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ORIGINAL PAPER

Preparation and colloidal dispersion behaviors of silica sol doped with organic pigment

Yunjie Yin · Chaoxia Wang · Youjiang Wang

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Abstract Silica sol doped with organic pigment was prepared by hydrolyzing tetraethoxysilane with a basic catalyst via dispersing pigment in silica sol. The colloidal properties of SiO_2/pigment hybrid sol and its deposited film were investigated. The presence of pigment in SiO_2/pigment hybrid sol affects the Zeta potential, particle size and surface tension compared to the silica sol without pigment. The SiO_2/pigment hybrid sol exhibited good dispersion stability in the centrifuge process. The maximum absorption wavelength was consistent with that of the pigment disperse solution, indicating that the pigment in SiO_2/pigment hybrid sol remained unchanged. Thermogravimetric analysis of the contents of organic component in silica sol and SiO_2/pigment hybrid sol were conducted, and the differential value was ascribed to the weight of the pigment and the condensate of polyoxyethylene octylphenol ether (OP-10) and γ-Glycidoxypropyltrimethoxysilane (KH-560). The surface topography of SiO_2/pigment hybrid silica film was characterized by AFM. The analysis of silica sol doped with organic pigment provides useful information for an effective pathway to disperse pigment on fiber and other substrates.

Keywords SiO_2/pigment hybrid sol · Colloidal property · Film · Stability · Gelation

Y. Yin · C. Wang (✉)
Key Laboratory of Eco-Textile, Ministry of Education, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China
e-mail: wangchaoxia@sohu.com

Y. Yin · Y. Wang
School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, USA

1 Introduction

Organic pigments are widely used as colorants for coatings, inks and plastics mainly because of their good color strength, brilliance, photosensitivity, transparence and high thermal stability [1, 2]. Different from dyes, pigments in textile industry usually present strong intermolecular aggregation and low polarity, and are insoluble in water due to no or few water-soluble groups. The pigments need to be finely ground and dispersed in an organic media to yield a gloss appearance, lighting efficiency, and high material utilization [3–7]. The principle for achieving a fine dispersion is a thermodynamically driven interaction among dispersant molecules, pigment particles and solvents in a collective manner by mutual non-covalent bonding, including electrostatic charge attraction, hydrogen bonding, p–p stacking, dipole–dipole interaction, and van der Waals forces. For practical applications, pigment dispersion is optimized for low viscosity, narrow range of size distribution, and long-term stability. Low molecular-weight surfactants are often used as dispersants for pigments, but they often lack the stability for long-term storage [3, 8, 9].

The sol–gel route is the most commonly employed method for the preparation of organic–inorganic hybrids at micro-scale and even at molecular level in mild conditions [10, 11]. The thin and transparent gel film can be formed on the surface of a substrate by a coating process [12]. They can improve the properties of the substrate effectively. Various precursors based on silicon, titanium, aluminum and zirconium have been used in sol–gel process for synthesis of the inorganic parts [10, 13, 14].

Organic pigments modified with silicon-based inorganic materials have attracted significant interest in recent years because of their inherent inert and superior durability properties derived from silicon-based materials [6, 15–18].

Jesionowski et al. [19] synthesized a silica, for use as a selective adsorbent of organic dyes by the sol–gel technique. Fei et al. [20] grafted a naphthol red pigment onto inorganic silica core to enhance the heat resistance, color strength, and dispersion stability of the pigment. No details are represented in the literature on basic hybrid silica sol doped with pigment and its film properties [21–23].

In previous work, the authors prepared several types of color hybrid silica sols doped with direct or reactive dyes which were then successfully coated on cellulose fibers [12, 24]. The current study reported focuses on color SiO_2/pigment hybrid sol as coating on textile fibers in order to improve their color fastness, hydrophobicity, anti-bacterial property, anti-UV, flame resistance, among others. To be used as an effective coating on fibers, a stable color SiO_2/pigment hybrid sol needs to be synthesized. During this paper, the authors deal mainly with the colloidal properties, such as particle size, Zeta potential, surface tension, stability and color property. The thermal property of the hybrid silica film is investigated and the surface morphology of the silica film is discussed.

