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Preparation and conductive mechanism of mica titania conductive pigment

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Abstract

Flake mica titania conductive pigment, which characteristically consists of both electrical conductivity and pearlescent effect when covered a layer of ATO (Antimony Doped Tin Dioxide) on its surface, has been prepared by using homogenous precipitation method with mica titania as substrate and urea as precipitant. The hydrolysis of urea and the conductive mechanism of the pigment were discussed and the different substrates of mica and mica titania were compared. Furthermore, this paper studied several critical technological parameters pertaining to the influences on electrical conductivity and pearlescent effect of the pigment such as molar ratio of Sn^{4+}/Sb^{3+}, coating quantity and the addition order, etc.

Keywords: Conductive pearlescent pigment; Molar ratio of Sn^{4+} to Sb^{3+}; Urea hydrolysis; Reflectivity; Resistivity

1. Introduction

As a kind of functional material, conductive pigments can make a coating to have the properties of electrical conductivity, anti-static and shielding to electromagnetic waves if added in a coating [1]. To coat conductive pigments on the surface of substance can avoid the formation of static electricity by friction and impaction of flowing of air and liquid, fire hazard due to static electricity aggregation to a certain degree and can also avoid irregular working of radar due to strong disturbance to the radio-receiver [2]. The conductive pigments have found a diverse range of application, such as in mining, oil-gas field, the chemical industry, automobile industry and the aerospace industry, etc. They are also used as packing materials for integrated circuits, printed circuit boards and electronic components. Thus, conductive pigments have an excellent development potentiality [3]. When the resistivity of a pigment is in the range of 10^{-5}–10^{-9} Ω cm, the pigment has electrical conductivity [4]. The most common conductive pigments are carbon series conductive pigments, metallic conductive pigment and metal oxide conductive pigments [5]. Carbon series conductive pigments have limited applications in conductive composites because they are dull and dark in coloring and have poor adhesive force and poor oil resistance [6]. The most metal conductive pigments have poor chemical stability, high cost and high specific densities to limit their application. Oxidation of the metal surface can

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also reduce the effective conductivity of the composite [7]. With the rapid development of the electronic industry especially personal computers and mobile phones, conductive undertint pigments with stable chemical properties and reliable electrical properties are becoming an increasing problem. A number of patents have reported about this project [3,8]. Mica or mica titania (mica titania was obtained by coating a layer of TiO_2 powders on the surface of mica) was selected for this project as they exist in the form of flakes of high aspect ratio [9]. If coated with one or more layers of semiconductor oxide, mica and mica titania have the potential to retain this advantage and at the same time become a light-colored conductive pigment–composite mica conductive pigment [10]. This pigment not only has electrical conductivity, anti-static and shielding to ultraviolet ray properties, but also gives ornaments magnificently pearlescent effect. In most existing reports, co-precipitation method was used to coat metal oxide on the surface of mica or mica titania with sodium hydrate (NaOH) as precipitant. Sodium hydrate, a strong base, was easy to cause the degree of supersaturation and maldistribution of the ions of forming crystal in system, and was difficult to control the nucleation rate to influence the homogenization of coating and further lead to poor electrical conductivity. Therefore, in the present study, an attempt has been made to prepare undertint flake mica titania conductive pigment with good electrical conductivity and pearlescent luster by a homogenous precipitation method by coating ATO on the surface of mica titania. The factors that influence electrical conductivity and pearlescent effect of the pigment, such as molar ratio of Sn^{4+}/Sb^{3+}, the addition of $SnCl_4$ and the addition order of substrate, etc. were discussed. The conductive mechanism and the hydrolysis of urea were also discussed in the paper.

2. Experimental

2.1. Materials

Tin tetrachloride: $SnCl_4$ (analytical reagent) and antimony butter: $SbCl_3$ (analytical reagent) were used as starting chemicals. Precursor solutions of $SnCl_4$ (1.0M) and $SbCl_3$ (0.1M) were prepared in distilled water. Urea: $CO(NH_2)_2$ (analytical reagent) was used as precipitant and mica titania made by myself was used as substrate [11].

