Environmentally friendly wollastonite@TiO₂ composite particles prepared by a mechano-chemical method

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A R T I C L E   I N F O

Article history:
Received 8 February 2017
Received in revised form 26 October 2017
Accepted 27 October 2017
Available online 15 February 2018

Keywords:
Wollastonite
TiO₂
Composite particles
Mechano-chemical method

A B S T R A C T

Core–shell wollastonite@TiO₂ (W@T) composite particles are prepared by a mechano–chemical method (MCM) to improve the dispersion of TiO₂ and reduce its dosage, and to achieve synergistic effects with the wollastonite mineral. The crystal structure, morphology, functional groups, and pigment properties of the as-prepared composite powders are determined. The W@T composite particles are formed by van der Waals force in addition to electrostatic attraction and chemical bonding. The anatase TiO₂ coating is anchored on the wollastonite surface by Si–O–Ti and Ca–O–Ti bonds. The W@T powders possess excellent characteristics such as whiteness of 96.6%, hiding power of 17.97 g/m², and oil absorption of 22.72 g/100 g. The properties of the W@T composite are similar to those of TiO₂ and the former, which is much cheaper, can potentially substitute the latter as a white paint in many applications.

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Introduction

Titanium dioxide (TiO₂), sometimes also referred to as titanium white, is one of the most important white pigments owing to its high refractive index, tintorial power, hiding power, and weather resistance. Anatase, rutile, and brookite are the three important polymorphs of TiO₂, and each polymorph possesses unique properties. For example, anatase has the smallest surface free energy, whereas rutile has the smallest bulk free energy and is the most thermodynamically stable phase. TiO₂ has been widely used in coatings, paper, rubber, inks, and other commercial products (Ren, Yin, Wang, Jiang, & Wada, 2007; 2008; Ren, Yin et al., 2009; Ren et al., 2010; Testino et al., 2007; Wang et al., 2009; Yang, Liao, & Mao, 2012; Zhang, Yin, Wang, Liu et al., 2010). However, the high cost and limited availability of titanium white have hampered its extensive use in various applications. For example, even though the ilmenite reserves in China are approximately 965 million tons, the overall grade is low and TiO₂ only constitutes approximately 200 million tons. Hence, China imports up to 50% of its ilmenite from other countries, such as Australia, India, and Vietnam, at a price of $250/t (Zhang et al., 2015).

To improve the use of non-metallic minerals, conserve resources, and protect the environment, much work has been performed (Wellmer & Becker-Platen, 2002) and with the continuous consumption of ilmenite, titanium is becoming scarcer. Therefore, it is critical to conserve titanium resources while seeking alternative titanium sources by identifying new materials and technologies to replace TiO₂. In this respect, significant efforts have been made to develop new core–shell TiO₂ composites, such as sericite@TiO₂ (Ren et al., 2008; Ren, Yin et al., 2009; Ren et al., 2010), SiO₂@TiO₂ (Ren, Zhao et al., 2009), and kaolin@TiO₂ (Yan, Lei, & Yuan, 2010). For example, wollastonite (CaSiO₃) is a metastable mineral that is abundant in nature (Ma, 2010). It has been used in products such as pigment dyes, paper, and plastic (Ding, Lu, & Du, 2011), owing to the notable advantages, including high whiteness, brightness, vitreous luster, chemical stability, alkali resistivity, low hygroscopicity (<4%), and oil absorption rate. Wollastonite is thus a potential mineral for preparing a mineral@TiO₂ composite.

The mechano-chemical method (MCM) uses the physical and chemical changes of the reactants by high-energy grinding (Čaplovičová et al., 2012; Huot et al., 2013). This method can be applied to solid–solid, solid–liquid, and solid–gas interactions where the mechanical force can be in the form of grinding, compression, impact, friction, shearing, or elongation. In this work, wollastonite@TiO₂ (W@T) composite particles were prepared by MCM and the crystal structure, morphology, functional groups, and...
pigment properties were determined systematically. The formation mechanism of TiO₂ on the wollastonite is proposed and discussed.