2 Materials and methods

2.1 Materials

Analytically pure tetraethoxysilane (TEOS, M.W. 208), ethyl alcohol (EtOH) (95 wt%), polyethylene glycol 600 (PEG 600) and $NH_3{\cdot}H_2O$ were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The pigment blue FFG (Fig. 1) was supplied by Jiangsu Multicolor Fine Chemical Industry Co., Ltd (Wuxi, China), which was of technical grade. The polyoxyethylene octylphenol ether (OP-10) was provided by Jiangsu Haian Petrochemical Co., Ltd (Haian, China), which was of technical grade.

2.2 Synthesis of silica sol doped with organic pigment

The basic silica sol was prepared by placing TEOS solution (diluted with 8.7 g EtOH and 15.8 g TEOS) into the mixture containing 3.2 g $NH_3{\cdot}H_2O$ (0.1 mol/L), 7.2 g EtOH, 1.6 g PEG and 13.5 g H_2O in a flask. The mixture was mixed with a magnetic stirring apparatus at room temperature [12, 25].

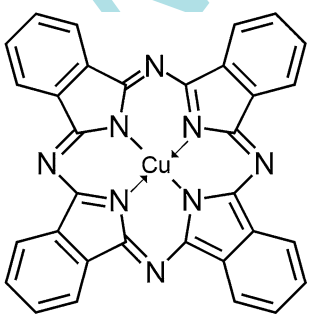

Fig. 1 The chemical formula of pigment blue FFG

2 g pigment blue FFG and 0.5 g OP-10 were added into 47 g H_2O, and then 0.5 g γ-Glycidoxypropyltrimethoxysilane (KH-560) was added into the mixture. After stirring for 30 min, the solution was dispersed with an ultrasonic homogenizer for 30 min.

The pigment disperse solution was doped into 50 g basic silica sol, then the mixture was stirred at 50 °C for 6 h with a magnetic stirring apparatus and aged for 48 h.

The control sample pigment disperse solution was prepared by doping 2 g pigment blue FFG into the mixture of 0.5 g OP-10 and 97.5 g H_2O.

2.3 Preparation of SiO_2/pigment hybrid film

The SiO_2/pigment hybrid film was prepared via spin-coating methods. 5 g SiO_2/pigment hybrid sol was dropped onto a mica sheet at the speed 800 rpm in 10 s. Then the rotor was sped up to 4,000 rpm to coat for 50 s. The coated mica sheet sample was dried at 60 °C for 20 min and finally baked at 150 °C for 3 min in a curing oven with a thermal annealing speed of 3 °C/min. The process is illustrated in Fig. 2.

2.4 Particle size measurement

The particle size distribution and Zeta potential of the sols was measured via Nano-ZS90 Zetasizer Nano series supplied by Malvern Instruments Ltd (Worcestershire, UK) at 25 °C. The scanning data and distribution curve were analyzed by DTS software.

2.5 Surface tension measurement

The surface tension was measured by Wilhelmy Plate method and the Du Noüy Ring method using the Krüss DSA100 Drop Shape Analysis System (Krüss GmbH, Hamburg, Germany) at 25 °C. The surface tension was recorded when the water drop was the largest below the sample pinhole, and calculated from,

$$\gamma = \mathrm{Fmg}/\mathrm{R} \quad (1)$$

where γ is the surface tension (N), F is a correction factor, m is the mass of the drop (kg), g is the acceleration of gravity (m/s^2), and R is the radius of the dripper (m). For the same device and experimental location, F, g and R are constants, and therefore the surface tension γ is proportional to the mass of the drop.

