Preparation of Photocatalyst with High Reactivity from Cellulose-based Graphitic Carbon

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A photocatalyst with high reactivity was prepared in liquid phase through the in situ deposition of TiO₂ on cellulose-based graphitic material that had been oxidized via Hummers' method that was followed by a heating treatment at 200 °C. The composite had excellent photocatalytic activity for degrading methyl orange (MO), and reducing hexavalent chromium (Cr(VI)) under ultraviolet irradiation as well as the reported graphene oxide/TiO₂ composite. Under the optimal condition, the reaction rates for treating MO and Cr(VI) using the new catalyst system were 4.6 and 1.6 times higher, respectively, than that of commercial TiO₂ (P25). In addition, the composite had good catalytic activity in acid solutions. Unlike the reported graphene oxide/TiO₂ composite, TiO₂ nanoparticles in the prepared composite aggregated to large particles of approximately 1 µm in size on the carbon substrate. When synthesized in the same procedure from other biomass materials, such as lignin, walnut shell, or fir sawdust, the composite had much lower reactivity, similar to that of neat TiO₂; the lower graphitic degree of those materials might be the reason for the disparity in reactivity.

Keywords: Photocatalyst; Graphitization; Cellulose; Composite

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INTRODUCTION

Treating contaminated water has occupied the attention of researchers for decades. Photocatalysis is widely utilized for the treatment of environmental pollutants, including atrazine (Youssef *et al.* 2019), organic dyes (Yang *et al.* 2005; Salama *et al.* 2018) or metallic pollutants (Litter *et al.* 2016) due to high efficiency and non-toxicity. Numerous kinds of photocatalysts had been synthesized, such as TiO₂ (Shen *et al.* 2008), CdS (Zhu *et al.* 2018), ZnO (Chen *et al.* 2017) or some composites containing Co (Natali *et al.* 2017), and Mn (Al-Oweini *et al.* 2014). Among these photocatalysts, TiO₂ is especially popular because of its physical and chemical stability and low cost. It is known that electrons (e^{-}) and holes (h^{+}), which are highly active during photoreaction, are generated in the surface of the catalyst when it is subjected to ultraviolet (UV) irradiation. However, the photo-generated electrons and holes always quickly recombine after they are generated, leading to limited catalytic efficiency on neat TiO₂ (Ozawa *et al.* 2014). Different methods to prevent the recombination have been reported to separate the photo-generated electron-hole pairs during the photocatalytic reaction. One of these methods is

to use conductive materials, including noble metals, such as Au (Ayati *et al.* 2014), Ag (Tada *et al.* 2004), or carbon materials, as modifiers to separate the electrons and holes. The application of cheaper but still highly conductive carbon materials, such as carbon nanotubes (CNTs) (Xiao *et al.* 2016), and C₆₀ (Zhang *et al.* 2010b), has become increasingly common in the photocatalysis field in recent years.

Recognized as a "star" carbon material since its discovery by Novoselov *et al.* in 2004, graphene has drawn a great deal of scientific interest due to its excellent electrical and thermal conductivity, its large specific surface area, and its great mechanical strength (Lee *et al.* 2008), all of which make it an outstanding candidate for promoting the photocatalytic effect based on its unique properties (Zhang *et al.* 2010a; Jiang *et al.* 2011). For example, a graphene-TiO₂ (P25) composite was prepared using a one-step hydrothermal method; the obtained composite demonstrated significant enhanced photocatalysis efficiency compared to that of neat TiO₂ (Zhang *et al.* 2010a). Additionally, in Jiang *et al.* (2011), a graphene oxide (GO)/TiO₂ composite with high photocatalytic reactivity was synthesized by a simple *in situ* depositing procedure in liquid phase followed by calcinating at 200 °C. The photo-reaction rates for methyl orange (MO) and Cr(VI) when using the composite were 7.4 and 5.4 times higher, respectively, than that of P25.

