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Effect of La^{3+} on evolution of TiO_2 coating layers on lamellar sericite and their pigmentary properties

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Abstract: TiO_2-coated sericite powders were prepared by the chemical deposition method starting from lamellar sericite and $TiCl_4$ in the presence of La^{3+}. After calcination at 900 ℃ for 1 h, the resultant TiO_2 nanoparticles on the sericite surfaces exist in anatase phase. The light scattering indexes of the TiO_2-coated lamellar sericite powders are dozens of times higher than those of the naked lamellar sericite powders, varying with different contents of La^{3+}. The presence of La^{3+} in the deposition solution is beneficial to the formation of the small-sized anatase TiO_2 nanoparticles. The presence of La^{3+} also favors the formation of the dense and uniform island-like TiO_2 coating layers in a large range of the mass ratio of TiO_2 to sericite from 5% to 20%. XPS analysis shows that when La^{3+} is absent in the reaction solution, TiO_2 coating layers anchor on the sericite surface via Ti—O—Si and Ti—O—Al bonds. The presence of La^{3+} causes the formation of Si—O—La and Al—O—La bonds on the sericite surface and Ti—O—La bond on the surface of TiO_2 coating layers.

Key words: lamellar sericite; TiO_2 coating; lanthanum

1 Introduction

Mica is a general name for a group of complex hydrous potassium-aluminum silicate minerals, such as sericite, biotite, lepidolite, muscovite, phlogopite, and vermiculite, with a lamellar structure and a high aspect ratio (ratio of diameter to thickness). Conventionally, mica is widely used as a filler for paint and plastics[1] and a substrate for preparation of mica-titania pearlescent pigment[2]. Recently, flat mica has been found as a facile substrate for preparation of conducting composites[3−4], colored pigments[5−8], indicators of halogen activities [9], glass-ceramics[10−11], radioactive metal ion adsorbent[12], and shielding materials of electromagnetic interference[13].

Coating of powdered materials improves their physicochemical performances, such as dispersibility, lasting quality, surface activity, and mechanical property [14]. The performance of the coating layers is usually affected by the combination manner between coating layer and substrate and the property of coating material. Modifying the properties of substrate and coating material is a practical route to improve the performance of resultant coating layers. In the production of commercial mica-titania pearlescent pigment by coating anatase TiO_2 on mica, muscovite as one type of mica has been widely used as a flat substrate[15]. But lamellar sericite with atomic flat surface as a subspecies of muscovite, occurring in large amounts in natural deposits, is seldom investigated.

Our present work aimed at the evolution of TiO_2 coating layers on the surface of lamellar sericite. The effects of La^{3+} present in the coating process on the morphology of TiO_2 coating layers were investigated. The resultant samples were investigated by X-ray photoelectron spectroscopy, X-ray diffractometry, and scanning electron microscopy. The pigmentary properties, such as yellowness, brightness, and relative light scattering index, of the resultant samples, were determined.

2 Experimental

2.1 Materials

Lamellar sericite, $K_{0.5-1}(Al, Fe, Mg)_2(SiAl)_4O_{10}$-

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$(OH)_2$ (30 μm), was supplied by Chuzhou Grea Minerals Co., Ltd., China. Titanium tetrachloride ($TiCl_4$, 98%), lanthanum(Ⅲ) nitrate hexahydrate ($La(NO_3)_3·6H_2O$), concentrated hydrochloric acid (37%), and sodium hydroxide, all in analytical grade, were purchased from Shanghai Chemical Reagent Co., Ltd., China, and used as received. Distilled water was used throughout the experiments.

2.2 Preparation of TiO_2-coated sericite in the presence of La^{3+}

Hundred grams of lamellar sericite powders were put into 800 mL of distilled water and stirred at 85 ℃. The pH value of the sericite suspension was adjusted to 2 by adding HCl (0.5 mol/L) aqueous solution. A given amount of $La(NO_3)_3$ (0.1 mol/L) aqueous solution was added dropwise into the sericite suspension while stirring at 85 ℃ for 0.5 h. Then the prescribed amounts of $TiCl_4$ (1.5 mol/L) and NaOH (2.0 mol/L) aqueous solutions were added into the suspension with two constant flow rate pumps. The feeding time was fixed at 2 h. The pH value of the reaction solution was kept at 2 during the coating process by adjusting the flow rate of the NaOH aqueous solution. After feeding, the resultant suspension was aged at pH 2 and 85 ℃ for 2 h. The precipitate was filtrated and washed with distilled water until the conductivity of the filtrate was less than 10 mS/m. The washed precipitate was dried in an electric oven at 100 ℃ for 8 h and calcined in a furnace at 900 ℃ for 1 h. The as-prepared samples were kept in a desiccator for characterization.

To illustrate the effect of La^{3+} on the evolution of TiO_2 coating layers, TiO_2-coated sericite samples were also prepared in the same procedures as described above in the absence of La^{3+}.

2.3 Characterization

X-ray diffraction(XRD) analysis was performed on a Phillips diffractometer using Cu K_α radiation with a scanning rate of 2 (°)/min. The morphologies of the as-prepared TiO_2-coated sericite powders were analyzed on a scanning electron microscope (JSM 7001F) operating at 10 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB 250 (Thermal Electron Corp.) spectrometer equipped with Al K_α X-ray source, operating at 150 W. For all the samples, the spectra of C 1s, Si 2p, Si 2s, O 1s, Al 2p, La $3d_{5/2}$, and Ti $2p_{3/2}$ were recorded. The binding energies were referenced to the C 1s binding energy at 284.5 eV. The yellowness, brightness, and the relative scattering index of the as-prepared TiO_2-coated sericite powders were analyzed on a spectrophotometer (CM-2500d), Minolta Co. LTD, XL-30, and D65 illuminant.

3 Results and discussion

3.1 XRD analysis

The powder X-ray diffraction patterns of the naked sericite and TiO_2-coated sericite powders are shown in Figs.1−3.