2.6 Centrifugal stability of the silica sols

The silica sol was placed into centrifuge tubes and centrifuged at 3,000 rpm for different time durations. Then the

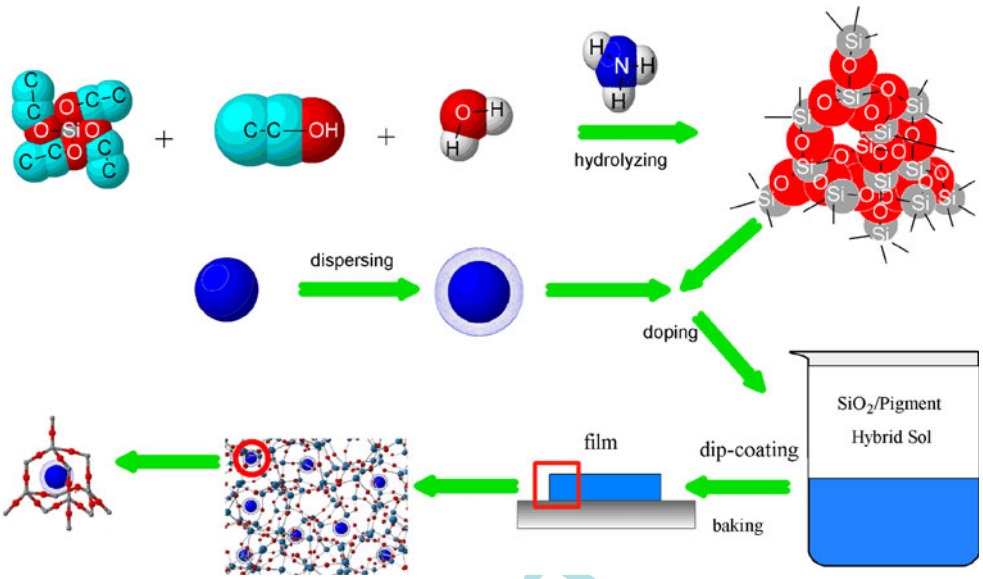

Fig. 2 Schematic of SiO_2/pigment hybrid sol doped with pigment and its gelation process

centrifuged solution was diluted with ethanol (1:40) and measured for absorbance with a TU-1901 UV–vis spectrophotometer (Puxi Tongyong Apparatus Ltd, Beijing, China) over the wavelength range of 550–750 nm.

2.7 Thermogravimetric (TG) analysis of the hybrid silica film

Thermogravimetric analysis of silica was carried out on a Q5000IR TGA (TA Instruments) Thermogravimetric Analyzer under air flow, at a heating rate of 20 °C/min and up to 650 °C.

2.8 Atomic force microscopy (AFM) measurement

The topography of the silica sol coatings on mica sheet was investigated at 25 °C and 40% relative humidity using a CSPM4000 AFM made by Benyuan Co., Ltd (Guangzhou, China) operating in contact mode. The tip slowly scanned across the surface of the coatings. The force between the atoms on the surface of the scanned material and those on the scanning tip lead to the tip to deflect. This deflection was recorded using a laser focused on the top of the cantilever and reflected onto a photodetector. The photodetector signals were used to map the surface characteristics of specimens with resolutions down to the nanometer scale.

3 Results and discussion

3.1 Zeta potential of silica sols

The Zeta potentials of silica sols with or without pigment are analyzed to estimating their disperse stability.

Figure 3 shows that the peak values of Zeta potential of the silica sol and SiO_2/pigment hybrid sol are −34.4 and −15.8 mV, respectively. After the pigment disperse solution compound is added, the Zeta potential distribution is changed due to charge redistribution in a more balanced state. As the disperse agent OP-10 is nonionic and the amount of anionic KH-560 is very small, the Zeta potential of the pigment disperse solution is low. After the two solutions are mixed, the negative charges in the silica sol component transfer to the pigment disperse solution component, causing a decrease in the overall Zeta potential and therefore a decrease in the disperse stability.