The usual starting material for preparing graphene is natural graphite; however, it is a non-renewable resource. Instead, abundant, cheap, and renewable biomass materials (Gao et al. 2017) have been studied as excellent candidates for producing a graphitic carbon that is favorable for further production of graphene (Herring et al. 2003; Sevilla et al. 2007; Sevilla and Fuertes 2010; Liu et al. 2013; Chen et al. 2018). Because biomass materials form non-graphitizable amorphous carbon after carbonization, a transition metal, such as Ni or Fe, is required as a catalyst during graphitization. For instance, cellulose-based graphitic carbon has been obtained by catalysis with Ni under laser irradiation at 2250 °C (Herring et al. 2003) or thermal treatment (Sevilla and Fuertes 2010). Similarly, activated carbon with between 3 and 8 ultra-thin graphitic layers has also been prepared from the leaves of Zizania latifolia at 900 °C with the assistance of Ni. In that case, the graphitic layers were thickened to approximately 30 layers when the temperature was raised to 1000 °C (Liu et al. 2013). Recently, this group successfully prepared graphitic carbon from microcrystalline cellulose at 1400 °C, utilizing Ni as a catalyst; the resulting cellulose-based graphitic carbon's crystallinity was as high as that of commercial flaky graphite (Chen et al. 2018). As mentioned above, graphene, which is prepared from graphite, can be further utilized in photocatalysis field; therefore, cellulose-based graphitic carbon can be applied for the syntheses of photocatalytic composite as well, and based on this group's survey of the literature, biomass-based graphitic material has not yet been applied in the photocatalysis field.

In this work, graphitic carbon was obtained from microcrystalline cellulose using Ni as a catalyst. The carbon was then oxidized using Hummers' method (Hummers and Offeman 1958) in liquid phase. The TiO_2 particles were assembled *in situ* on the oxidized carbon, and the photocatalyst composite was finally obtained after calcination. Both MO and hexavalent chromium Cr(VI) were chosen as the target pollutants for testing the photo-reactivity of the composite. In addition, different biomass materials – lignin, walnut shell, and fir sawdust – were used to prepare the composite according to the same procedure as with the control samples.

EXPERIMENTAL

Materials

Preparation

Graphitic carbon was prepared from microcrystalline cellulose (Aladdin Co., Ltd., Shanghai, China) as the authors have previously reported (Chen *et al.* 2018). In brief, cellulose was carbonized at 500 °C followed by impregnating with a NiCl₂ solution overnight. The mixture was then dehydrated and calcinated in a sealed crucible at 1400 °C for 3 h. The obtained sample was washed with HCl (37%) to remove metal residue and was dehydrated overnight. To prepare the control samples, different raw materials – lignin (Duly Biotech Co., Ltd., Nanjing, China), walnut (*Juglans regia*) shell (Shihezi, Xinjiang Province, China), and fir (*Cunninghamia lanceolata*) sawdust (Yushan, Jiangxi Province, China) – were carbonized and then graphitized following the same procedure.

After graphitization, the obtained carbon was oxidized using Hummers' method, similarly to the process for preparing graphene oxide (GO). For convenience, the product was named cellulose-based graphitic carbon oxide (CGO). The composite was prepared via an in situ decomposing method in aqueous phase as previously reported (Jiang et al. 2011). First, CGO was added into distilled water and ultrasonicated for 30 min to achieve a dark-brown CGO solution. Both boric acid (H_3BO_3) and ammonium hexafluorotitanate $[(NH_4)_2 TiF_6]$ were added into the CGO solution and continuously stirred. The hydrolysis reaction occurred at 60 °C for 2 h in a water bath, and the light-brown CGO/TiO₂ product was separated and washed via filtration. The obtained product was dried in a DHG-9036A electrothermal constant-temperature drying box (Jinghong Experimental Equipment Co., Ltd., Shanghai, China) and heated in an SX-5-22 muffle furnace (Boluo Experimental Equipment Co., Ltd., Shanghai, China) at 200 °C for 1 h, and the final gray-colored product was obtained. The products before and after calcination were defined as cellulose-based graphitic carbon/titanium dioxide (CGT) and CGT-X, where X is the heating temperature. The control samples of lignin, walnut shell, and fir sawdustbased composites were prepared in the same way, and the products were defined as LGT, WGT, and FGT, respectively. Neat TiO₂ was also prepared using the same procedure but without adding CGO. Commercial Deguassa TiO₂ (P25) (Evonik Deguassa Co., Ltd., Essen, Germany) was also purchased for comparison.