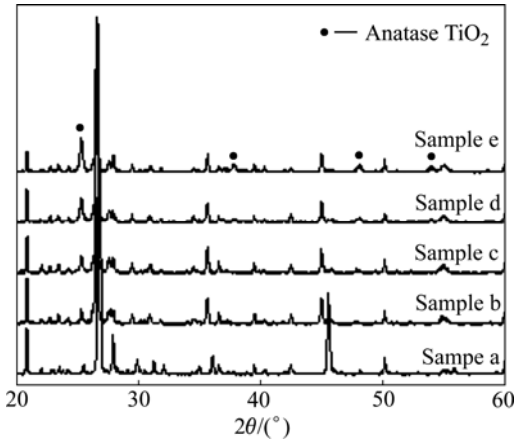

Fig.1 XRD diffraction patterns of naked lamellar sericite (sample a) and TiO_2-coated sericite powder samples prepared with mass ratios of TiO_2 to sericite of 1% (b), 5% (c), 10% (d), and 20% (e), respectively

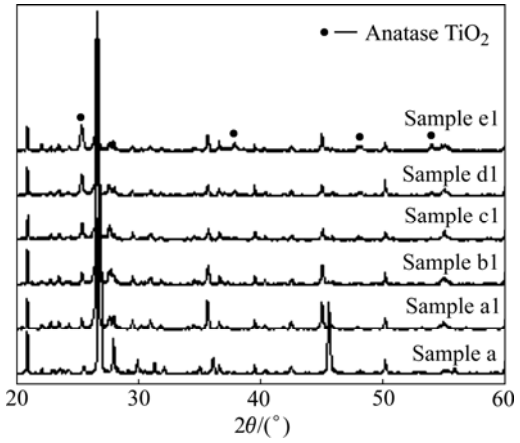

Fig.2 XRD diffraction patterns of naked lamellar sericite (sample a) and TiO_2-coated sericite powder samples prepared in the presence of La^{3+} in reaction solution with mass ratio of La^{3+} to sericite of 1% and mass ratios of TiO_2 to sericite of 0 (a1), 1% (b1), 5% (c1), 10% (d1), and 20% (e1), respectively

The XRD peaks appearing at 2θ=26.8°, 27.8°, 36.06°, and 45.57° are ascribed to sericite. For the samples prepared in the presence of La^{3+} in the reaction solution with mass ratios of La^{3+} to sericite of 1% and 5%, respectively, there is no any lanthanum species found by XRD analysis, meaning that La^{3+} is well dispersed in the samples. For the TiO_2-coated sericite powders prepared in the absence or presence of La^{3+}, the XRD peaks appearing at 2θ=25.28°, 37.80°, 48.05°, and

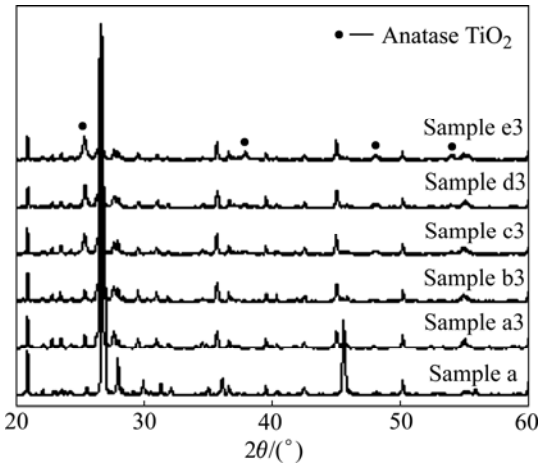

Fig.3 XRD diffraction patterns of naked lamellar sericite (sample a) and TiO_2-coated sericite powder samples prepared in the presence of La^{3+} in reaction solution with mass ratio of La^{3+} to sericite of 5% and mass ratios of TiO_2 to sericite of 0(a3), 1%(b3), 5%(c3), 10%(d3), and 20%(e3), respectively

55.06° ascribed to anatase TiO_2 (PDF #21-1272) are observed when the mass ratio of TiO_2 to sericite is up to 10%. The intensity of the XRD peaks of the anatase TiO_2 increases with further increasing the mass ratio of TiO_2 to sericite to 20%. Therefore, it can be concluded that the anatase TiO_2 is formed on the sericite surface and the anatase TiO_2 loading increases with the increase in mass ratio of TiO_2 to sericite. Although the presence of La^{3+} has no obvious effect on crystal phase transformation of TiO_2, the presence of La^{3+} significantly affects the morphology of TiO_2 coating layers on lamellar sericite surfaces as certified by SEM analysis.

3.2 Morphology of TiO_2-coated sericite

The SEM image of the naked sericite shows that the sericite has a smooth surface (Fig.4(a)). When TiO_2-coated sericite powders are prepared by the deposition of TiO_2 in the absence of La^{3+} cations, the sericite powders are partially coated by the TiO_2 nano-