2.2. Analysis

MYI-50 sheeter was used to obtain the resistivity of the pigment by applying a pressure of 2.5 ton to the resultant pigment powders or ATO powders to be a pellet of 12 mm diameter, then putting the pellet between two copper plates of known dimensions. The resistivity was calculated with the formula $\rho = R \cdot \frac{A}{d}$, where ρ is the resistivity, R is the measured resistance, A is the cross sectional area of pellet, and d is the thickness of pellet. The measured resistance was obtained by using universal meter and the thickness of pellet was measured by vernier caliper. Color measurement instrument (JFY-AB_1) was used to obtain the spectral reflectance of the pigment. The thermogravimetric analysis (TG) of Sb_2O_3 powders and differential thermal analysis (DTA) of Sb_2O_3 powders were done by using differential thermal gravimetric analysis apparatus (WC-T). Finally, the phase analysis of the resultant pigment powders was carried out by X-ray diffractometer (XRD BDX-3300).

2.3. Preparation method

Mica titania (2.0 g) were dissolved in 20 ml distilled water to be a suspension. A mixture of $SnCl_4$ solution and $SbCl_3$ solution was treated in 250 ml reaction vessel with the molar ratio of $Sn^{4+}/Sb^{3+} = 12.5:1$ to be uniform with continuous stirring, followed by adding 18.0 g of urea. This mixing solution was heated to 368 K to react. The mica titania suspension was added in this mixture to coat before the hydrolysis of Sn^{4+} or Sb^{3+} ions to form precipitate. When the pH value of reaction system reached 5.0–6.0, the reaction was finished and the ions of Sn^{4+} or Sb^{3+} had precipitated completely at this time. The resultant pigment powders were washed several times to remove Cl^- ions and dried at 353 K, and finally were calcined at 973 K for 0.5 h to get the conductive pigment powders with pearlescent luster.

3. Results and discussion

3.1. Hydrolysis of urea

The conductive pigment with pearlescent effect was prepared by coating ATO on the mica titania surface with urea as precipitant. The process of urea hydrolysis is a critical step in the whole reaction. Thus, to discuss the hydrolysis of urea under different conditions is necessary, firstly.

3.1.1. Hydrolysis of urea with temperature

Since the hydrolysis of urea is an endothermic reaction, the hydrolysis rate increases with temperature. When the concentration of urea is 0.5 mol l^{-1} and the reaction time is 0.5 h, the hydrolysis of urea expressed as pH value at different temperatures are shown in Fig. 1.

3.1.2. Relationship of urea concentration and its hydrolysis

The hydrolysis of urea is shown in Fig. 2 under the conditions of 368 K of reaction temperature and 0.5 h of reaction time only by varying the concentration of urea.

3.1.3. Variation of urea hydrolysis with reaction time

The hydrolysis of urea with reaction time is shown in Fig. 3 under a limited set of conditions (taking urea concentration of 0.5 mol l^{-1} and 353 K as reaction temperature).

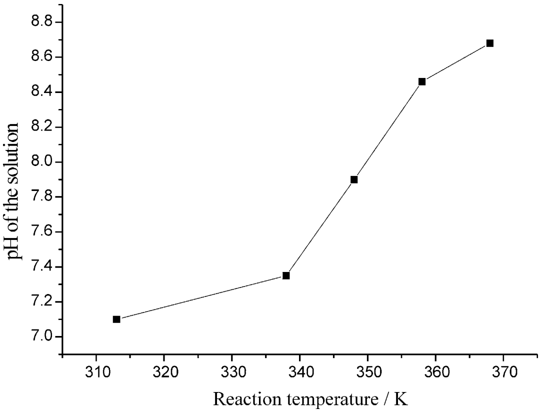

Fig. 1. Hydrolysis of urea at different temperatures.

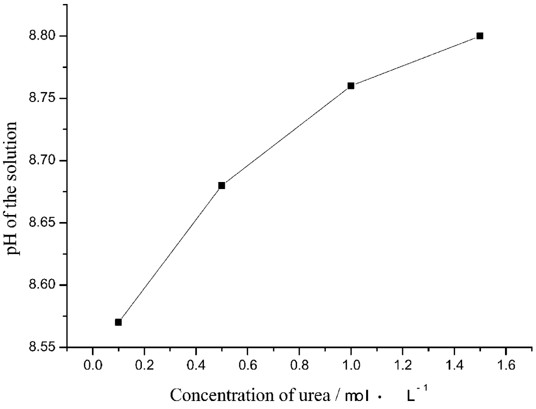

Fig. 2. Relationship of urea concentration and its hydrolysis.