**Experimental**

Wollastonite was provided by Beijing Lanning Trade Co., Ltd. (China) with properties as presented in Table 1. The particle size was measured by Mastersizer 2000 to be \(d_{50} = 11.77 \, \mu m\) and \(d_{90} = 29.20 \, \mu m\). The whiteness, hiding power, and oil absorption were 94%, 272.65 g/m², and 11.20 g/100 g, respectively. The TiO₂ (anatase) was provided by Henan Billions Chemicals Co., Ltd. (China). The particle size was \(d_{50} = 0.35 \, \mu m\) and \(d_{90} = 0.54 \, \mu m\). The whiteness, hiding power, and oil absorption were 96.2%, 14.72 g/m², and 25.03 g/100 g, respectively.

**Preparation of W@T**

Wollastonite was smashed and blended with TiO₂ into superfine wollastonite/TiO₂ composite particles by the MCM. The optimized processes are described as follows. The wollastonite was ground by corundum balls. The slurry concentration, dispersing agent (sodium silicate), ratio of grinding media to materials, rotational speed of the agitating mill, and milling time were 35%, 0.3%, 5:1, 1400 rpm, and 20 min, respectively. In dispersing the TiO₂, the slurry concentration, dispersing agent (sodium silicate), and jitter time were 35%, 0.3%, and 30 min, respectively. The wollastonite and TiO₂ were produced with a TiO₂ dosage, a ratio of grinding media to materials, a rotational speed of the agitating mill, milling time, and pH of 45%, 4.5:1, 1400 rpm, 15 min, and 8, respectively. The balls and materials were separated and dried at 100 °C to obtain the composite powders.

**Characterization**

Powder X-ray diffraction (XRD) was performed in a D8 Advance diffractometer (Bruker Corporation, Germany) at 40 kV and 40 mA with Cu Kα radiation (\(\lambda = 0.15406 \, nm\)) and the scanning rate was 40/ min. The morphology and chemical composition were determined on an SU-70 high-resolution field-emission scanning electron microscope (FE-SEM, Hitachi, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS). Selected-area electron diffractions (SAED) were obtained on a Tecnai 20U Twin high-resolution transmission electron microscope (Phillips, Netherlands) at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5000 (PHI, USA) that was equipped with an Al Kα X-ray source operated at a power of 250 W. The Ti2p1/2, Ti2p3/2, Ca2p1/2, Ca2p3/2, Si2p, and O1s spectra were recorded. Fourier transform infrared spectroscopy (FT-IR) was performed using the KBr pellet technique on a Fourier transform infrared spectrometer (Nicolet 750, USA) to determine the interfacial bonding. Zeta-potential measurements were performed on a Zeta potential instrument (BDL-B, China). The sample (0.2 g) was dispersed in 200 mL of distilled water and the suspension was added in an ultrasonic bath for 20 min prior to Zeta potential measurement. The dispersion rate of the samples was determined on a particle size distribution analyzer (Mastersizer-2000, Malvern, UK) with a dynamic laser scattering (DLS) mode. Here, the sample (0.1 g) was dispersed in 150 mL of distilled water and the suspension was placed in an ultrasonic bath for 20 min prior to the measurements.

**Table 1**

<table>
<thead>
<tr>
<th>Items</th>
<th>SiO₂ (%)</th>
<th>CaO (%)</th>
<th>Fe₂O₃ (%)</th>
<th>Whiteness (%)</th>
<th>pH</th>
<th>Screenings</th>
<th>Oil absorption (g/100 g)</th>
<th>Burning loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indexes</td>
<td>≥48</td>
<td>≥43</td>
<td>≤0.2</td>
<td>≥92</td>
<td>7–9</td>
<td>≤0.5</td>
<td>≤12</td>
<td>≤3</td>
</tr>
</tbody>
</table>
through hydration yielding Si–O–Ti and Ca–O–Ti. Consequently, the wollastonite became coated with TiO$_2$ (Ren, Shen, & Lu, 2005). XRD results indicated that the W@T particles were not a simple mixture of wollastonite and TiO$_2$, possibly owing to the chemical bonds formed during the mechano-chemical process which formed the TiO$_2$ coating on the wollastonite particles.