Methods

Photocatalytic experiments

The MO (10 mg/L) and Cr(VI) (0.2 mM) were chosen as the target pollutants. The solutions were prepared by dissolving certain amounts of MO or $K_2Cr_2O_7$ (both purchased from Tianjin Chemical Reagent Institute Co., Ltd.) into distilled water. Photocatalytic tests were conducted in a glass reactor (Sichuan Shubo (Group) Co., Ltd., Chongzhou, China) in which 50 mL of solution and 0.020 g of catalyst were thoroughly mixed *via* magnetic stirring at room temperature. The pH value of the solution was adjusted through adding HCl or NaOH before the photocatalytic reaction was started (pH 4 for MO and pH 2 for Cr(VI), if not otherwise stated). A 15 W UV lamp with maximum emission of 254 nm was positioned at approximately 10 cm above the reactor. The suspension was magnetically stirred in the dark for approximately 30 min before irradiation to favor the adsorption-desorption equilibration, and then the concentration was recorded as the initial concentration (c_0) to discount the adsorption. At certain time

intervals, *e.g.*, 2 min, 5 min, or 10 min, 2 mL of solution was removed from the suspension and centrifuged at 10000 rpm for 8 min to remove catalyst particles for analysis.

Analysis

X-ray powder diffraction (XRD) patterns for all samples were obtained on a Bruker D8 instrument (Bruker Corporation, Karlsruher, Germany) operating at 40 kV and 20 mA with Cu K α radiation ($\lambda = 0.15406$ nm) and a measuring angle from 10° to 80°. The determination of the graphitized samples and control sample was performed on a Raman Thermo DXR532 microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA), in the range of 50 cm⁻¹ to 3500 cm⁻¹. X-ray photoelectron microscopy (XPS) spectra were recorded on a Kratos Axis Ultra DLD spectrometer (Kratos Analytical Co., Ltd., Manchester, UK). The surface morphology of CGT and neat TiO₂ were recorded by a JEM-7600F scanning electron microscope (SEM) (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan). To observe the morphology of cellulose-based graphitic carbon and CGO, the samples were first well dispersed into alcohol and treated with an ultrasonic processor (Hechuang Ultrasonic Instrument Co., Ltd., Kunshan, China), followed by coating to copper grids (Gilder Grids Ltd., Grantham, UK). The coated grids were placed into a JEM2100 high-resolution transparent electron microscope (TEM) (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan), operated at 200 kV accelerating voltage. The concentration of MO was analyzed by measuring the absorbance at 465 nm (pH \ge 4) or 510 nm (pH < 4). The diphenylcarbazide photometric method, according to the Chinese national standard GB/T 7466 (1987), was utilized to measure the concentration of Cr(VI) at 540 nm. The absorbance of all solutions was analyzed by a Shimadzu UV 2550 UV-vis spectrophotometer (Shimadzu Corporation, Kyoto, Japan). The photo reaction rate constant k was obtained by utilizing a pseudofirst-order equation listed below,

$$\ln\frac{c_t}{c_0} = -kt \tag{1}$$

where c_0 is the initiate concentration (mg/L), c_t is the concentration at a certain reaction time (mg/L), k is the rate constant (min⁻¹), t is the reaction time (min). It was obvious that $(\ln \frac{c_t}{c_0})$ presented a linear relationship with t and k is the slope that can be directly known from the linear equation.