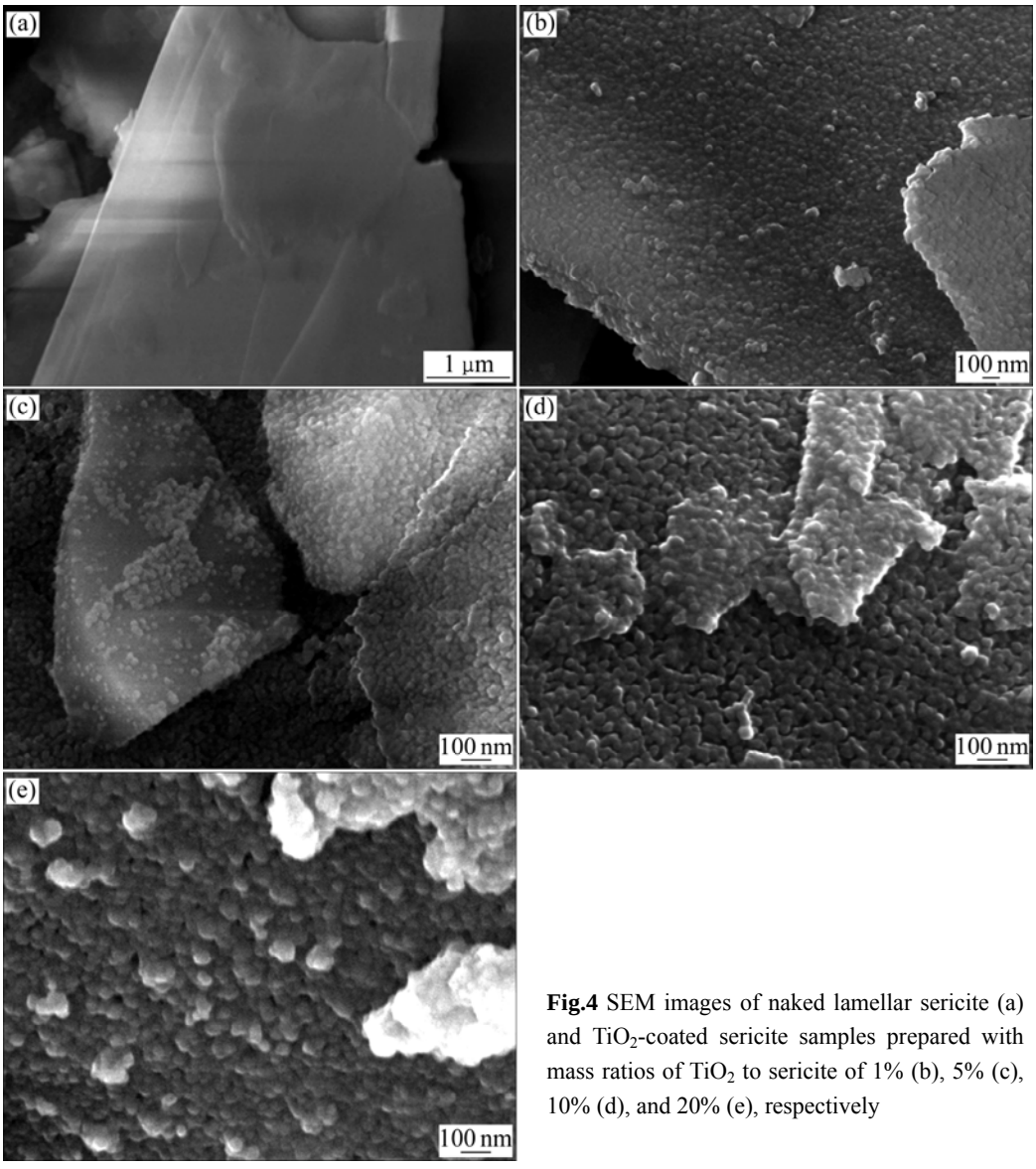

Fig.4 SEM images of naked lamellar sericite (a) and TiO_2-coated sericite samples prepared with mass ratios of TiO_2 to sericite of 1% (b), 5% (c), 10% (d), and 20% (e), respectively

particles with an average particle size of 26 nm as the mass ratio of TiO_2 to sericite is 1% (Fig.4(b)). While increasing the mass ratio of TiO_2 to sericite to 5%, the surfaces of the sericite powders are almost completely coated by the TiO_2 nanoparticles with an average particles size of 23 nm (Fig.4(c)). With further increasing the mass ratios of TiO_2 to sericite to 10% and 20%, the SEM images show that dense and uniform TiO_2 coating layers have been formed on sericite surfaces and the average particle sizes of TiO_2 nanoparticles are 28 and 40 nm, respectively (Figs.4(d) and (e)).

Figs.5 and 6 show the SEM images of the TiO_2-coated sericite powders prepared with different TiO_2 loadings in the presence of La^{3+} with the mass ratios of La^{3+} to sericite of 1% and 5%, respectively.

While sericite powders are only treated with La^{3+}, the sericite surface has the same smoothness as that of the naked sericite (Figs.5(a) and 6(a)), meaning that no lanthanum species is formed on the sericite surface.

While TiO_2-coated sericite powders are prepared with different TiO_2 loadings in the presence of La^{3+} cations with a mass ratio of La^{3+} to sericite of 1%, the SEM images (Fig.5) show that small-sized TiO_2 nanoparticles with an calculated average particle size of 14 nm are uniformly dispersed on the sericite surface as the mass ratio of TiO_2 to sericite is 1% (Fig.5(b)). When the mass ratios of TiO_2 to sericite are elevated to 5%, 10%, and 20%, the dense and uniform TiO_2 coating layers are formed on the surfaces of sericite powders and the average particle sizes of TiO_2 nanoparticles are 19, 21, and 24 nm, respectively (Figs.5(c) and (e)).

With further increasing the mass ratio of La^{3+} to sericite to 5%, the SEM images show that when the mass ratio of TiO_2 to sericite is 1%, the TiO_2 nanoparticles are uniformly dispersed on the sericite surface with an calculated average particle size of 12 nm (Fig.6(b)). With