Also from Fig. 3, two peaks are seen in the SiO_2/pigment hybrid sol distribution curve. The weak peak is near Zeta potential peak of silica sol (−34.4 mV), suggesting that the charges of SiO_2/pigment hybrid sol may not be very uniform and there are some regions with high silica sol concentration.

3.2 Particle sizes of silica sols

The particle size reflects the degree of aggregation the sol particles. The higher the aggregation degree, the larger the particle size of the sol. The particle size is usually directly

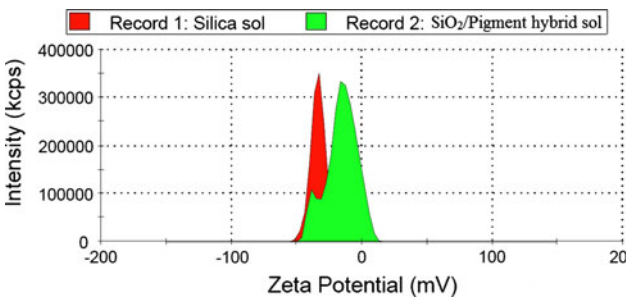

Fig. 3 The comparison of Zeta potential distributions between silica sol and SiO_2/pigment hybrid sol

affected by the Zeta potential which affects particle dispersion.

As seen from Fig. 4, the average particle size of the silica sol is 32.7 nm, that of the pigment disperse solution is 91.3 nm, and that of the SiO_2/pigment hybrid sol is much larger at 220.2 nm. The silica sol is a dispersion system that is thermodynamically unstable. According to the Zeta potential of the SiO_2/pigment hybrid sol (Fig. 3), the decrease of the Zeta potential can result in the aggregation of the silica sol particles. From the data of the particle size in Fig. 4, the pigment surface is surrounded by multilayer silica sol particles. The silica sol particles tend to automatically sequence themselves around the pigment particles under the electrostatic repulsion forces. Because a single layer of particles are thermodynamically unstable, the particles have a tendency to distribute in multilayers.

3.3 Surface tensions of silica sols

Surface tension of silica sol is closely related to its interaction with substrates in terms of the wetting and adsorption. The surface tension was measured according to the sessile drop method (Fig. 5).

From Fig. 5, the surface tension of silica sol is found to be 28.7 mN/m and that of SiO_2/pigment hybrid sol is 43.6 mN/m. Among the components in silica sol, ethanol and surfactant exhibit low surface tension and they will reduce the surface tension of the mixture. When the pigment disperse solution is doped into the silica sol, the large amount of water added (surface tension of water is about 72 mN/m), leads to an increase of the surface tension in the pigment disperse solution [26], from 28.7 to 43.6 mN/m.

3.4 Color properties of silica sols

From Fig. 6, the absorbance of the SiO_2/pigment hybrid sol at the maximum absorption wavelength is slightly lower than that of the pigment disperse solution. The absorbance of pigment disperse solution is 0.58 while the absorbance of SiO_2/pigment hybrid sol is 0.55. The change is mainly due to the disparate polarities of the solutions. In these two solutions, the polarity of the pigment disperse solution, which contains more H_2O, is stronger, while the polarity of SiO_2/pigment hybrid sol, which contains more ethanol, is weaker. The color of pigment blue is aroused by the $\pi \rightarrow \pi^*$ energy transition when the chromophore groups

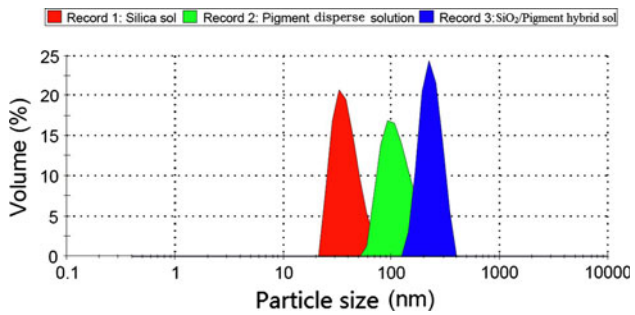

Fig. 4 The comparison of particle sizes among silica sol, pigment disperse solution and SiO_2/pigment hybrid sol