RESULTS AND DISCUSSION

Characterization of the Catalysts

From the (SEM) images of CGT-200 shown in Figs. 1(a) and 1(b), it was clearly seen that the prepared product had large spherical particles with diameters of approximately 500 nm, which were in fact composed of numerous TiO_2 nanoparticles with diameters of 20 to 40 nm, and the substrate was hardly observed. This surface morphology was remarkably different from the composite prepared from flaky graphite as reported by Jiang *et al.* (2011). In the authors' previous report (Chen *et al.* 2018), the cellulose-based graphitic carbon was an annular shape, as seen in Fig. 2(a), a structure that was completely different from common flaky graphite. As shown in Fig. 2(b), after oxidation and ultrasonic procedures, the obtained CGO still retained its original annular

structure. Because CGO could not be exfoliated into sheets like flaky graphite, the surface of CGO may have been unfavorable for the effective distribution of TiO₂ nanoparticles. Instead, TiO₂ nanoparticles aggregated into larger particles similar to those generated with neat TiO₂, as seen in Figs. 1(c) and 1(d). Due to that structure, the Brunauer-Emmett-Teller (BET) specific surface area of CGT-200 was determined as 38 m²/g, which was much lower than the reported GO/TiO₂ composite (80 m²/g) (Jiang *et al.* 2010) and even lower than P25 (53 m²/g).



Fig. 1. SEM images of CGT-200 (a and b) and TiO₂-200 (c and d)



Fig. 2. TEM images of (a): cellulose-based graphitic carbon and (b): CGO

According to the morphology of CGT-200, the synthesis procedure could be described as shown in Fig. 3.



Fig. 3. Schematic illustration for the synthesis of CGT-200

The XRD patterns demonstrated that TiO₂ in the composites appeared in the form of anatase (the (1 0 1) diffraction peak for anatase appears at $2\theta = 25.4^{\circ}$), as can be seen in Fig. 4. The intensity of the peak was greatly enhanced as the heating temperature increased from 100 °C to 300 °C, indicating that heating promoted the crystallinity of TiO₂. When the heating temperature was raised to 400 °C, the intensity of the diffraction peak only slightly increased. Therefore, heating at 300 °C was enough to produce anatase crystallinity growth. No observable peaks for CGO, graphite, or graphene appeared in any of the samples, and this was probably due to the low carbon content in the composites or their being obscured by the diffraction signals of the TiO₂.



Fig. 4. XRD patterns for the photocatalysts heated at different temperatures

Raman spectroscopy is a common method for the characterization of ordered or disordered microstructures of carbonaceous materials. There are generally two distinct peaks in Raman spectra: the D band at around 1350 cm⁻¹ and the G band at around 1580 cm⁻¹, which are caused by defects and/or disordered structures and sp² sites, respectively (Ferrari and Robertson 2000). In the Raman spectrum of CGT, as shown in Fig. 5(a), the D and G bands were observed at 1347 and 1596 cm⁻¹, and the two bands slightly shifted to 1333 and 1599 cm⁻¹, respectively. The intensities of the two bands, I_D and I_G , are

usually used to evaluate the disorderedness of carbon networks. It was noticeable that the I_D and I_G ratios of CGT and CGT-200 were 0.99 and 1.10, respectively. The increase of the I_D and I_G ratios after heating were probably due to the decrease of sp² regions (Ferrari 2007) caused by the release of heteroatoms during the heating procedure. Furthermore, both CGT and CGT-200 had 2D and S3 bands that were caused by resonant processes and lattice disorders, respectively. Besides, the color of CGT changed from light brown to light grey after heating at 200 °C, as can be seen in Fig. 5(b). The darkened color indicated the reduction of CGO, during which the conjugate structures in the carbon substrate recovered, leading to obviously stronger light absorption.



Fig. 5. (a): Raman spectra for CGT and CGT-200; (b): Color comparison of CGT and CGT-200

The chemical state of Ti in the composite was measured *via* XPS spectra, as illustrated in Fig. 6(a). Two distinct peaks were located at binding energy 464.5 and 458.7 eV, which were respectively assigned to Ti $2p_{1/2}$ and $2p_{3/2}$ spin-orbital splitting photoelectrons in the Ti⁴⁺ chemical state. The peak-to-peak separation was 5.8 eV, indicating that TiO₂ in CGT-200 existed in a normal state. From the C 1s spectra, as shown in Fig. 5(b), there were three peaks positioned at 284.7, 285.8, and 288.7 eV, which can be attributed to C-C, C-O-C, and O-C=O, respectively, revealing that carbon also existed in the common chemical state in the composite.