**Morphology**

As shown in Fig. 2(a), the wollastonite particles were smooth and had a fibrous or columnar structure. The diameter of the particles varied between 3.0 and 4.0 μm and EDS analysis revealed the presence of Ca, Si, and O. The TiO$_2$ particles had a spherical or ellipsoidal morphology with a particle size between 0.2 and 0.3 μm (Fig. 2(b)). Fig. 2(c)–(d) present the SEM and EDS results of the W@T particles, which confirmed that the surface of wollastonite was covered by a uniform and compact film composed of nano-scale TiO$_2$. The TiO$_2$ coating was thicker at the edges of the wollastonite than at the surface. The large number of unsaturated bonds and hydroxy groups formed on the surface of the columnar wollastonite were attributed to the MCM. The probability of binding the hydroxyl groups present in TiO$_2$ with the columnar wollastonite was high owing to the large electrical charge, electrostatic attraction, reactivity, and energy. In addition, the peak intensities of Ca and Si were relatively low in the EDS spectra, while those of Ti and O were relatively higher, which corroborated that the wollastonite particles were coated with TiO$_2$.

**Chemical structure**

The IR spectra of wollastonite, TiO$_2$, and composite particles are depicted in Fig. 3. The absorption peaks of wollastonite could be further divided into two parts. The peaks between 900 and 1300 cm$^{-1}$ corresponded to the asymmetric stretching of Si–O–Si and stretching of O–Si–O (Fig. 3(a)), while those between 500 and 700 cm$^{-1}$ represented the symmetrical stretching of Si–O–Si. These included three repetitive permutations of an oxygen–silicon tetrahedron in the wollastonite structure. Fig. 3(b) shows a weak TiO$_2$ absorption peak at 3438 cm$^{-1}$, which corresponded to the stretching of O–H, which was attributed to the H$_2$O that was physically adsorbed on the particle surface. The bands at 1642, 1400, 670, and 520 cm$^{-1}$ were assigned to the O–H flex vibration, background peak of KBr, and Ti–O stretching, respectively. As shown in Fig. 3(c), the absorption peaks of the composite particles ranged between 900 and 4000 cm$^{-1}$, which was indicative of wollastonite. The absorption bands of the stretching vibration of O–H at 3450–3500 cm$^{-1}$ were formed by wollastonite hydroxylation, and were broad and shifted to lower wavenumbers after coating with TiO$_2$. The data provide evidence of hydroxyl condensation of TiO$_2$ during cleavage of wollastonite. In addition, the characteristic peaks of Si–O–Si at 470 cm$^{-1}$ disappeared and those of Si–O–Ti at 950 cm$^{-1}$ and Ca–O–Ti at 620 cm$^{-1}$ appeared (Creutz & Chou, 2008; Gan, Wang, Hao, Xu, & Chen, 2005; Kawano & Yamane, 2010; Park & Kang, 2005; Zhou & Jiang, 2002).
Zeta potential

There are two types of interactions among the particles in water; the first is a short-range force within the grains, at a distance of less than 2 nm, and the other is a long-range force within the particles, at a distance between 5 and 100 nm. The long-range force includes van der Waals force, electrostatic force, steric effects, solvent membrane force, and hydrophobic interactions. The long-range force includes van der Waals force and electrostatic force in this system. The two kinds of forces determine the interfacial interactions among particles and the interactions between wollastonite and TiO$_2$ affected the reaction. They were close to each other and participated in the reaction according to their structure and morphology. The reaction rate is decreased if the particles are repulsive.