It is obtained from Figs. 1–3 that both the reaction temperature and time have a very significant effect on the hydrolysis rate of urea, while concentration has a small effect on urea hydrolysis. Therefore, to control the formation and growth rate of crystal nuclei of SnO_2 and Sb_2O_3 by controlling the reaction temperature and time can achieve the goal of coating them on the surface of mica titania uniformly.

3.2. Choice of substrate

Mica and mica titania as substrate were coated respectively under the same conditions, based on the preparation method (Section 2.3). Their resistivities and spectral average reflectivities of samples obtained are given in Table 1.

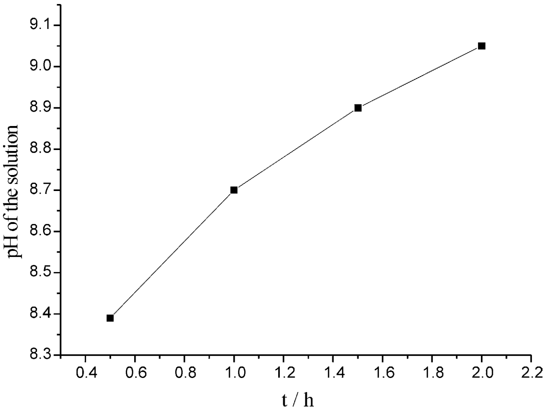

Fig. 3. Hydrolysis of urea with reaction time.

Table 1
Resistivities and reflectivities of different substrate samples

Substrate	Resistivity (Ω cm)	Reflectivity (%)
Mica	1.841×10^4	22.31
Mica titania	3.437×10^3	60.59

The electrical conductivity described by the resistivity and the pearlescent effect reflected by spectral average reflectivity with mica titania as substrate are better than that with mica as substrate from Table 1. Thus, mica titania was selected to be substrate.

3.3. *Molar ratio of Sn^{4+} to Sb^{3+}*

In order to get the flake conductive pearlescent pigment with good electrical conductivity, the optimum molar ratio of Sn^{4+}/Sb^{3+} in coating layer has been investigated. A series of ATO semiconductor powders were prepared by varying the molar ratio of Sn^{4+}/Sb^{3+} with other experimental conditions fixed. The resistivities of the powders measured are shown in Fig. 4.

Based on Fig. 4, at the beginning, the resistivity decreases with molar ratio of Sn^{4+}/Sb^{3+}, which shows that the electrical conductivity of powders is increasing. The electrical conductivity of SnO_2 powders is at its best, when the molar ratio is 12.5 (mean 100:8). After this, the electrical conductivity decreases with the decreasing molar ratio. The reason is that at the outset, the aim of doping a few of antimony trioxide as impurity is to form crystal defect, and further to form conductive current carrier to make SnO_2 powders to have electrical conductivity property. But when the amount of Sb_2O_3 doped was too much, too many impurity ions of antimony hindered the migration moving of conductive current carrier and affected the doping effect and further leaded to a decrease in electrical conductivity [12]. The flake conductive pigment was prepared by taking molar ratio of $Sn^{4+}/Sb^{3+} = 12.5$ to coat mica titania, according to the experiment method of Section 2.3. The resistivity of the pigment obtained is 3.437×10^3 Ω cm and the spectral average reflectivity is 60.59%, which show that the flake pigments have not only good electrical conductivity but also pearlescent effect.

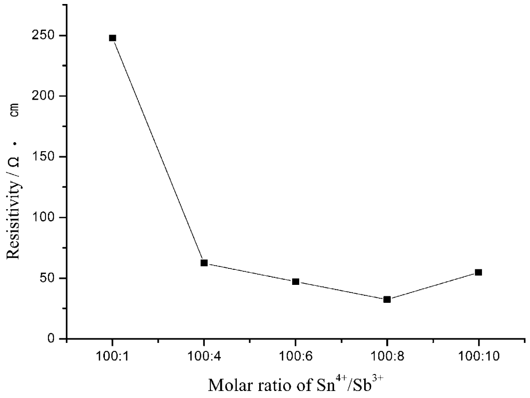

Fig. 4. Relationship of resistivity and molar ratio of Sn^{4+}/Sb^{3+} in composite oxide.