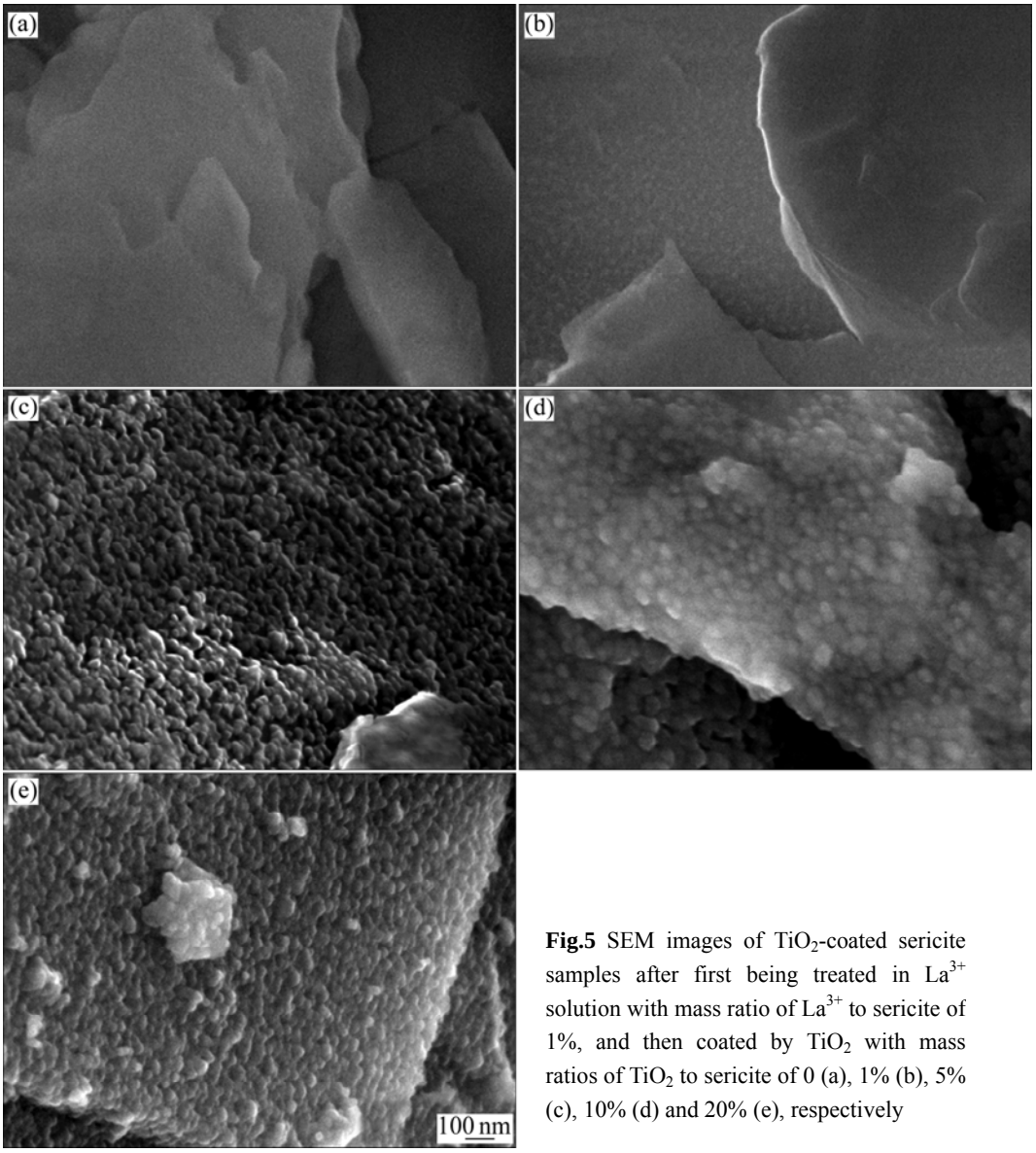

Fig.5 SEM images of TiO_2-coated sericite samples after first being treated in La^{3+} solution with mass ratio of La^{3+} to sericite of 1%, and then coated by TiO_2 with mass ratios of TiO_2 to sericite of 0 (a), 1% (b), 5% (c), 10% (d) and 20% (e), respectively

