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Preparation and Characterization of Silanized TiO₂ Nanoparticles and Their Application in Toner

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ABSTRACT: Surface modification of TiO₂ nanoparticles with 3-methacrylic acyloxy propyl trimethoxysilane (KH570) was carried out in the liquid phase. The modified TiO₂ nanoparticles, as charge control agents (CCAs), were added to toner. Infrared and X-ray photoelectron spectroscopies provided strong indications of the formation of organic links between the TiO₂ and the KH570. The thick coating layer of KH570 deposited on the surface of TiO₂ nanoparticles was determined to be about 2–5 nm by transmission electron microscopy. The hydrophobicity of the modified toner decreased when the amount of coated KH570 reached 5.28 wt % and then increased with further increasing amount of coated KH570. The charge-to-mass ratio (*Q/M*) of the modified toner shifted in the negative direction with increasing amount of coated KH570; however, with increasing amount of modified TiO₂, the value of *Q/M* shifted in the positive direction. The reason for this difference is that the OH groups existing on the surface of TiO₂ transferred from the toner to the carrier after friction.

INTRODUCTION

Surface modification of TiO₂ nanoparticles and their application in various organic matrixes, for example, electronic ink, have been extensively discussed.^{1,2} Polymer/TiO₂ composites have aroused widespread interest in many fields, such as biology,³ optics,⁴ and electrics.⁵ However, at present, the use of modified TiO₂ nanoparticles as functional additives in toner has seldom been discussed.

Toner, with charges and a coloring function, is often applied in xerographic laser printers. The essential component of toner is polymer resin;⁶ however, the tribocharging, dispersion, and fluidity of raw toner are not ideal for application. Hence, it is necessary to modify the toner to meet the requirements for use in xerographic laser printers.

Charge control agents (CCAs) are included in toner formulations to control the sign and magnitude of the toner charge.⁷ TiO₂ nanoparticles were employed as a CCA for the toner in our work; however, TiO₂ nanoparticles have little interaction with the organic matrix in the interface because of the hydrophilic surfaces. Segregation and agglomeration of the inorganic phase are usually observed.⁸ Many efforts have been made to overcome the interfacial incompatibility between the fillers and the matrix by enhancing the hydrophobicity and decreasing the surface energy of the fillers.⁹ Silane coupling agents are common grafting agents for increasing the interfacial adhesion between inorganic fillers and organic matrix.^{9–12}

The primary material property that determines the behavior of xerographic laser printer development is the toner charge distribution.¹³ It is well-known that toner with charges of the wrong sign should degrade image quality. It is very important to determine the charge-to-mass ratio (*Q/M*) of toner for its application. A fundamental understanding of the material parameters that determine toner charging would be a revolutionary advance in xerographic laser printers.¹⁴ TiO₂ nanoparticles, as CCAs, play a vital role in regulating the

toner charge. In this study, we modified TiO₂ with KH570 and employed the resulting particles as CCAs for toner. The characterization of the modified TiO₂ nanoparticles is described first, and then the charge-to-mass ratio and wettability of the modified toner are also discussed.

EXPERIMENTAL SECTION

Materials. 3-Methacrylic acyloxy propyl trimethoxysilane [CH₂=C(CH₃)COO(CH₂)₃Si(OCH₃)₃, KH570] was obtained by Aladdin Chemistry Co., Ltd. (Shanghai, China). Bare TiO₂ (TiO₂ P2S) supplied by Degussa was composed of anatase and rutile with a ratio of 80:20 (wt %). Absolute ethanol was supplied by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Toner kindly provided by ICMI Co., Ltd. (Guangdong, China), was employed as an organic matrix.

Grafted Modification of TiO₂ Nanoparticles with KH570.

The grafted modification of TiO₂ nanoparticles was carried out in the liquid phase. TiO₂ nanoparticles were dispersed in ethanol, and then, KH570 was added to the solution phase. The KH570/TiO₂ nanoparticle weight ratio varied from 10 to 200 wt %. The slurry was subjected to ultrasonic treatment for 15 min and was then stirred for 1 h in a 40 °C water bath. The reaction mixture was washed several times with ethanol, filtered, and then dried in a vacuum oven at 50 °C for 24 h.