3.4. *Optimum amount of ATO*

In order to get the pigments with both electrical conductivity and pearlescent effect, the appropriate SnO_2 film coated on the surface of substrate of mica titania is necessary. The samples of conductive pigments were obtained by varying the amount of $SnCl_4$ with other conditions fixed, and were tested to get their resistivities and spectral average reflectivities. The results are given in Table 2.

Table 2 shows that when the amount of $SnCl_4$ added is small, the spectral average reflectivity of pigment is high and the luster of the pigment is good, while the electrical conductivity is poor to lead to a main property of mica titania of the insulation property. The increasing of the amount

Table 2
Variation of resistivity and reflectivity with addition of $SnCl_4$

Addition of $SnCl_4$ (ml)	Resistivity (Ω cm)	Reflectance (%)	Existence of free ions of Sn^{4+} or Sb^{3+} in resultant powders
2.5	∞	71.64	Have not
4.0	5.14×10^6	71.34	Have not
6.0	1.26×10^4	55.10	Have not
7.0	1.09×10^4	59.90	Have not
8.0	4.42×10^3	52.13	Have not
9.0	343.7	60.99	Have not
10.0	1.84×10^4	40.30	Have

of $SnCl_4$ solution doped with $SbCl_3$ means that SnO_2 film coated on mica titania surface thickens and the resistivity of pigment decreases. The resistivity is at its lowest by adding 9.0 ml of $SnCl_4$ solution, while the spectral average reflectivity is high relatively, which indicates that the thickness of the film on the surface of mica titania is appropriate and the pigments obtained have an ideal pearlescent effect and good electrical conductivity. On the contrary, the resistivity increases rapidly while the reflectivity decreases when more $SnCl_4$ was added and there were free ions of Sn^{4+} or Sb^{3+} in resultant powders out of the substrate surface observed by a microscope further to influence electrical conductivity and pearlescent effect of the pigments. Therefore, the optimum amount coated on the surface of 2.0 g mica titania should be the amount of chloride produced by hydrolysis of the mixture solution of 9.0 ml of 1.0 mol l^{-1} $SnCl_4$ and 7.2 ml of 0.1 mol l^{-1} $SbCl_3$.

3.5. Addition order of substrate

It was found that under above experimental conditions, the order to feed mica titania also affected the electrical conductivity and pearlescent luster of the pigments. With other experimental conditions fixed, we took two different feeding orders, one was to add mica titania at the outset of reaction, another was to add it just before the hydrolysis of Sn^{4+} or Sb^{3+} ions to form precipitate. The resistivity and spectral average reflectivity of samples obtained by the two ways separately were measured and shown in Table 3. The results of Table 3 indicate the second method is better. This is likely to be caused by that substrate (mica titania) are influenced by the effect of shear force over a long period if mica titania is added too early, possibly, TiO_2 film on mica titania have detached partially to be free in the solution, according to the first feeding order. In this case, the particles produced by the hydrolysis of Sn^{4+} or Sb^{3+} ions will precipitate with TiO_2 particles as nuclei, apart from on the surface of mica titania. This phenomenon leads to the scatter to light and the decrease of pearlescent effect. The film formed is non-uniform with many gaps to affect the electrical conductivity of the pigments.