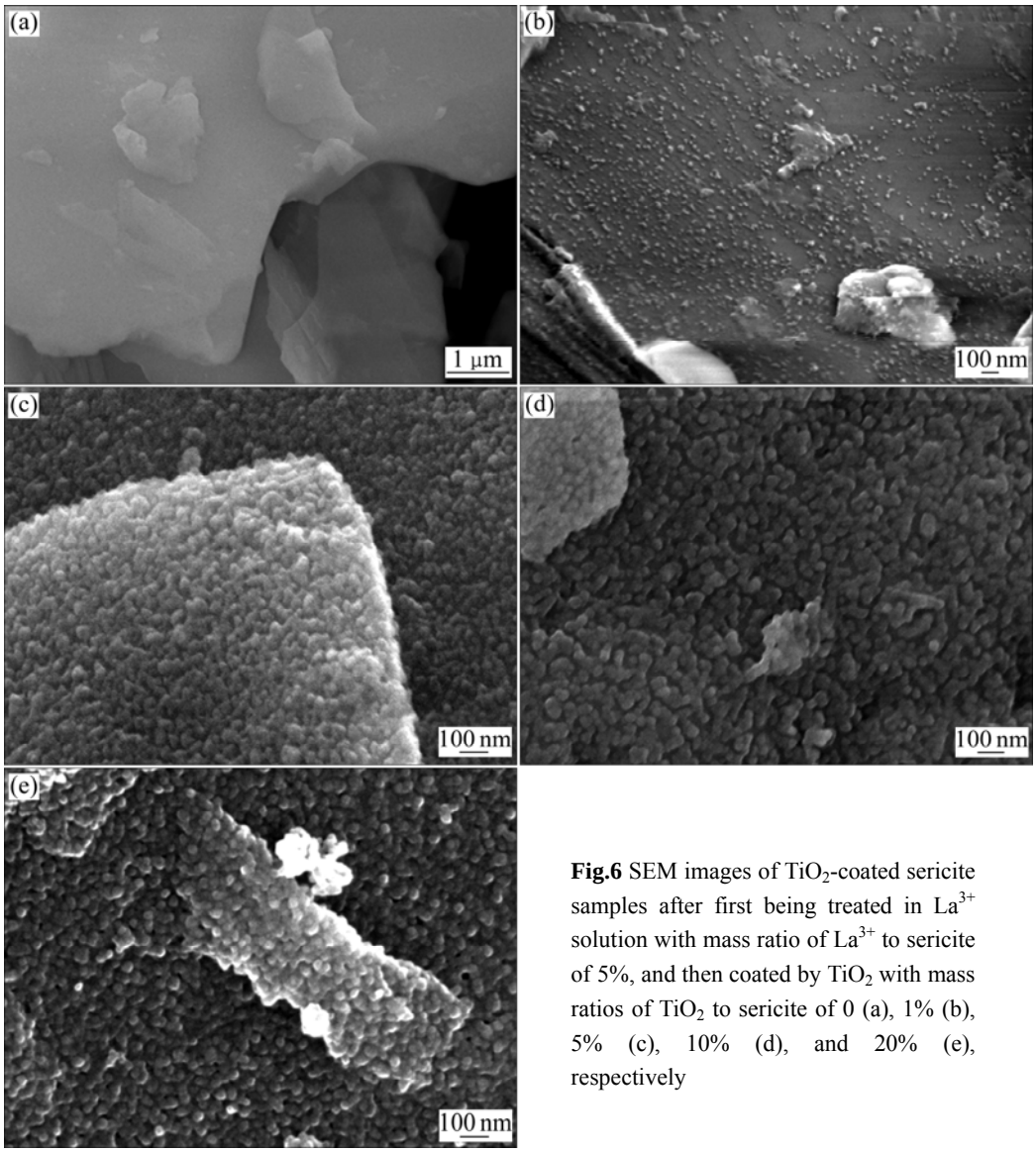

Fig.6 SEM images of TiO_2-coated sericite samples after first being treated in La^{3+} solution with mass ratio of La^{3+} to sericite of 5%, and then coated by TiO_2 with mass ratios of TiO_2 to sericite of 0 (a), 1% (b), 5% (c), 10% (d), and 20% (e), respectively

further increasing the loadings of the TiO_2 nanoparticles to 5%, 10%, and 20%, the dense and uniform TiO_2 coating layers also have been formed on the surfaces of sericite powders and the average particle sizes of the TiO_2 nanoparticles are 21, 24, and 24 nm, respectively (Figs.6(c) and (e)).

The results show that the presence of La^{3+} in the reaction solution is beneficial to the formation of the small-sized TiO_2 nanoparticles and promotes the dispersibility of the TiO_2 nanoparticles on the sericite surfaces, resulting in the formation of the dense and uniform TiO_2 coating layers. The effect of La^{3+} on the formation of dense and uniform TiO_2 coating layers with small particle sizes is obvious even the mass ratio of La^{3+} to sericite is at a lower lever of 1%.

3.3 XPS analysis

Fig.7 shows the O 1s, Al 2p, Si 2p, and Ti $2p_{3/2}$ peaks of the naked sericite and the TiO_2-coated sericite powders prepared in the absence of La^{3+}. The binding energy of O 1s of the naked sericite is 532.00 eV. When the TiO_2-coated sericite powders are prepared with the mass ratios of TiO_2 to sericite of 1% and 20%, the binding energies of O 1s are 531.53 eV and 529.63 eV, respectively. The O 1s peaks shift to a lower level of binding energy with an increase in TiO_2 loading. The O 1s peak located at 532.00 eV should be ascribed to sericite and the O 1s peak at 529.63 eV to Ti—O bond of anatase TiO_2[16]. The binding energies of Si 2p and Al 2p of the naked sericite are 102.53 eV and 74.20 eV, respectively. When the TiO_2-coated sericite powders are prepared with the mass ratios of TiO_2 to sericite of 1% and 20%, the binding energies of the Si 2p, Al 2p, and Ti $2p_{3/2}$ of the samples are 102.17, 74.00, 457.90 eV; and 101.86, 73.70, 458.05 eV, respectively. Increasing TiO_2 loading makes the Si 2p and Al 2p peaks shift to a lower