The van der Waals force between particles is expressed as (Lifshitz & Pitaevskii, 1992):

$$ U = -\frac{A}{r^2}, $$

(1)

$$ F = -\frac{AR}{(12r^2)}, $$

(2)

where $U$, $F$, $R$, $H$, and $A$ represent the van der Waals energy, van der Waals force, particle radius, distance between particles, and Hamaker constant, respectively. The driving force is the interattraction if $U$ has a negative value. If $U$ has a positive value, the particles are repelled. The sign of $U$ is opposite to that of $A$. The effective Hamaker constant of heterogeneous particles 1 and 2 in the medium of particles 3 is shown as follows (Brown & Jaffe, 2006):

$$ A_{13} = (A_{11}^{1/2} - A_{33}^{1/2}) (A_{22}^{1/2} - A_{33}^{1/2}). $$

(3)

In the present system, the Hamaker constant of wollastonite was $A_{11} = 9.1 \times 10^{-20}$ J, the Hamaker constant of TiO$_2$ was $A_{22} = 19.7 \times 10^{-20}$ J, and the Hamaker constant of aqueous medium was $A_{33} = 5 \times 10^{-20}$ J (Ren et al., 2005). This gave $A_{13} = 4.4 \times 10^{-20}$ J. Obviously, $A_{13} > 0$ and $U < 0$ indicated that the van der Waals force between wollastonite and TiO$_2$ particles was attractive in this reaction.

The relationship between the zeta potential and pH is demonstrated in Fig. 4. The z potential decreased gradually as the pH was increased above 7. The z potential was negative as the pH was increased. When the pH was approximately 8.2, the z potential became 0, which indicated that the zero electric point of wollastonite in water was ~8.2. The pH of TiO$_2$ in the aqueous medium was 5.8. In the neutral system (pH = 7), the electrostatic force was attractive because the wollastonite surface was positively charged and the surface of TiO$_2$ was negative. The strong attraction between wollastonite and TiO$_2$ arose from van der Waals and electrostatic interactions, which were the prerequisite and necessary conditions for the two particles to interact.

Mechanism of formation of the TiO$_2$ coating on wollastonite

The W@Ti particles were produced with TiO$_2$ as the shell, reacting with wollastonite, which represented the core, by the liquid MCM. First, wollastonite and TiO$_2$ particles formed functional groups on the surface of the cleavage plane and then these groups were combined. Clearly, the morphology and properties of the functional groups were the internal factors that determined the reactions between the TiO$_2$ and wollastonite.

The TiO$_2$ surface was hydrophilic owing to the hydroxyl groups (Nakamura, Kobayashi, Kuzuya, Komatsu, & Mochizuka, 2006). The crystal structure of the (101) cleavage plane is presented in Fig. 5(a), where the red atom represents oxygen and the grey octagon represents the TiO$_6$ octahedron. Fig. 5(c) shows the hydroxyl groups on the (101) cleavage plane and the six functional groups at the interface were very reactive.

Fig. 4. $\zeta$–pH curves of wollastonite in an aqueous medium.

Fig. 5. (a) Crystal structure of the {101} cleavage plane of TiO$_2$; (b) crystal structure of the {100} cleavage plane of wollastonite; (c) surface functional group distribution in TiO$_2$; (d) surface functional groups distribution in wollastonite.
Wollastonite is a silicate having a chain structure. The Si–O bond is mainly covalent with a bond energy of 443.08 kJ/mol, whereas the Ca–O bond is mainly ionic with a bond energy of 133.76 kJ/mol. The crystal structure of wollastonite, as viewed from the (100) cleavage plane, is presented in Fig. 5(b). The red atom represents oxygen and the green represents calcium. They form a CaO6 octahedron and SiO2 tetrahedron. The surface functional groups of wollastonite are presented in Fig. 5(d). The weak bond of Ca–O could be easily broken along the (100) cleavage plane, under mechanical shock and shear, and the Si–O groups exposed on the surface of the (100) cleavage plane tended to form Si–OH, Ca–OH, and other active groups in the aqueous medium.