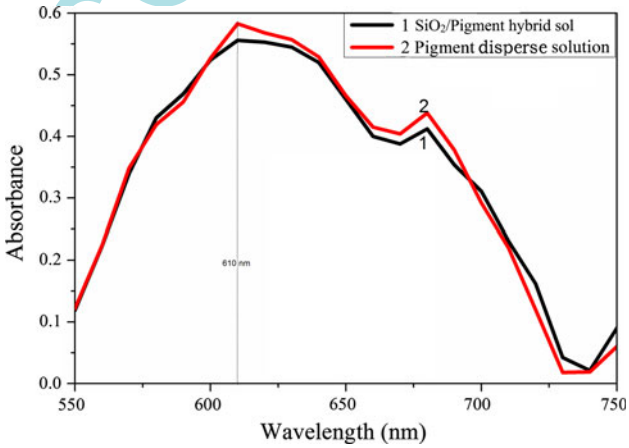

Fig. 6 The comparison of solution colors between pigment disperse solution and SiO_2/pigment hybrid sol

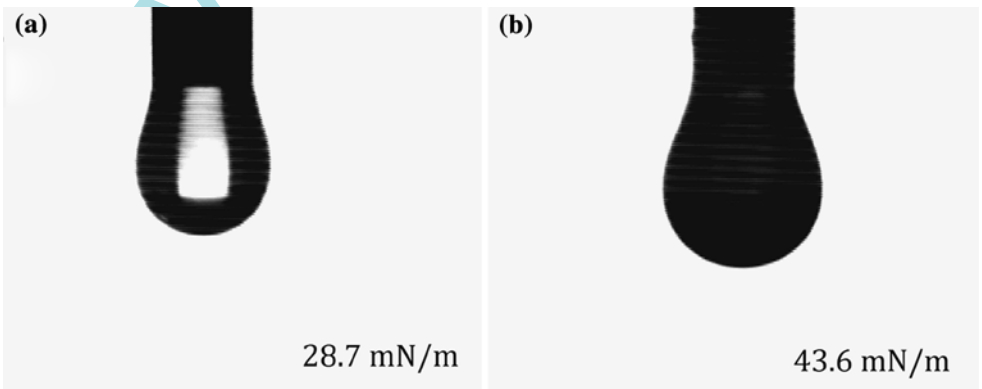

Fig. 5 Surface tensions of silica sol (**a**) and SiO_2/pigment hybrid sol (**b**)

are irradiated. The ionization of the dye molecules increases in a solution with high polarity (such as H_2O), and the electric charge in the conjugated system can transport more easily, which leads to an increases in the absorbance [12, 27].

From Fig. 6, the maximum absorption wavelengths for both systems remain the same at 610 nm. This indicates that the chromophore groups of the pigment blue are not damaged in the SiO_2/pigment hybrid sol and the conjugated systems are essentially not altered, and therefore the color hue of the hybrid sol remains identical to that of the pigment disperse solution.

3.5 Centrifugal stabilities of pigment disperse solution and SiO_2/pigment hybrid sol

The centrifugal stabilities of the pigment disperse solution and SiO_2/pigment hybrid sol represent the ability of the pigment and silica sol to resist external force.

From Fig. 7, the absorbance of the pigment disperse solution at the maximum absorption wavelength (610 nm) is 0.57 while centrifuging 15 min, and while centrifuging 60 min, the absorbance of the pigment disperse solution at the wavelength 610 nm is 0.53. From Fig. 6, the absorbance of the original pigment disperse solution at the maximum absorption wavelength (610 nm) is 0.58. The decrease (0.05) of absorbance between the original solution and the centrifuged solution for 60 min indicates good stability.