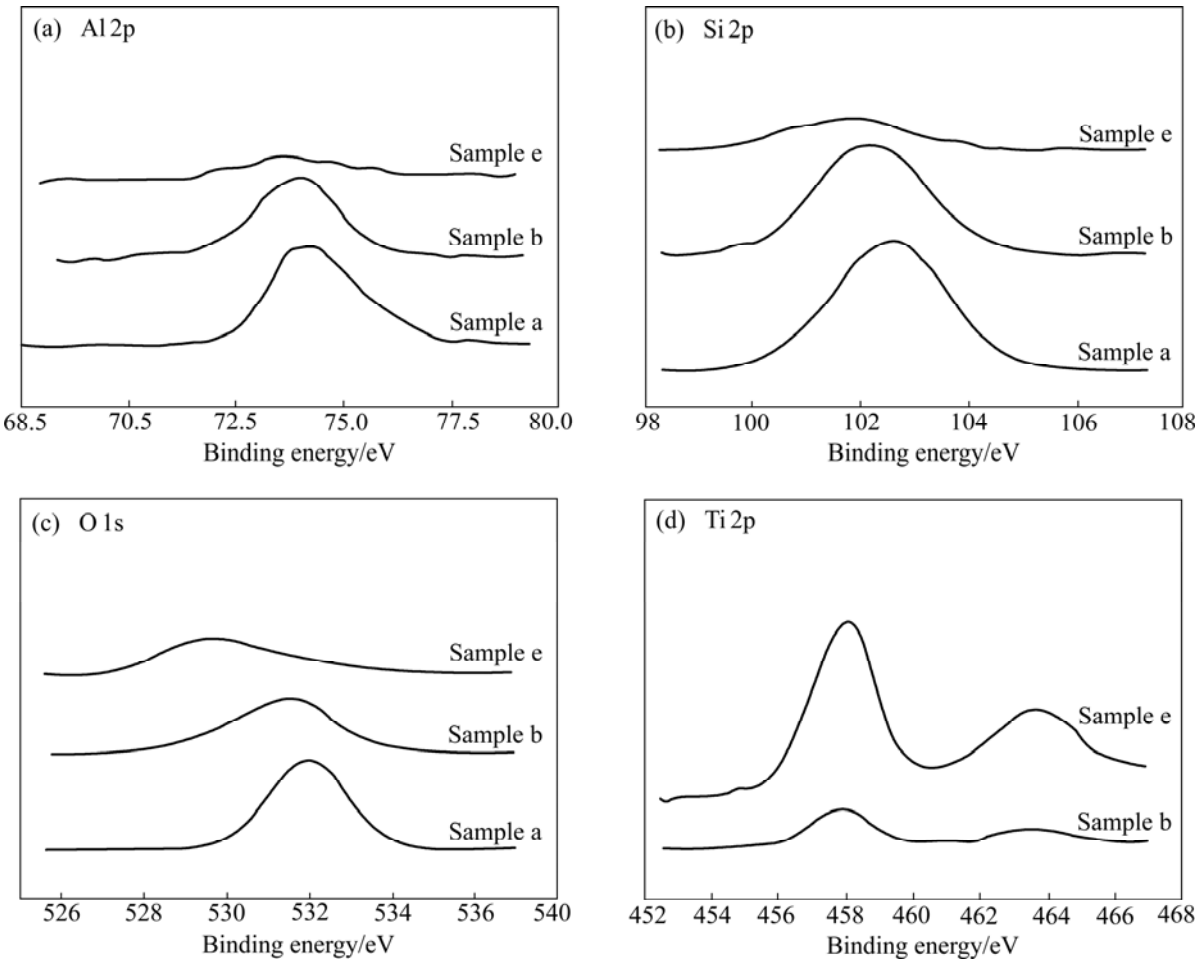

Fig.7 XPS spectra of naked lamellar sericite (sample a) and TiO_2-coated sericite powder (samples b and e) prepared with mass ratios of TiO_2 to sericite of 1% and 20 %, respectively

binding energy, while the Ti $2p_{3/2}$ peaks shift to a higher binding energy. The shifts of the O 1s, Si 2p, Al 2p, and Ti $2p_{3/2}$ peaks reveal that the chemical states of O, Si, Al, and Ti are changed. From SEM images, it is found that TiO_2 coating layers tightly anchor on the surfaces of sericite powders. Therefore, it is reasonable to conclude that TiO_2 coating layers anchor on the sericite surface by the formation of Ti—O—Si and Ti—O—Al chemical bonds at the interface of the TiO_2 coating layer and the sericite powders.

The O 1s, Al 2p, Si 2s, Ti $2p_{3/2}$, and La $3d_{5/2}$ peaks of the naked sericite and TiO_2-coated sericite powders prepared in the presence of La^{3+} are shown in Fig.8. The binding energies of O 1s, Si 2s, Al 2p, and La $3d_{5/2}$ of the sericite powders solely treated with La^{3+} cations are 531.83, 153.41, 74.00, and 836.53 eV, respectively. The binding energy of Si 2s of the naked sericite is 153.57 eV. By comparing the binding energy of La $3d_{5/2}$ with that known in Ref.[17], lanthanum can be confirmed to be in the chemical state of La^{3+}. The O 1s, Si 2s, and Al 2p peaks of the sericite powders solely treated with La^{3+} cations shift to lower binding energy as compared with those of the naked sericite, meaning that La^{3+} can combine on the sericite surface. The molar percentage of La^{3+} on the sericite surface is only 0.29% as certified by XPS analysis. Therefore, it is reasonable to conclude that no lanthanum compound is formed on the sericite surface in a large scale and that the La^{3+} should be chemically adsorbed on the sericite surface via Si—O—La and Al—O—La bonds.

With increasing the mass ratio of TiO_2 to sericite from 1% to 20%, the binding energies of O 1s, Si 2s, Al 2p, Ti $2p_{3/2}$, and La $3d_{5/2}$ of the TiO_2-coated sericite powders prepared in the presence of La^{3+} cations are 531.55, 153.24, 74.00, 458.20, 836.30 eV; 530.05, 153.14, 73.98, 458.78, 835.07 eV, respectively. The binding energy of Al 2p keeps constant in the presence of La^{3+}, certifying that the Al sites on the sericite surfaces are dominantly occupied by La^{3+} before the deposition of TiO_2. The binding energies of O 1s and Si 2s of the TiO_2-coated sericite powders shift to lower value, while the binding energy of Ti $2p_{3/2}$ shifts to higher value, with