The formation process could be divided into three stages: mechanical grinding of wollastonite, surface hydroxylation of particles, and connection with TiO2 particles by hydration. Wollastonite was activated by liquid MCM leading to a lattice distortion and the increasing number of defects decreased the activation energy. The condensation reaction between the hydroxy on the (100) cleavage plane of wollastonite and the hydroxyl on the (101) cleavage plane of TiO2 formed two new Si–O–Ti bonds, with a bond energy of 366.7 kJ/mol, and one Ca–O–Ti bond, with a bond energy of 500.1 kJ/mol (Plotnikov & Stolyarova, 2005). Ca2+ in the wollastonite was still present in the water (pH = 7). The Ca2+ ions on the particle surface increased as new cleavage planes were continuously generated by ultrafine grinding. The hydrolysis rate of Ca2+ increased with the number of particles on the surface and the amount of Ca(OH)2 increased accordingly. In addition, the hydration reaction of SiO2 with water was a major reaction on the wollastonite surface. The hydration reaction of SiO2 became more intense owing to the high diffusing rate.

The reaction mechanism between wollastonite and TiO2 is demonstrated in Fig. 6. The wollastonite, hydroxyl groups, and TiO2 were close to each other owing to van der Waals and electrostatic forces (Fig. 6(a) and (b)). With a high mechanical energy input, the hydroxyl groups on the two cleavage sites were linked, which resulted in a hydration reaction (Fig. 6(c)). They formed Si–O–Ti and Ca–O–Ti on the cleavage plane, which produced TiO2 on the wollastonite surface.

**Chemical states of TiO2 and TiO2 coating on wollastonite**

Fig. 7 shows the XPS results of anatase TiO2, naked fibrous wollastonite, and wollastonite@TiO2 powders prepared by the MCM. The binding energies of Ti2p1/2, Ti2p3/2, and O1s of the anatase TiO2 were 464.14, 458.45, and 529.65 eV, respectively (Fig. 7(a)–(c)). The binding energies of Ca2p1/2, Ca2p3/2, Si2p, and O1s of the pristine fibrous wollastonite were 350.45, 346.92, 102.09, and 529.65 eV, respectively (Fig. 7(d)–(e)), whereas the binding energies of Ti2p1/2, Ti2p3/2, Ca2p1/2, Ca2p3/2, Si2p, and O1s were 463.42, 457.73, 350.07, 346.53, 101.80, and 528.98 eV, respectively (Fig. 7(f)–(i)). The wollastonite@TiO2 powders prepared by the MCM exhibited weight ratios of TiO2 to wollastonite of 60% and 40%, respectively.

The binding energies of the Ti2p1/2, Ti2p3/2, Ca2p1/2, Ca2p3/2, Si2p, and O1s peaks shifted to lower values in the W@T composites, when prepared by the MCM, which suggested changes in the chemical
states of Ti, Ca, Si, and O. The SEM images in Fig. 2 show that the TiO2 coatings were tightly bonded on the surface of the wollastonite powders. Therefore, it was reasonable to conclude that the TiO2 coatings were anchored on the wollastonite surface by the formation of a Ti–O bond (Hou, Ding, Zheng, & Wang, 2013; Ren et al., 2008; Ren, Yin et al., 2009; Ren et al., 2010; Zhou & Jiang, 2002) between Si–O–Ti (Agraval, Gupta, Pich, Zafeiropoulos, & Stamm, 2009; Zhang, Yin, Wang, Ren et al., 2010) and Ca–O–Ti (Brown & Jaffé, 2006; Chen, Liu, & Fang, 2011) bonds at the interface between the TiO2 coating and wollastonite. The presence of Ti, Ca, Si, and O was detected by EDS on the W@T powders (Fig. 2(c)).

**Pigment properties of the wollastonite@TiO2 powders**

As presented in Tables 1 and 2, the whiteness and hiding power of the W@T composite particles were improved compared with the pristine wollastonite. The whiteness was slightly higher than that of TiO2, whereas the hiding power and oil absorption were similar to those of TiO2 (Hou, Ding, Li, Cao, & Wang, 2010). The W@T particles exhibited similar white pigment characteristics as TiO2 and are a good substitute for TiO2 in some products.

**Use of wollastonite@TiO2 powders in pigment dyes**

UV–vis spectra were acquired from wollastonite, TiO2, and W@T, and the range of 210–400 nm showed the UV capability. It was clear, as shown in Fig. 8, that the pristine wollastonite showed no UV absorption and/or scattering but TiO2 showed both. The ranges of 210–240 and 350–400 nm should be attributed to absorption and that of 240–350 nm to scattering of TiO2.