Table 3
Relationship of resistivity and reflectivity and addition order of substrate

Addition order of substrate	Resistivity (Ω cm)	Reflectance (%)
Feed from the outset	3.44×10^3	60.59
Feed before appearance of precipitate	2.07×10^3	62.32

3.6. Conductive mechanism

Mica titania coated with pure SnO_2 crystal has not the property of electrical conductivity. The foreign substance introduced by doping leaded to the deviation of SnO_2 crystal from stoichiometry to form crystal defects. The imperfection of grain boundary will destroy the periodicity of potential function at the place where the defects locate. The energy band theory and the simple hydrogen-like model indicate that at the place where the periodic potential function is destroyed, localized energy level will enter into forbidden band [13], which can supply conductive current carrier for materials to make the materials have the properties of semiconductor. When a localized energy level is near to the bottom of conduction band, the electron on the energy level can be excited to conduction band to become a conductive electron if accepted energy, thus this energy level is called donor level. While a localized energy level near to the top of valence band is called acceptor level, because the electron in the top of valence band will be excited to this energy level and leave a conductive vacancy at valence band when supplied energy by outside. The electronegativity of tin is 1.8 and the electronegativity of antimony is 1.9, they are very close to each other. The radius of Sn^{4+} ion is near to that of Sb^{3+} and Sb^{5+} ion, the radius of Sn^{4+} ion is 71 pm, and the radius of Sb^{3+} ion and Sb^{5+} ion are 76 and 62 pm separately. And the atomic radius of tin and antimony are more similar, they are $r_{Sn}=162$ pm, $r_{Sb}=159$ pm. When the difference of atomic radius between two elements is less than 15%, these atoms can be substituted each other and form a substitutional impurity defect [14]. Thus, both Sb^{3+} ions and Sb^{5+} ions may substitute the lattice of Sn^{4+} ions to form substitutional defect. To clarify the conductive mechanism, the analysis for pure SnO_2 and ATO powders calcined at 973 K with molar ratio = 12.5 were undertaken by using X-ray diffraction pattern as shown in Fig. 5.

The X-ray diffraction pattern shows that the peaks of pure SnO_2 and ATO powders are same completely. The absence of Sb_2O_3 peak indicates that the Sb_2O_3 phase is not present to show that antimony substituted the lattice of Sn^{4+} ions and formed impurity defect. In order to confirm further whether Sb^{3+} ions or Sb^{5+} ions substitute Sn^{4+} lattice, single Sb_2O_3 powders were calcined at different temperatures to be analyzed by using X-ray diffraction patterns. The results are shown in Fig. 6.

Fig. 6 [1] (the XRD pattern of single Sb_2O_3 powders calcined at 673 K) shows that there is no diffraction peak of Sb_2O_4 (the composite of $Sb_2O_3{\cdot}Sb_2O_5$). The X-ray diffraction patterns of single Sb_2O_3 powders calcined at 773 and 973 K show that there are peaks of Sb_2O_4 apart from Sb_2O_3 diffraction peaks and 2θ angles of the peaks of Sb_2O_4 are 29.00, 30.30, 33.72, 37.34, 48.82°, etc. The peaks strengthen with the temperature increasing. The differential thermal analysis matches very well with the XRD patterns of single Sb_2O_3 and the TG–DTA curve of Sb_2O_3 is shown in Fig. 7.

There is an exothermic peak at 855 K in DTA curve (Fig. 7). This is likely to be caused by the oxidation of Sb^{3+} ions to Sb^{5+} ions. The increase in weight in TG curve further suggests that Sb_2O_3 are oxidized to Sb_2O_5 partially. The X-ray diffraction pattern of Sb_2O_3 calcined at 1173 K (Fig. 6[4]) shows a weakening of the peak of Sb_2O_4, most likely due to the partial reduction of Sb^{5+} ions to Sb^{3+} ions. Both Sb^{3+} ions and Sb^{5+} ions are possible to substitute Sn^{4+} lattice. The reasons are explained as follows. The resistivities of SnO_2 with doping ratio = 12.5 calcined at different temperatures separately were measured to get that the resistivity of the sample calcined at 673 K was 758.20 Ω cm. This sample has the properties of semiconductor and due to the absence of Sb^{5+} ion in this sample (Fig. 6[1]), which indicates that Sb^{3+} ions substitute the lattice of Sn^{4+} ions to form substitutional impurity defect. This defect is equal to a negative electricity center bound with a vacancy flabbily ($Sb'_{Sn}+h^{\cdot}$),