Fig. 6. XPS spectra for (a) Ti 2p and (b) C 1s core level in CGT-200

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Photocatalytic Reaction of MO and Cr(VI) on the Catalysts

The photocatalytic performances of the prepared composites were evaluated by the discoloration rate of MO and reduction rate of Cr(VI), respectively. To discount adsorption of the substrate on the catalyst, the suspension was magnetically stirred for 20 min in the dark before photocatalytic reaction. The rapid degradation of MO by CGT-200 was clearly demonstrated from the obvious change in the UV-vis absorption spectra of MO, as shown in Fig. 7(a). Within 8 min, approximately 90% of the added MO (10 mg/L) was removed by CGT-200, whereas approximately 20 min were necessary for the total removal of MO for P25, and only 20% of the added MO was degraded for TiO₂-200 after 40 min, as can be seen in Fig. 7(b). Utilizing the pseudo-first-order equation, it was calculated that the rate constant for removing MO by CGT-200 was 0.440 min⁻¹, which was 4.6 and 67 times higher than P25 (0.0965 min⁻¹) and TiO₂-200 (0.0065 min⁻¹), respectively.



Fig. 7. (a) UV-Vis spectra for the degradation of MO by CGT-200 and (b) photocatalytic degradation of MO by CGT-200, P25, and TiO₂-200

It was evident during the preparation process that heat treatment caused structural and chemical variation in CGT: first, the crystallinity of TiO₂ was greatly promoted, and second, the oxygen-containing groups were removed, leading to the formation of reduced CGO (rCGO). Both changes occurred and were beneficial for the promotion of photocatalytic reactivity. The photocatalytic reactivity of CGT treated at different temperatures is summarized in Fig. 8(a). Although the crystallinity of TiO₂ constantly increased from 100 °C to 400 °C, the photocatalytic reactivity clearly dropped when the heating temperature was higher than 200 °C. This phenomenon also was involved in the case of the GO/TiO₂ composite in the previous report (Jiang *et al.* 2011); the decrease in the photocatalytic reactivity was probably due to partial decomposition or combustion of the CGO substrate.

The CGO in the composite also played an important role in promoting the photocatalytic reactivity. For this reason, the authors also investigated the effect of CGO content on the photocatalytic reactivity. Composites with different CGO content were prepared by using CGO solutions with different concentrations in the hydrolysis procedure. As can be seen in Fig. 8(b), when the CGO content was increased from 0.5 to 1.0%, the reaction rate constant for degradation of MO was greatly increased from 0.252 to 0.440 min⁻¹, and the rate constant dropped to 0.414 min⁻¹ when CGO content rose to 2.0%. It has been reported that an initial increase of GO content helps enhance the

photocatalytic reactivity, while too much GO impedes the reaction due to the photoabsorbing and scattering of GO (Jiang *et al.* 2011).



Fig. 8. Effect of (a) heating temperature, (b) CGO amount, (c) CGT-200 concentration, and (d) pH values on the photocatalytic degradation of MO