Preparation of the Modified Toner. The modified TiO₂ nanoparticles and toner were fixed at a suitable ratio. Then, the two materials were mixed with a mixer (Joyoung processor, JYL-C020) to obtain the mixture (called modified toner in this work).

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FTIR Analysis. Fourier transform infrared (FTIR) analysis of the bare and modified TiO_2 nanoparticles was performed on potassium bromide pellets in a spectrometer (Tensor 27, Bruker, Karlsruhe, Germany) collecting 32 scans in the 400–4000 cm^{-1} range with 4 cm^{-1} resolution.

XPS Studies. X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra DLD X-ray photoelectron spectroscopy/ESCA (electron spectroscopy for chemical analysis) instrument under a pressure of $\sim 5 \times 10^{-9}$ Torr. XPS spectra were excited by a monochromatized Al $\text{K}\alpha$ (15 kV, 10 mA) X-ray source. All binding energies were referenced to the C 1s peak at 284.6 eV of the surface-adventitious carbon.

Morphology Analysis. Micrographs of the bare and modified TiO_2 nanoparticles were recorded by transmission electron microscopy (TEM) (JEOL JEM-2100HR, Japan). All of the TiO_2 samples were dispersed in anhydrous ethanol with an ultrasonic generator for a specified time and then dropped onto a copper grid to dry.

Amount of Coated KH570 Calculations. The amount of coated KH570 was calculated by thermogravimetric analysis (TGA, STA449C, NETZSCH Corporation, Selb, Germany) in the temperature range of 0–550 °C.

Contact Angle Measurements. Contact angle was used to investigate the wettability of the TiO_2 nanoparticles and the modified toner. Contact angles were measured in air by the sessile drop method using a contact angle goniometer (OCA40Micro, Dataphysics, Filderstadt, Germany). Readings were made after a droplet was put onto the surface (the experimental error range was from about –0.1 to 0.1°). For each sample, the data were collected five times to get an average value.

Toner Charge Measurements. Toner charge measurements were based on the ASTM Standard (F 1425-06). This standard suggests that a toner concentration of 3–4% will yield charge-to-mass ratios of 5–25 $\mu\text{C/g}$ for typical negative toners. For the toner to have an opportunity to tribocharge, the friction time should be long enough. In our work, we fixed the toner concentration and friction time at 4% and 20 min, respectively. Then, we also investigated the influences of toner concentration and friction time on toner charge.

First, the modified toner and carrier (Fe_3O_4) were rubbed by a mixed friction instrument (Labmill-8000, Cole Parmer, Vernon Hills, IL) at a suitable ratio for a certain time. Second, 1.0 g of the composites was placed in a Faraday cage to measure the charge-to-mass ratio (Q/M) with an electrometer (model T-150 Tribo Tester, Vertex).

RESULTS AND DISCUSSION

FTIR Spectroscopy of the TiO_2 Nanoparticles. FTIR spectra of the bare and modified TiO_2 nanoparticles are shown in Figure 1. In the spectrum of the bare TiO_2 (Figure 1b), the band at $\sim 3400 \text{ cm}^{-1}$, corresponding to the hydroxyl groups on the TiO_2 nanoparticle surface, was observed. The peak was strong and broad because of overlapping with the peak related to physically adsorbed water on the TiO_2 nanoparticle surface.¹⁵ The band at 3374 cm^{-1} (Figure 1a) can be ascribed to hydroxyl groups on the modified TiO_2 nanoparticle surface. Compared with the bare TiO_2 , a blue shift was observed in the spectral line of the modified TiO_2 , probably due to the formation of intermolecular or inner molecular hydrogen bonds.¹⁶ The weak peak indicated that some hydroxyl groups on TiO_2 nanoparticle surface had reacted with KH570. The

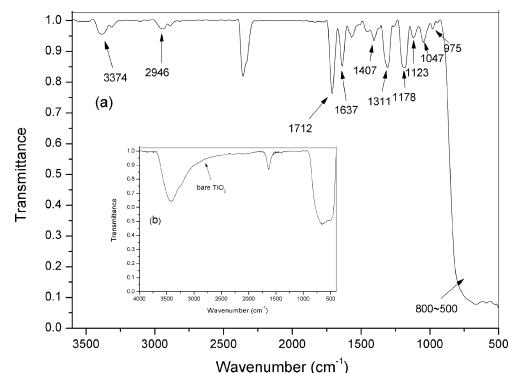


Figure 1. FTIR spectra of (a) modified and (b) bare TiO_2 nanoparticles.

decrease in the amount of hydroxyl groups also suggests an improvement in the hydrophobicity of the TiO_2 nanoparticles.