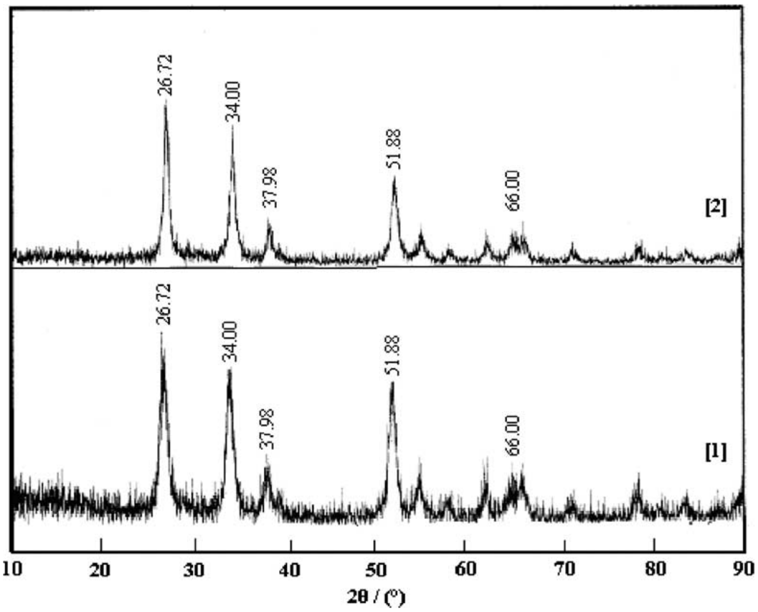

Fig. 5. X-ray diffractogram of pure SnO_2 and antimony doped SnO_2 powders: [1] pure SnO_2 powders; [2] antimony doped SnO_2 powders.

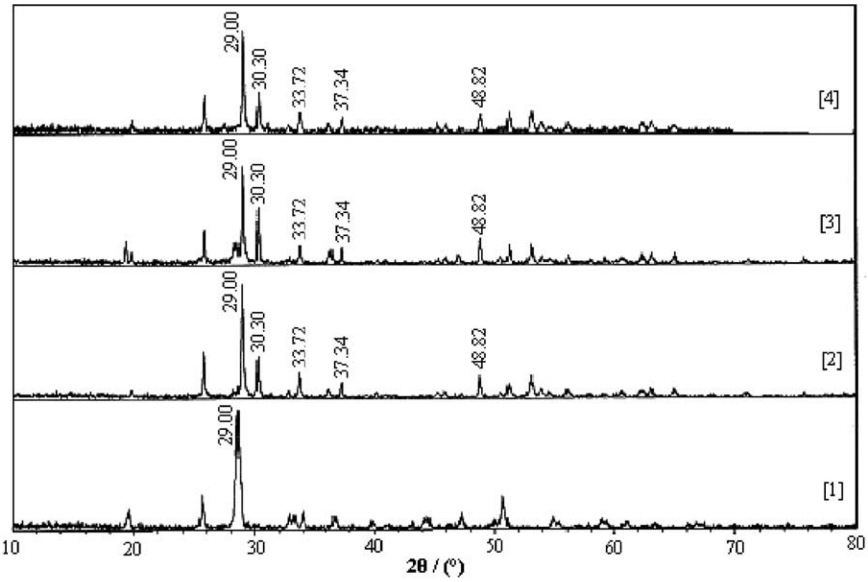

Fig. 6. X-ray diffractogram of single Sb_2O_3 calcined at different temperatures: [1] 673 K; [2] 773 K; [3] 973 K; [4] 1173 K.