The effect of CGT-200 concentration on the degradation of MO was also investigated, as shown in Fig. 8(c). The degradation rate constant continuously increased from 0.177 to 0.440 min⁻¹ as the concentration of CGT-200 was increased from 0.1 to 0.4 g/L. When the CGT concentration was increased to 0.5 g/L, the rate constant k was calculated as 0.478 min⁻¹. Hence, 0.4 g/L of CGT-200 was seen as sufficient to induce high photocatalytic efficiency. In addition, as shown in Fig. 8(d), CGT-200 had good photocatalytic reactivity for degradation of MO only in acid solutions, and the photocatalytic reactivity noticeably dropped at pH values higher than 4. The rate constants were calculated as 0.328, 0.446, 0.440, 0.065, and 0.039 min⁻¹ at solution pH values of 2, 3, 4, 5, and 6, respectively. Generally, it is believed that pH affects the photoreduction rate of MO by 1) changing the surface charge of photocatalyst which changes the contact ability with MO molecules and 2) changing the structure of MO molecules. To investigate the reason, the zeta potential of both CGT-200 and P25 under different pH values was measured, as shown in Fig. 9(a). Obviously, the surface of both CGT-200 and P25 was positively charged when pH value was lower than 5, and even P25 had a higher potential than CGT-200. Thus, surface charge is not an important influence factor. As a pH indicator, MO molecules are sensitive to pH values, as shown in Fig. 9(b). The molecules exist mainly in quinoid structure at pH below 3.1, mainly in azo

structure at pH above 4.4, and in both quinoid and azo structures at pH between 3.1 and 4.4. It is known that the quinoid structure has lower bond energy than the azo structure (Niu and Hao 2011); therefore, the obvious enhancement of the photocatalytic reactivity of CGT-200 under lower pH values might due to the existence of quinoid structure.



Fig. 9. (a) Zeta potential of CGT-200, P25 and (b) molecular transformation of MO



Fig. 10. Photocatalytic reduction of Cr(VI) by CGT-200, P25, and TiO₂-200

The composite CGT-200 also showed good photocatalytic activity for reducing Cr(VI), which is a highly toxic and carcinogenic inorganic pollutant. It had previously been demonstrated that during photocatalytic procedure, Cr(VI) could also be reduced by photo-generated electrons, and the less toxic reduction product, Cr(III), could be easily further removed *via* precipitation in alkaline solution (Wang *et al.* 2008). Fig. 10 shows that the rate constant for reducing Cr(VI) by CGT-200 was 0.0241 min⁻¹, which was 1.6 times and 11.5 times higher than that over P25 (0.0153 min⁻¹) and TiO₂-200 (0.0021 min⁻¹), respectively.

The photocatalytic reactivity for degrading MO and reducing Cr(VI) by the control samples, LGT-200, WGT-200, and FGT-200, were also determined and are listed in Fig. 11 and Table 1. It is clearly shown that none of the prepared control samples had high photocatalytic reactivity for degrading MO or reducing Cr(VI) as CGT-200. Rather, the photocatalytic reactivity of the control samples was only slightly higher than TiO₂-200, indicating that the carbon substrates contributed little towards enhancing the photocatalytic reactivity.



Fig.11. UV-spectra for the degradation of MO in the presence of (a) P25, (b) WGT-200, (c) LGT-200 and (d) FGT-200

Table 1. Kinetic Data for Photocatalytic Degradation of M	C and Reduction of
Cr(VI) by Different Composites	

Catalyst	CGT-200	LGT-200	WGT-200	FGT-200	P25	TiO ₂ -200
<i>к</i> мо (min⁻¹)	0.440	0.0182	0.0322	0.0112	0.0956	0.0065
<i>k</i> cr (min ⁻¹)	0.0241	0.0029	0.0067	0.0037	0.0153	0.0021

Discussion of the Reasons for High Photocatalytic Reactivity

According to previous reports, the GO/TiO₂ composite had extra high photocatalytic reactivity mainly due to a two-dimensional nanostructure, large specific surface areas, and effective separation of photogenerated electrons and holes (Jiang *et al.* 2011). Nevertheless, it can be clearly seen from Fig. 1 that CGT-200 had almost the same structure as neat TiO₂. Besides, all the prepared catalysts had almost the same XRD patterns and morphologies, as shown in Fig. 12(a) and (b), respectively. Therefore, the high reactivity of CGT-200 was not attributable to a structural reason. Accordingly, the specific surface area of CGT-200 was measured as only 38 m²/g, which was much smaller than the reported GO/TiO₂ composite (80 m²/g) and even lower than P25 (53 m²/g). However, CGT-200 had similar photocatalytic reactivity as that of the reported GO/TiO₂ composite. Hence, it was concluded that the reason for such high photocatalytic reactivity was the quick transfer of photogenerated electrons from the conducting band of TiO₂ to the conductive substrate rCGO during the photoreaction, as illustrated in Fig. 12(c).