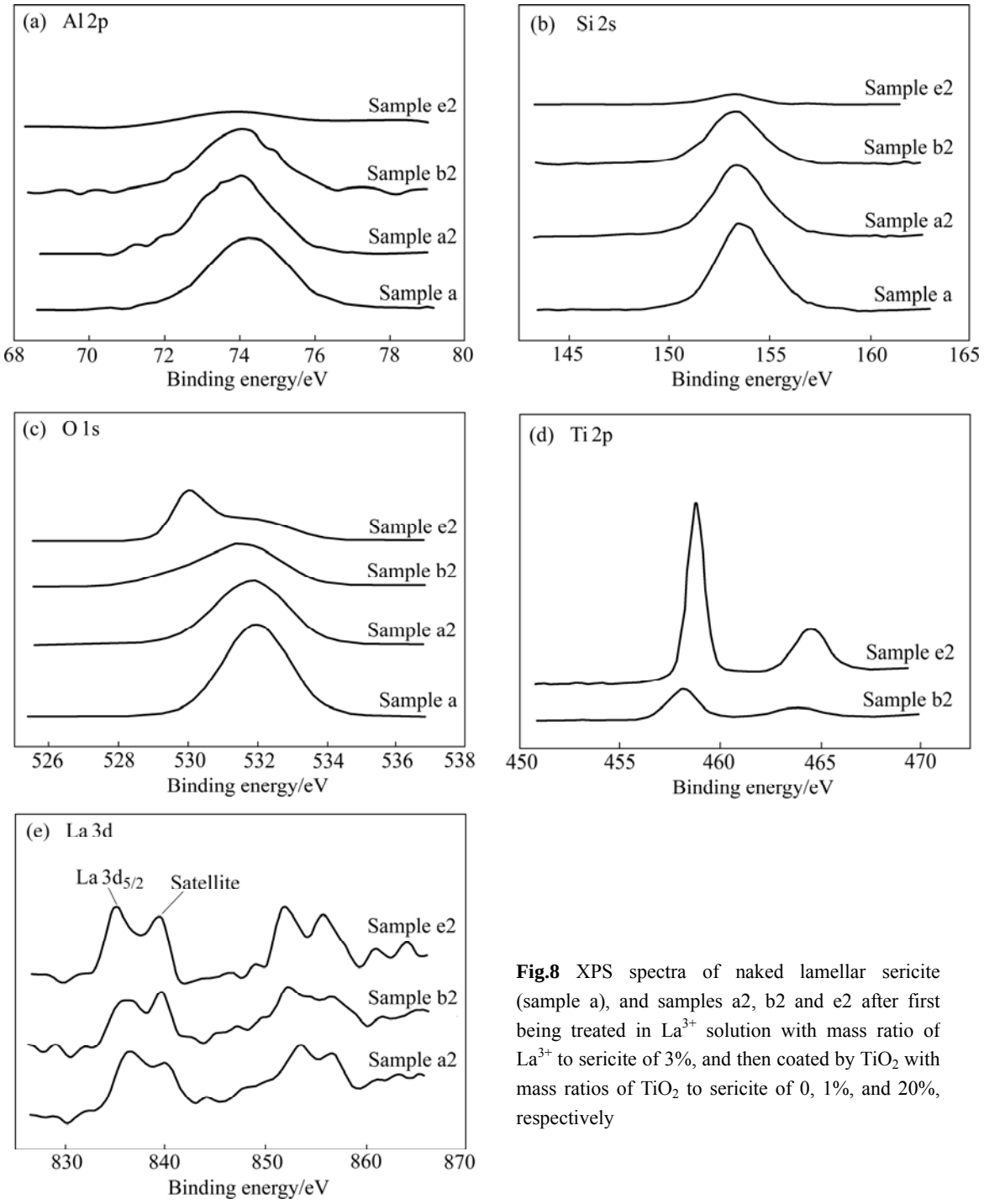

Fig.8 XPS spectra of naked lamellar sericite (sample a), and samples a2, b2 and e2 after first being treated in La^{3+} solution with mass ratio of La^{3+} to sericite of 3%, and then coated by TiO_2 with mass ratios of TiO_2 to sericite of 0, 1%, and 20%, respectively

increasing TiO_2 loading, conforming that in the presence of La^{3+}, TiO_2 coating layers anchor on the sericite surfaces mainly via Ti—O—Si bond. On the other hand, the binding energies of Ti $2p_{3/2}$ of the TiO_2-coated sericite powders prepared in the presence of La^{3+} are higher than those prepared in the absence of La^{3+}. The binding energy of La $3d_{5/2}$ is markedly decreased by 1.23 eV as increasing the mass ratio of TiO_2 to sericite from 1% to 20%. Therefore, it can be concluded that La^{3+} also reacts with TiO_2 on the surfaces of the resultant TiO_2 nanoparticles through Ti—O—La bonding. Furthermore, XPS analysis shows that the molar percentage of La^{3+} in the TiO_2-coated sericite prepared with a TiO_2 loading of 20% is 0.4%, which is higher than that of the sericite solely treated with La^{3+}, revealing the existence of the interaction between La^{3+} and the surfaces of the TiO_2 coating layers.

3.4 Pigmentary properties of TiO_2-coated sericite

Table 1 shows that when TiO_2 coating layers are

formed on the sericite surface, the yellowness of the TiO_2-coated sericite powders is increased while the lightness is slightly decreased as compared with that of the naked sericite. In the substrate, sericite ($K_{0.5-1}(Al, Fe, Mg)_2(SiAl)_4O_{10}(OH)_2$), iron ions coexist with potassium, magnesium, and aluminum ions to balance the negative charges of lamellar sericite[18]. Therefore, when sericite powders are deposited by TiO_2 at a lower pH value of 2 and then calcined at 900 ℃, iron-containing compounds probably form and move to the surface of the TiO_2-coated sericite, resulting in the increase of the yellowness and the decrease of the lightness.

The light scattering properties of the TiO_2-coated sericite powders are listed in Table 2. The light scattering indexes of the TiO_2-coated sericite powders are increased with the increasing of TiO_2 loading, which could be explained as being due to the increase of anatase TiO_2 coverage on sericite surface. Furthermore, the TiO_2-coated sericite powders prepared in the presence of La^{3+} cations have higher light scattering indexes than those prepared in the absence of La^{3+}, which should be due to the evolution of dense and uniform TiO_2 coating layers with small-sized TiO_2 nanoparticles in the presence of La^{3+}.

Table 1 Color schemes of TiO_2-coated sericite samples (in system CIE)

Sample	Yellowness	*L**	*a**	*b**
a	7.77	93.29	−1.17	5.11
c	22.49	87.39	3.82	14.15
d	19.93	88.67	3.40	12.55
e	14.86	90.77	2.71	9.33
c1	22.31	88.44	3.26	14.19
d1	15.95	91.56	2.31	10.15
e1	14.70	90.72	2.56	9.22
c3	18.95	87.39	3.82	14.15
d3	19.03	88.44	3.26	14.19
e3	15.76	90.72	2.56	9.22

*L** means brightness; *a** means red-green index; *b** means yellow-blue index; Preparation conditions of samples are same as those described in Figs.1, 2 and 3.