In addition, as shown in Figure 1a, the band at 2946 cm^{-1} corresponds to C—H asymmetrical stretching vibration.^{17–19} C=O and C=C stretching vibration occurred at 1712 and 1637 cm^{-1} , respectively.¹⁵ This clearly shows that the intensity of the C=O band was stronger than that of the C=C band. Bands at 1407 and 1311 cm^{-1} can be attributed to $-\text{CH}_3$ deformation vibration.¹⁶ The band at $\sim 1178 \text{ cm}^{-1}$ is due to the Si—O—Si bond,^{15,17} which indicates a condensation reaction between silanol groups. Bands at 1123 and 1047 cm^{-1} can probably be assigned to O—Si asymmetric flexible vibration.¹⁷ The peak at 975 cm^{-1} , corresponding to stretching vibration of Ti—O—Si bond,¹⁵ reconfirms the condensation reaction between methoxy groups of KH570 and the TiO_2 nanoparticle surface hydroxyl groups.⁹ The broad and strong peak appearing at 800–500 cm^{-1} , which is related to Ti—O—Ti bonds, was assigned to the characteristic peak of TiO_2 .¹⁵ Wang et al.¹⁵ and Sabzi⁹ also researched the FTIR spectrum of silanized TiO_2 . Their results are similar to ours. Therefore, it was clear that KH570 was successfully grafted onto the surface of TiO_2 nanoparticles.

XPS Studies of the TiO_2 Nanoparticles. XPS was utilized to investigate the properties of the TiO_2 surface. Figure 2 shows a survey spectrum of the modified TiO_2 nanoparticles. It contains Si 2p and C 1s peaks in addition to the O 1s and Ti 2p peaks.²⁰ The C 1s spectrum consists of peaks at 284.6 and 288.4 eV, corresponding to alkyl and carboxylate carbon, respectively (Figure 3).²¹ The high-resolution XPS spectrum of the O 1s peaks of the modified TiO_2 after extraction is given in

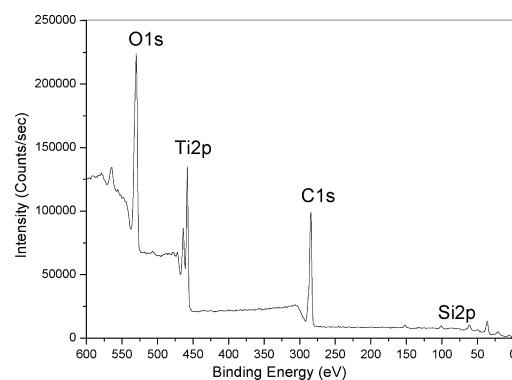


Figure 2. XPS survey of the modified TiO_2 nanoparticles after extraction.

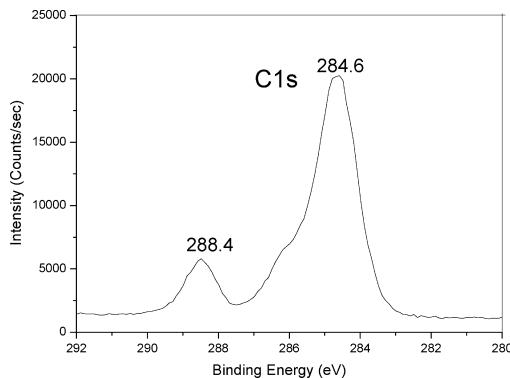


Figure 3. XPS spectrum of the close-up survey of the C 1s peak of the modified TiO_2 nanoparticles.