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Fig. 12. (a) XRD patterns for the photocatalysts (b) SEM images of the composites synthesized from different raw materials (c) Mechanism of the photocatalytic reaction on CGT-200

The UV spectra of the degradation of MO at 5 min in the cases of P25, CGT-200 and TiO₂-200 are displayed in Fig. 13(a). It's clear that in the case of CGT-200, a new peak appeared at wavelength around 245 nm, which could not be found in the case of P25 or TiO₂-200.



Fig. 13. Comparison of UV spectra of MO treated by (a) P25, CGT-200, TiO₂-200 for 5 min and (b) CGT-200 for 2 min and P25 for 10 min

The new peak might be the intermediate that was relatively stable during degradation. For further investigation, the spectra were compared for MO treated by CGT-200 and P25 for 2 min and 10 min, respectively, as illustrated in Fig. 13(b). In both cases, the absorbance of MO at wavelength around 465 nm was almost the same. However, the new peak mentioned at above could be clearly seen in the case of CGT-200. It was concluded that the new peak might be attributed to a certain intermediate with weak acidic which led to the slight shift of maximum wavelength. The degradation of MO might follow a different pathway in the case of CGT-200, and further investigation is being carried out.

It was also demonstrated *via* the XRD patterns in Fig. 14(a) that after the same graphitization procedure, the crystallinity of cellulose-based carbon was almost as high as graphite, but the graphitization products from the other raw materials had much lower graphitic crystallinity. As shown in Fig. 14(b), the graphitized products had different conductivities corresponding to various graphitic crystallinities. Therefore, the high photocatalytic reactivity of CGT-200 was attributed to the effective separation of photogenerated electrons and holes by the conductive substrate rCGO. Moreover, it was noticeable that the rate constant for reducing Cr(VI) by CGT-200 was only 1.6 times higher than that by P25, and was much slower than the reported GO/TiO₂ composite (Jiang *et al.* 2011). During photocatalytic reaction, the photogenerated electrons that were of vital importance for the reduction of Cr(VI), transferred to the conductive substrate rCGO where large TiO₂ particles were located. Therefore, the contact of Cr(VI) and electrons may have been affected by these large particles, which led to a relatively slower rate.



Fig. 14. (a) XRD patterns and (b) conductivity of graphitized products from different raw materials

CONCLUSIONS

- 1. A photocatalyst composite with high reactivity was prepared from cellulose-based graphitic carbon oxide (CGO) in liquid phase through *in situ* deposition followed by calcination at 200 °C. Large TiO₂ particles approximately 500 nm in size and composed of anatase TiO₂ nanoparticles were evenly deposited on the carbon substrate.
- 2. The degradation rate of methyl orange (MO) and reduction rate of Cr(VI) under

ultraviolet light in the presence of CGT-200 were 4.6 and 1.6, respectively, times higher than the degradation and reduction rates in the case of P25. Such high photocatalytic reactivity of CGT-200 was probably due to the quick transfer of photogenerated electrons from TiO_2 to the conductive substrate.

3. Among the four prepared composites, only CGT-200 exhibited excellent photocatalytic reactivity as it had the highest graphitic content and because of the electron conductivity of the substrate rCGO.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Project No. 31770629), the National Key R&D Program of China (Project No. 2017YFD0601206), and Biomass Energy & Materials Laboratory of Jiangsu Province (JSBEM-S-201506). The authors are grateful for the analytic support of the Instrument Analysis Center and Pulp and Paper Research Lab at the Institute of Chemical Industry of Forest Products, CAF, Nanjing, China.

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Article submitted: February 7, 2019; Peer review completed: April 20, 2019; Revised version received and accepted: July 16, 2019; Published: July 29, 2019. DOI: 10.15376/biores.14.3.7213-7228