiNT/CNT/Fe$_3$O$_4$ composites with varied amount of Fe$_3$O$_4$ were measured at room temperature using VSM analysis, as illustrated in figure 5. The values of saturation magnetization and coercivity are shown in table 2. The observed value of saturation magnetization for the prepared magnetic iron oxide, Fe$_3$O$_4$ is 79.7 emu/g. Magnetic properties depend on the amount of magnetic phase (Fe$_3$O$_4$) fraction in the materials. The decrease in the saturation magnetization in composite is due to the lower content of magnetic iron oxide in materials and the presence of non-magnetic materials [7]. It seems that the reduction of saturation magnetization value is not proportional to the amount of Fe$_3$O$_4$. This result is similar to XRD result which shows that the difference between the peak height of magnetite phase of TiNT/CNT/Fe$_3$O$_4$ (1:0.015:0.05) and TiNT/CNT/Fe$_3$O$_4$ (1:0.015:0.03) is not significant. As explained before, this phenomenon might happen due to the oxidation process of Fe$_3$O$_4$ (see XRD Characterization Section). Superparamagnetic behavior of material can be seen from the low value of coercivity. The coercivity value of those two magnetic composites are similar to each other and lower than 100 oe, which indicates that those composites have superparamagnetic behavior [7]. In the other hand, TiNT/CNT/Fe$_3$O$_4$ (1:0.015:0.01) has low saturation magnetization value and great coercivity value (> 100 oe), which means the composite could not be categorized as superparamagnetic material. Superparamagnetic behavior is needed for the field application to facilitate recovering the magnetic composite efficiently from treated water by the assistance of magnetic field [7].
Figure 5. Hysteresis curve of Fe$_3$O$_4$ nanoparticles and TiNT/CNT/Fe$_3$O$_4$ composites with varied amount of Fe$_3$O$_4$.

Magnetic separation test for the samples was conducted and the images of the test can be seen on Figure 6. TiNT/CNT sol was very stable, so that after 60 minutes there were no significant differences. Even though the sol was left for 24 hr, the sol was still stable. Magnetic composites were shown to have magnetic response to the magnetic field, produced by magnetic bar. The separation time until the supernatant became transparent for TiNT/CNT/Fe$_3$O$_4$ (1: 0.015: 0.1), TiNT/CNT/Fe$_3$O$_4$ (1: 0.015: 0.3), and TiNT/CNT/Fe$_3$O$_4$ (1: 0.015: 0.5) composites were 60, 24, and 9 minutes respectively, which means that the separation time of the magnetic composite was inversely proportional to the amount of magnetic phase. However, for TiNT/CNT/Fe$_3$O$_4$ (1: 0.015: 0.3) and TiNT/CNT/Fe$_3$O$_4$ (1: 0.015: 0.5) composites, it is a bit contrary to the result of VSM analysis which shows that the magnetic strength of those two composites are quite similar. This phenomenon can be understood if we also consider the factor of composite density, which would also increase as the amount of Fe$_3$O$_4$ increased. High density of composite would make the composite to sink faster in water. In this case, it can be concluded that the separation time of a composite was determined not only by magnetic response but also the density of the composite.

For field application, it is demandable to have decent rate of composite separation. In this case, using rather small amount of Fe$_3$O$_4$, like on TiNT/CNT/Fe$_3$O$_4$ (1: 0.015: 0.1) is not recommended, because the separation process would take fairly long time. Using high amount of magnetic phase (≥ 0.5 times the amount of photocatalyst), iron oxide is not recommended too, because it might lead to excessive photodissolution effect. Therefore, using medium amount of Fe$_3$O$_4$ will be sufficient to produce composite which can be efficiently separated from the treated water by the assistance of magnetic field. From these outcomes, it could be concluded that the optimal amount of Fe$_3$O$_4$ was 0.3 times the amount of TiNT. The composition was chosen in order to minimize the negative drawbacks to photocatalytic activity because of the presence of magnetic phase. Yet, the composition still can make magnetic composite owned supermagnetic behavior to enable the magnetic separation process for composite recovery. Photodegradation test of the samples to investigate the performance of the composites for eliminating organic waste and the photodissolution effect is still in progress.
4. Conclusion
The TiNT/CNT/Fe$_3$O$_4$ composite had been successfully prepared by ultrasonic assisted in-situ process, which the composite had good magnetic properties. In the magnetic composites, TiNT and CNT were attached to each other due to electrostatic attraction force and Fe$_3$O$_4$ nanoparticles were formed on the surface of TiNT/CNT in cluster structure. Based on the experimental results, the optimum amount of Fe$_3$O$_4$ in the magnetic composite was 0.3 times the amount of TiNT to minimize the photo dissolution effect. Yet, with the chosen composition, the superparamagnetic behavior could be maintained, with the saturation magnetization and coercivity values were 21.1 emu/g and 84.4 Oe respectively. It would not be effective to add more Fe$_3$O$_4$, because the magnetic characteristic would insignificantly increase. On the contrary, it could increase the photo dissolution effect. Photo degradation test of the samples is still in progress.

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