Figure 4. In the O 1s core line, three O contributions were fitted and assigned according to literature values.^{20,22} The peak

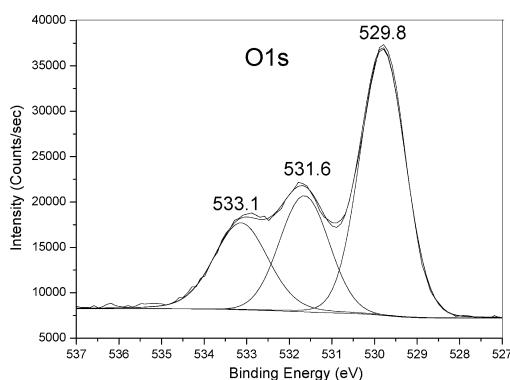


Figure 4. High-resolution XPS spectra of the O 1s region of the modified TiO_2 nanoparticles after extraction.

at 529.8 eV was assigned to O atoms in TiO_2 .²² The second peak at 531.6 eV was attributed to either surface termination oxygen^{23,24} or hydroxyl groups (OH^-),²⁰ as well as to carbonyl groups ($\text{O}=\text{C}$).²⁵ The final oxygen peak at 533.1 eV was attributed to ether groups ($\text{C}-\text{O}$)^{26,27} and the oxygen species $\text{Ti}-\text{O}-\text{Si}$.²⁰ These results demonstrate that the nanoparticles have a TiO_2 core and an organic surface layer. According to the FTIR and XPS results, we can confirm that KH570 was bonded to the surface of the TiO_2 nanoparticles.

TEM Analysis of the TiO_2 Nanoparticles. The TEM images of the TiO_2 nanoparticles (see Figure 5) clearly demonstrate that surface silanization decreased nanoparticle aggregation. Usually, untreated TiO_2 formed hard aggregates on the micrometer scale (Figure 5a).²⁸ After silanization, the aggregates were considerably diminished, and an increase in the particle diameter of the modified TiO_2 could be noticed (see Figure 5b–f). It was observed clearly that the silane coupling agent deposited on the particle surface and formed an outer layer (Figure 5e,f). An obvious interface could be observed. We deduced that the core–shell microstructure might appear gradually as the silane shifted to TiO_2 surface. The shape and size of the modified TiO_2 nanoparticles were diverse, and the coating thickness varied. For example, Figure 5e displays a thick coating layer of about 5 nm, whereas the coating layer in Figure 5f is only about 2 nm.

Using the method described in ref 29, the average coating thickness (d) of KH570 on the TiO_2 nanoparticles was

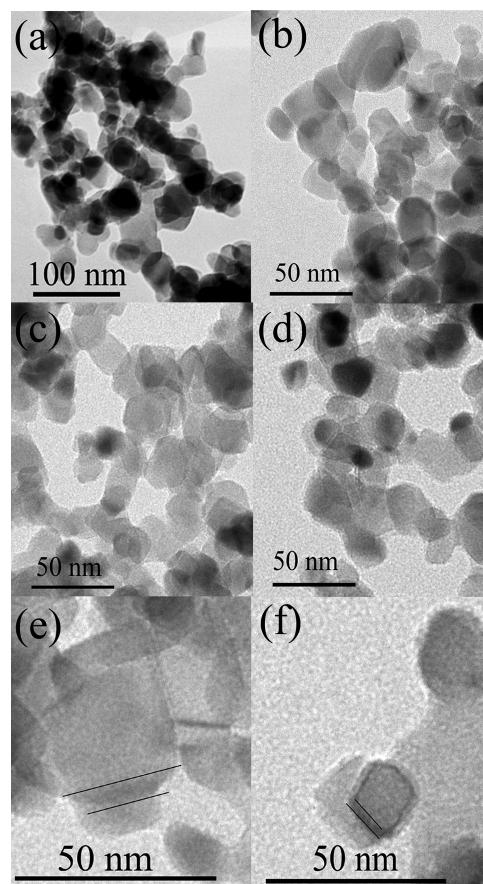


Figure 5. TEM images of (a) untreated TiO_2 and (b–f) TiO_2 modified with (b) 100, (c,e) 120, and (d,f) 200 wt % KH570.