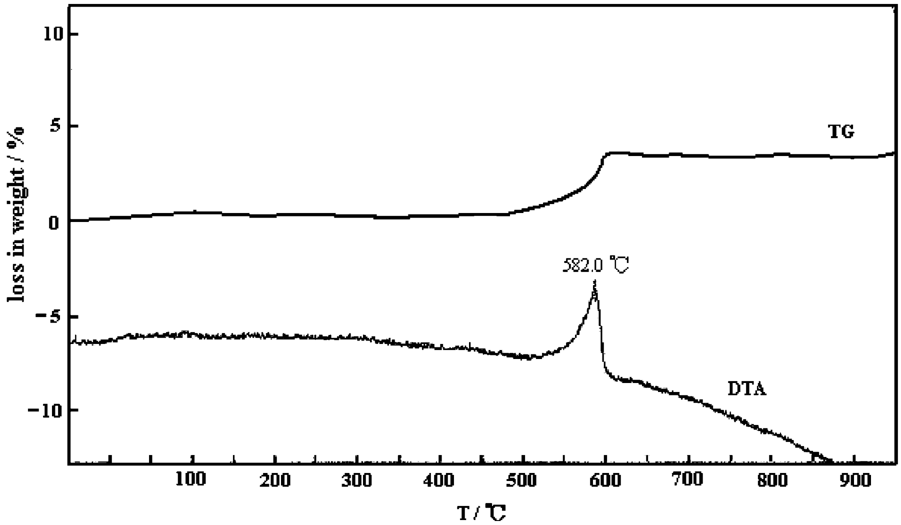

Fig. 7. TG–DTA curve of Sb_2O_3.

and the notation and effective electric charge of this defect can be expressed as $Sb^{\times}_{Sn}$ [14]. The energy level of this defect is generally near to the top of valence band of conduction band to be a donor level. The vacancy bound flabbily is easy to be excited to fall in valence band when accept a little of energy because the interaction between the negative electricity center and the vacancy is weak. The vacancies in valence band have the properties of electrical conductivity and thermal conductivity to make SnO_2 crystal a semiconductor to be P-type semiconductor. The resistivity of the sample calcined at 773 K or above 773 K has a significant decrease. At this time, Sn^{4+} lattice were substituted not only by Sb^{3+} ions but also by Sb^{5+} ions because of the oxidation of Sb^{3+} ions to

Table 4
Cell parameters and cell dimension of ATO calcined at different temperatures

Calcining temperature (K)	Cell parameters			Cell dimension (nm^3)
	a (nm)	*b* (nm)	*c* (nm)	
673	0.47484	0.47484	0.31881	0.07188
773	0.47218	0.47218	0.31881	0.07108
1073	0.47424	0.47424	0.31784	0.07148

Sb^{5+} ions from Fig. 6. When one Sb^{5+} ion substitutes one Sn^{4+} ion to form a defect, this defect is equal to a univalent positive ion bound by an electron flabbily ($Sb^{+}_{Sn} + e^{-}$) because Sb^{5+} ion has one more positive charge than Sn^{4+} ion, the effective electric charge mark of this defect can be expressed as $Sb^{\times}_{Sn}$. This defect will give out electron with the formula of $Sb^{\times}_{Sn} + E_D \rightarrow Sb\cdot_{Sn} + e'$ to be a donor defect. The localized energy level formed by this defect is located in the forbidden band under the bottom of conduction band. When an electron accepts energy equal to or larger than E_D, this electron will be excited into conduction band and form conductive current carrier to further make SnO_2 crystal a semiconductor to be N-type semiconductor. The substitution of Sb^{3+} ion for Sn^{4+} lattice is more difficult than that of Sb^{5+} ion relatively, because the mobility rate of electron is larger than that of cavity [15] and the radius of Sb^{3+} ion is larger than that of Sn^{4+} while the radius of Sb^{5+} ion is less than that of Sn^{4+} ion. So the electrical conductivity increases with calcining temperature at the outset, while when calcining temperature > 1073 K, the resistivity increases on the contrary and the electrical conductivity decreases, most likely because Sb^{5+} ions are reduced to Sb^{5+} ions partially. The change trend of the cell parameters and the cell dimension of SnO_2 doped by antimony calcined at different temperatures form Table 4 suggests the change of oxidation state of antimony.

4. Conclusion

Homogenous precipitation method with urea as precipitant is successfully used to prepare flake conductive pigment with both electrical conductivity and pearlescent luster by coating antimony doped tin dioxide on mica titania surface. The optimum technological parameters during preparation are as follows: the temperature of urea hydrolysis is 368 K, the final pH value is 5.0–6.0, the molar ratio of Sn^{4+}/Sb^{3+} is 12.5:1 and mica titania is added just before the hydrolysis of Sn^{4+} or Sb^{3+} ions to form precipitate. The conductive mechanism is mainly caused by the substitution of Sb^{3+} ions or Sb^{5+} ions for Sn^{4+} lattice and the formation of impurity defect.

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