Table 2 Light scattering performances of TiO_2-coated sericite samples

Sample	*k*/*s*	Relative light scattering index/%
a	95.302 643	100
c	10.615 692	898
d	3.200 388	2978
e	1.428 763	6670
c1	7.676 740	1241
d1	2.422 301	3934
e1	1.369 843	6957
c3	10.368 244	923
d3	3.054 929	3120
e3	1.389 061	6861

k means absorption coefficient; *s* means light scattering coefficient; Preparation conditions of samples are same as those described in Figs.1, 2 and 3.

4 Conclusions

1) In the absence of La^{3+} in the reaction solution, the dense and uniform TiO_2 coating layers form on the sericite surface by the direct deposition of TiO_2 when the mass ratio of TiO_2 to sericite is up to 10%. The TiO_2 coating layers anchor on the sericite surface via Ti—O—Si and Ti—O—Al bonding. The light scattering indexes of the TiO_2-coated sericite powders are greater than those of the naked sericite powders.

2) While La^{3+} is present in the reaction solution, small-sized TiO_2 nanoparticles form since the formation of Ti—O—La bonds on TiO_2 surfaces inhibits TiO_2 crystal growth. La^{3+} anchors on the sericite surface by the formation of La—O—Al and La—O—Si bonds and the aluminum sites on the sericite surface are dominantly occupied by La^{3+}. When sericite is pretreated with La^{3+}, TiO_2 anchors on the sericite surface via Ti—O—Si bonds, giving a higher dispersibility of TiO_2 nanoparticles, subsequently, constructing dense and uniform TiO_2 coating layers. The light scattering indexes of the TiO_2-coated sericite powders prepared in the presence of La^{3+} are higher than those prepared in the absence of La^{3+}.

References

[1] MAINE F W, SHEPHERD P D. Mica reinforced plastics: A review [J]. Composites, 1974, 5(5): 193−200.

[2] ATWOOD F C. Method of treating mica: USA 2306292 [P]. 1942−12.

[3] TAN J, SHEN L, FU X, HOU W, CHEN X. Preparation and conductive mechanism of mica titania conductive pigment [J]. Dyes Pigments, 2004, 62: 107−114.

[4] SEMALTIANOS N G, WILSON E G. Investigation of the surface morphology of thermally evaporated thin gold films on mica, glass, silicon and calcium fluoride substrates by scanning tunneling microscopy [J]. Thin Solid Films, 2002, 366: 111−116.

[5] TOHIDIFAR M R, NASSAJ E T, ALIZADEH P. Optimization of the synthesis of a nano-sized mica-hematite pearlescent pigment [J]. Materials Chemistry and Physics, 2008, 109: 137−142.

[6] BERTAUX S, REYNDERS P, SCHWEDA E. The reaction of ceria coatings on mica with H_2S: An in-situ X-ray diffraction study [J]. Materials Research Bulletin, 2004, 39: 793−801.

[7] ŠTENGL V, ŠUBRT J, BAKARDJIEVA S, KALENDOVA A, KALENDA P. The preparation and characteristics of pigments based on mica coated with metal oxides [J]. Dyes and Pigments, 2003, 58: 239−244.

[8] TAN J, FU X, HOU W, CHEN X, WANG L. The preparation and characteristics of a multi-cover-layer type, blue mica titania, pearlescent pigment [J]. Dyes Pigments, 2003, 56: 93−98.

[9] COULSON I M, DIPPL E G M, RAUDSEPP M. Evolution of HF and HCl activity in magmatic volatiles of the gold-mineralized Emerald Lake Pluton, Yukon Territory, Canada [J]. Mineralium Deposita, 2001, 36: 594−606.

[10] ALIZADEH P, YEKTA B, JAVADI T. Sintering behavior and mechanical properties of the mica-diopside machinable glass-ceramics [J]. Journal of the European Ceramic Society, 2008, 28: 1569−1573.

[11] TARUTA S, SUZUKI M, YAMAKAMI T, YAMAGUCHI T, KITAJIMA K. Preparation and ionic conductivity of transparent glass-ceramics containing a large quantity of lithium-mica [J]. Journal of Non-Crystalline Solids, 2008, 354: 848−855.

[12] KODAMA T, HARADA Y, UEDA M, SHIMIZU K, SHUTO K, KOMARNENI S. Selective exchange and fixation of strontium ions with ultrafine Na-4-mica [J]. Langmuir, 2001, 17: 4881−4886.

[13] JIANG G, GILBERT M, HITT D J, WILCOX G D, BALASUBRAMANIAN K. Preparation of nickel coated mica as a conductive filler [J]. Composites: Part A, 2002, 33: 745−751.

[14] SONG J, ZHANG L M, LI J G, SONG J R. Introduction of coating technology of superfine particle surface [J]. Surface Review and Letters, 2007, 14(2): 199−208.

[15] MAHÉ M, HEINTZ J M, RÖDEL J, REYNDERS P. Cracking of titania nanocrystalline coatings [J]. Journal of the European Ceramic Society, 2008, 28: 2003−2010.

[16] FEI H L, LIU Y P, LI Y P, SUN P C, YUAN Z Y, LI B H, DING D T, CHEN T H. Selective synthesis of borated meso-macroporous and mesoporous spherical TiO_2 with high photocatalytic activity [J]. Microporous and Mesoporous Materials, 2007, 102: 318−324.

[17] HUANG Y, ZHU W, FENG X, MAN Z. The effects of La^{3+} doping on luminescence properties of $PbWO_4$ single crystal [J]. Journal of Solid State Chemistry, 2003, 172: 188−193.

[18] REN M, YIN H B, WANG A L, JIANG T S, WADA Y. Mica coated by direct deposition of rutile TiO_2 nanoparticles and the optical properties [J]. Materials Chemistry and Physics, 2007, 103: 230−234.

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