calculated from the amount of coated KH570. According to the TEM images, the average radius (R) of the modified TiO_2 nanoparticles is about 20 nm (Figure 5e), and the d value was calculated to be about 1.53 nm. In Figure 5f, the R and d values are probably 7 and 0.45 nm, respectively. According to TGA, the coating of KH570 was extremely thin; as a result, the theoretical coating thickness of the silane was too small to be observed by TEM. Compared with the TEM results, the coating thickness obtained from TGA was much smaller. The reason for this difference is that we assumed that the TiO_2 nanoparticles were spherical when calculating the coating thickness according to TGA; however, the actual particles were not regular spheres. Because of the irregular shape, the reaction activity was different in different surface microdomains of the TiO_2 nanoparticles, leading to different coating thicknesses, as seen in Figure 5e,f. García-González⁸ suggested that the thickness of the coating layer should be about 2 nm for it to be observed by TEM when a silane with a large C_{18} alkyl chain is employed. Fortunately, the thick coating layer of the silane was over 2 nm because of nonuniform deposition so that the shell could be observed by TEM.

Contact Angle Analysis. We used ethanol wettability to estimate the surface wettability of the modified TiO_2 nanoparticles because ethanol was employed as the reaction solvent. Contact angles are usually used to evaluate the surface wettability of materials. As shown in Figure 6, the grafting modification clearly had an influence on the contact angle of the TiO_2 . The contact angle increased sharply (from $91.82^\circ \pm 1.01^\circ$ to $150.92^\circ \pm 1.15^\circ$) as the coated KH570 increased to

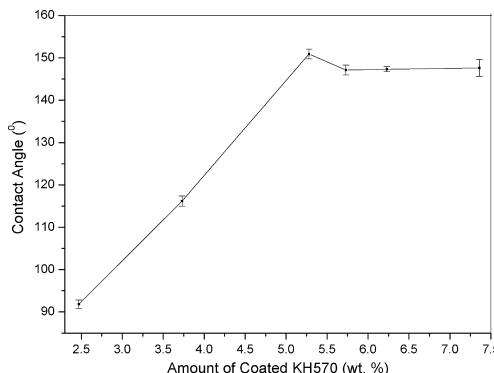


Figure 6. Contact angles of ethanol droplets on the surface of the modified TiO_2 nanoparticles. The error bars represent the standard error.

5.28 wt %; then, the curve became constant when the amount of coated KH570 further increased, with values of $147.12^\circ \pm 1.15^\circ$ at 5.73 wt %, $147.30^\circ \pm 0.61^\circ$ at 6.23 wt %, and $147.64^\circ \pm 1.98^\circ$ at 7.36 wt %. This behavior can be attributed to the effect of steric hindrance and the limited number of OH groups on the surface of the TiO_2 nanoparticles.⁹ In short, these results further confirm that the reaction of TiO_2 nanoparticles with KH570 occurred, resulting in a hydrophobic surface.

We used the water contact angle to investigate the wettability and the influence of the modified TiO_2 nanoparticles on the contact angle of toner. Figure 7 illustrates the relationship

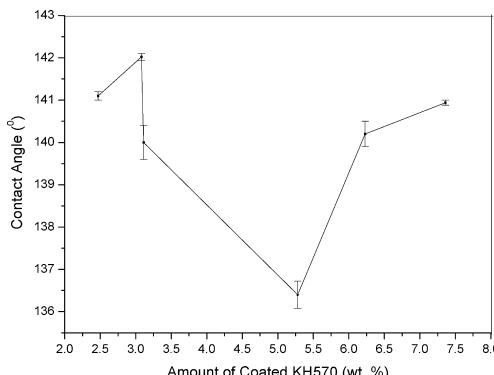


Figure 7. Effect of the amount of coated KH570 on the water contact angle of the modified toner at a constant modified TiO_2 /toner weight ratio of 1:99. The error bars represent the standard error.