The UV absorption spectra of the W@T composite particles lay between those of wollastonite and TiO2 in the UV region. There was an increase in absorption in the UV range for the W@T particles. The higher the amount of TiO2, the more uniform was the coated wollastonite. The effect of the composites upon UV radiation was similar to that of TiO2. Obviously, the absorption property of the W@T particles (60 wt%:40 wt%, and 50 wt%:50 wt%) was similar to that of TiO2 and as a result, the W@T particles showed similar physical and chemical features as TiO2. The results were consistent with previous studies (Chen, Ding, & Wang, 2015).

To study the performance and chemical stability of the rutile TiO2 (R-TiO2), anatase TiO2 (A-TiO2), and wollastonite@TiO2 (W@TiO2) powders, coatings with 15% powders were prepared (Tarng et al., 2010) and the samples were exposed to UV, according to the National Standard of the People’s Republic of China, JGT23-2001. The thin films were prepared on glass substrates (Fig. 9) and irradiated with UV for various durations (Fig. 9(a), (f): 0 h; Fig. 9(b), (g): 100 h; Fig. 9(c), (h): 250 h; Fig. 9(d), (i): 400 h; and Fig. 9(e), (j): 600 h). Fig. 9 shows the images of the R-TiO2, A-TiO2, and W@TiO2 powders (15% coating) after UV light exposure. From a visual perspective, the R-TiO2 and A-TiO2 powders treated this way were never yellow. The sample in Fig. 9(e) was irradiated with UV light for more than 600 h (simulating exposure for two years in nature), and exhibited no microcracks. It can be concluded that the coating plays a critical role in aging and yellowing resistance. The W@TiO2 composite powders deliver a similar performance to R-TiO2 and A-TiO2 and can indeed substitute titanium dioxide as white paint in some products.

The SEM images of rutile TiO2 (R-TiO2), anatase TiO2 (A-TiO2), and wollastonite@TiO2 (W@TiO2), after irradiation for different periods, are displayed in Fig. 10. Without irradiation, the dispersion of the coating in W@TiO2 prepared by the MCM was similar to that of R-TiO2 and A-TiO2 (Fig. 10(a)–(c)). The coating was uniform and stable and adhered tightly even after UV irradiation. After exposure for 600 h, the W@TiO2 composite was similar to R-TiO2 and A-TiO2. Thus, the wollastonite @TiO2 powders have a large potential as a white pigment dye.

**Conclusions**

The crystal structure, morphology, and functional groups of W@T composite particles were determined. The wollastonite was uniformly coated with TiO2. The W@T particles were formed by the combination of a chemical bond, van der Waals force, and electrostatic forces. The anatase TiO2 coating was bonded on the
Fig. 10. SEM images of the rutile TiO$_2$, anatase TiO$_2$, and wollastonite@TiO$_2$ (W@TiO$_2$) powders with the 15% coating irradiated by UV light for different durations: (a)–(c): 0 h; (d)–(f): 100 h; (g)–(i): 250 h; (j)–(l): 400 h; and (m)–(o): 600 h.

wollastonite surface by Si–O–Ti and Ca–O–Ti bonds. The results show that the mechano-chemical process has notable effects on the interfacial reaction. The pigment properties of the W@T composite particles were examined. The whiteness, hiding power, and oil absorption were 96.6%, 17.97 g/m$^2$, and 22.72 g/100 g, respectively. The white pigment performance was similar to that of TiO$_2$ (anatase), which indicated that the W@T composite has a high potential for replacing pure titanium dioxide in some products.

Acknowledgements

This work was financially supported by the Fundamental Research Funds for the Central Universities of China (No. 2011PY0169), National Natural Science Foundation of China (NSFC) (Nos. 51144011 and 51474194), and City University of Hong Kong Applied Research Grants (ARG), China, Nos. 9667104 and 9667122.
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