between the amount of coated KH570 and the water contact angle of the modified toner. The weight ratio of the modified TiO_2 nanoparticles and toner was fixed at 1:99. According to preliminary measurements, the water contact angle of bare toner was $144.74^\circ \pm 0.80^\circ$. As seen in Figure 7, the water contact angle of the modified toner first decreased with increasing amount of coated KH570 and then increased when the amount of coated KH570 was above 5.28 wt %. The contact angle of a water droplet on the surface of a solid polymer depends on whether a hydrophilic moiety of the polymer molecule is oriented toward the air interface or toward the bulk of the solid.³⁰ In addition, if the modified TiO_2 nanoparticles and toner particles are assumed to be spherical and the radius of the toner ($\sim 5.8 \mu\text{m}$) and the average specific surface area of the modified TiO_2 nanoparticles ($\sim 40 \text{ m}^2/\text{g}$) are taken into consideration, then the modified TiO_2 /toner surface area ratio

can be calculated as $\sim 9.6 \times 10^8$. Here, we use the coverage rate to express the degree of dispersion. It can be inferred that the degree of dispersion increased with increasing coverage rate. Assuming that a uniform distribution existed in the composite particles, it can be inferred that multilayer coverage of the modified TiO_2 nanoparticles was produced on the surface of the toner. Therefore, we propose a model of double layers of adsorption to explain the interaction mechanism between the modified TiO_2 and toner (Figure 8).

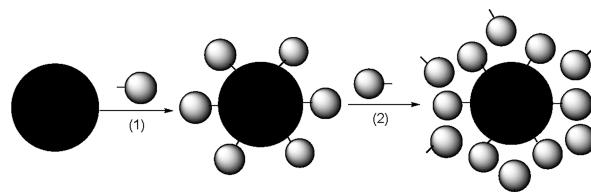


Figure 8. Schematic plot of the interaction mechanism between modified TiO_2 and toner. The black and white circles represent toner and TiO_2 , respectively, and the short lines represent the organic chain of KH570.

Nanocomposites follow the “like dissolves like” principle. When the surface functional groups and structure of nanoparticles are similar to those of an organic matrix, the nanoparticles have strong adhesion with the matrix.³¹ The thicknesses of the coating layers of KH570 deposited on the TiO_2 surface were $\sim 5 \text{ nm}$ (Figure 5e) and $\sim 2 \text{ nm}$ (Figure 5f) when the radii of the modified TiO_2 nanoparticles were ~ 20 and $\sim 7 \text{ nm}$, respectively. Compared with the diameter of the modified TiO_2 nanoparticles, the thickness of the coating layer of KH570 was very small. Nevertheless, one can assume that it had a short tail to bridge the TiO_2 nanoparticles and the toner particles. According to ref 31, one can infer that the organic groups in KH570 acted as a molecular bridge and reacted with the organic matrix when the modified TiO_2 nanoparticles were added to the toner, as presented in Figure 8. As a result, the TiO_2 nanoparticles displayed on the surface of the toner were oriented toward the air interface. According to our preliminary study, the surface of the bare TiO_2 nanoparticles was hydrophilic ($62.60^\circ \pm 1.91^\circ$); therefore, the water contact angle of the modified toner decreased.

For each sample, the weight ratio of the modified TiO_2 and toner was fixed at 1:99. Thus, the percentages of modified TiO_2 that could interact with the toner increased when the amount of coated KH570 increased. When the amount of coated KH570 increased to 5.28 wt %, the number of modified TiO_2 nanoparticles displayed on the surface of the toner was maximized. If the amount of coated KH570 was increased further, the surplus modified TiO_2 nanoparticles formed double layers of adsorption. Hence, the organic chains in KH570 were exposed outward and were oriented toward the air interface, leading to increasing water contact angles.

The above inference was further confirmed by Figure 9. The mass fraction of modified TiO_2 nanoparticles added to the toner was varied from 0.1% to 2.0%. The changing tendency between the water contact angle and the mass fraction of modified TiO_2 was similar to that in Figure 7. Figure 9 can also be explained by the model of double layers of adsorption (Figure 8). In short, Figure 7 is consistent with Figure 9, and both suggest that our model (Figure 8) is reasonable.

Toner Charge Analysis. The primary material property that determines the behavior of a xerographic laser printer is

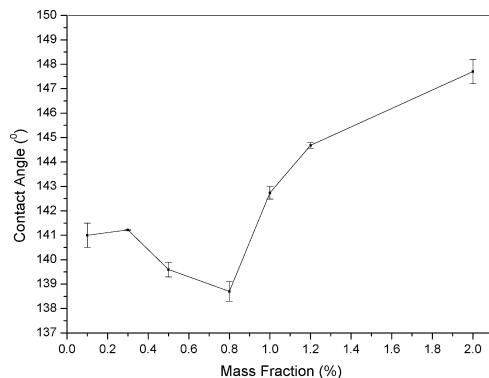


Figure 9. Effect of the mass fraction of modified TiO_2 nanoparticles on the water contact angle of modified toner. The error bars represent the standard error.

the toner charge distribution.¹³ A fundamental understanding of the material parameters that determine toner charging would be a revolutionary advance in the field of xerographic laser printers.¹⁴ As is well-known, toner charging is strictly requested as an important parameter. The amount of toner transferring to the organic photoconductor (OPC) drum is intimately related to the amount of charge in the toner. If the toner charging is too great, the transfer rate should decrease, and the bottom ash should increase.

In previous publications, several models of origin of the electrostatic charge have been presented. Gutman and Hartmann³² and Anderson³³ described the exchange of electrons between surface electronic states in polymers. Diaz and Alexander³⁴ demonstrated a model for the exchange of ions. Another model on contact charging involves material transfer.³⁵ When the transferred material carries charge, charge transfer will occur.³⁶ The surface state theory is currently given to describe electrostatic charge, concerning either electron or ion transfer. It can be distinguished from other theories of ion transfer.^{34,37} It has two limits: the low-density limit and the high-density limit.³⁸

Two different materials being rubbed against each other can be called “frictional electrification”, “triboelectric charging”, or simply “tribocharging”.³⁵ In our work, the modified toner was rubbed against ferroferric oxide, and then a developer sample of known weight was placed in a Faraday cage to determine the Q/M value of the toner.

Without a charge control agent (CCA), the Q/M value of the toner was $-24.43 \mu\text{C/g}$ as determined by the total blow-off technique; however, the Q/M values of the modified toner increased regardless of the measurement conditions (see Figure 10). When the toner/carrier weight ratio and friction time were varied, all of the Q/M values exhibited similar changing tendencies, as shown in Figure 10a–f. However, the values of Q/M were different. In fact, toner charging can be controlled through physical factors, such as the friction time, the toner particle size, and especially the mass ratio of toner and carrier in the developer.⁷ Figure 10 also demonstrates that the Q/M value of the modified toner shifted in a negative direction with increasing amount of coated KH570. Birkett and Gregory³⁹ envisioned small mobile ions of the CCA diffusing from the toner surface to the carrier particles to explain how CCAs operate. Medley⁴⁰ suggested that the acidic or basic groups promote water absorption on the surface, which provides H^+ and OH^- ions that can transfer between materials. Therefore, the phenomenon demonstrated in Figure 10 can be understood. The toner/carrier surface area ratio was $\sim 6.9 \times 10^{-4}$ based on the radii of the toner ($\sim 5.8 \mu\text{m}$) and carrier ($\sim 45 \mu\text{m}$), so that the carrier had enough space to transfer OH^- groups from the toner surface. A higher amount of coated KH570 meant a smaller amount of OH^- groups on the surface of the TiO_2 nanoparticles. After the friction, OH^- groups were transferred to ferroferric oxide from the surface of the toner. The lower the number of OH^- groups, the lower number of the negative charges transferring to the carrier. Thus, the Q/M value of the modified toner shifted in the negative direction with increasing amount of coated KH570.

In addition, we investigated the influence of the mass fraction of the modified TiO_2 nanoparticles on the toner charging. Figure 11 shows that the Q/M value of the modified toner shifted in the positive direction with increasing amount of

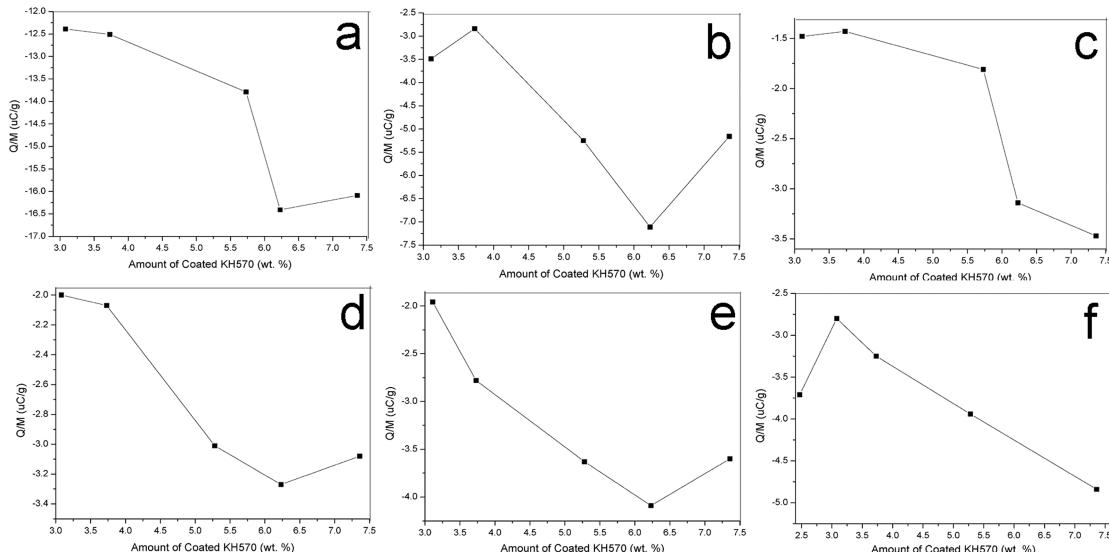


Figure 10. Effect of the amount of coated KH570 on the Q/M ratio of modified toner. The toner/carrier weight ratio was fixed at (a) 1:24, (b) 1:19, and (c) 1:9 at the friction time of 20 min. Then, the friction time was fixed at (d) 16, (e) 10, and (f) 2 min for a weight ratio of 1:24.

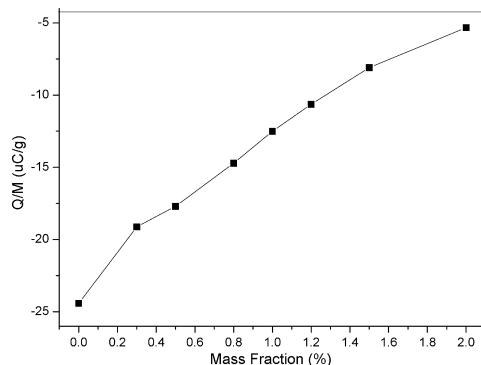


Figure 11. Effect of the mass fraction of modified TiO_2 nanoparticles on the Q/M ratio of modified toner. The toner/carrier weight ratio was fixed at 1:24, and the friction time was 20 min.

modified TiO_2 . The higher the amount of modified TiO_2 nanoparticles, the higher the amount of OH^- groups transferring to the carrier from the surface of the toner. The Q/M value of the modified toner shifted in the positive direction because of the increasing number of modified TiO_2 nanoparticles. Therefore, according to the changing regularity, one can adjust the toner charge to meet the requirements of xerographic laser printers. Advances in CCAs will improve the development of toners.

In summary, the modified TiO_2 investigated in this work was found to have excellent dispersion and a uniform core–shell microstructure. The modified toner exhibited good fluidity and proper toner charging. These materials are promising for applications in xerographic laser printers.

CONCLUSIONS

Based on the results reported herein, it can be concluded that KHS70 was successfully grafted onto the surface of TiO_2 nanoparticles. The O 1s peak at 533.1 eV in the high-resolution XPS spectrum was attributed to the oxygen species $\text{Ti}=\text{O}-\text{Si}$, demonstrating that the nanoparticles had a TiO_2 core and an organic surface layer. The layer of KHS70 deposited on the surface of the TiO_2 nanoparticles was also confirmed by TEM, and a core–shell structure was obtained. The thickness of the coating layer was about 2–5 nm. The ethanol contact angle of the modified TiO_2 nanoparticles became constant when the amount of coated KHS70 was above 5.28 wt % because of the effect of steric hindrance and the limited number of OH groups. For the modified toner, the water contact angle decreased to $136.4^\circ \pm 0.32^\circ$ when the amount of the coated KHS70 reached 5.28 wt %. The change tendency of the contact angle can be explained by a model of double layers of adsorption. The Q/M values of the modified toner shifted in the negative direction with increasing amounts of coated KHS70, whereas they shifted in the positive direction with an increase in the modified TiO_2 mass because of the transfer of OH groups after friction.

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Notes

The authors declare no competing financial interest.

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