From Fig. 7, the absorbance at the maximum absorption wavelength (610 nm) of the SiO_2/pigment hybrid sol shows a slight decrease with the increase of centrifugal time from 0.54 to 0.52, which indicates that the SiO_2/pigment hybrid sol is relatively stable. Fig. 7 also shows that the maximum absorption wavelengths are not changed, and the total absorbance curves remain similar. This illustrates that the pigment in the SiO_2/pigment hybrid sol is stably dispersed. The stability of the hybrid silica sol is mainly due to the Zeta potential of the sol. From Fig. 3, the Zeta potential of the sol is negative, and the electrostatic repulsion among the hybrid silica sol particles keeps the particles separated other, even under the centrifugal condition.

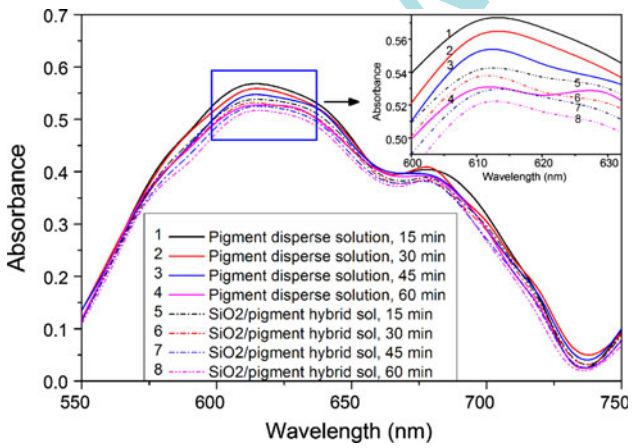

Fig. 7 Centrifugal stabilities of pigment disperse solution and SiO_2/pigment hybrid sol in different time

3.6 TG analysis of silica film

TG analysis provides information on content of the components in the silica sol and the SiO_2/pigment hybrid sol which is useful to investigate the properties of the silica deposition.

From Fig. 8, the organic components in the silica sol and SiO_2/pigment hybrid sol begin to degrade at about 275 °C, and end at about 625 °C. The weight loss of the silica film is 4.9%, and the weight loss of hybrid silica film is 7.1%. The weight loss at temperature below 275 °C mainly is attributed to H_2O and the weight loss of silica sol at temperature range between 275 and 625 °C mainly is the residual siloxane branched chains. For the hybrid silica film, besides the residual siloxane branched chains, pigment and the condensate of OP-10 and KH-560 contribute to addition weight loss.

3.7 AFM measurement of silica film

After spin-coating on the mica plate, the film is characterized by AFM. The particle size and height of hybrid silica film are analyzed by an imager analysis software (Fig. 9).

From Fig. 9a, the micro-surface topography of the film is scraggly, reflecting the pigment particles packed by SiO_2/pigment hybrid sol. The average height of the deposition is 35.9 nm. From Fig. 9b, the particle size distribution spans over a wide range with an average particle size

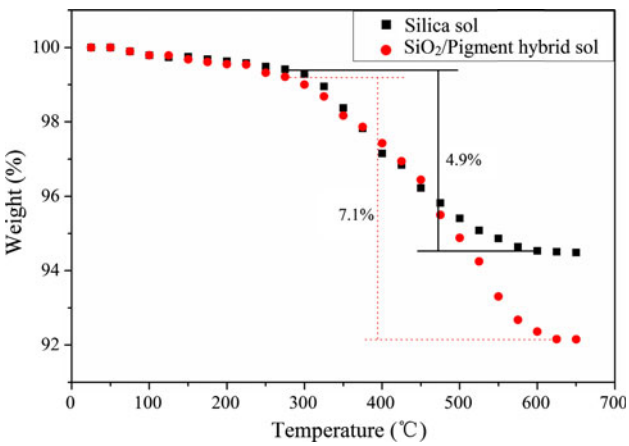

Fig. 8 TG analysis of the silica sol and SiO_2/pigment hybrid sol

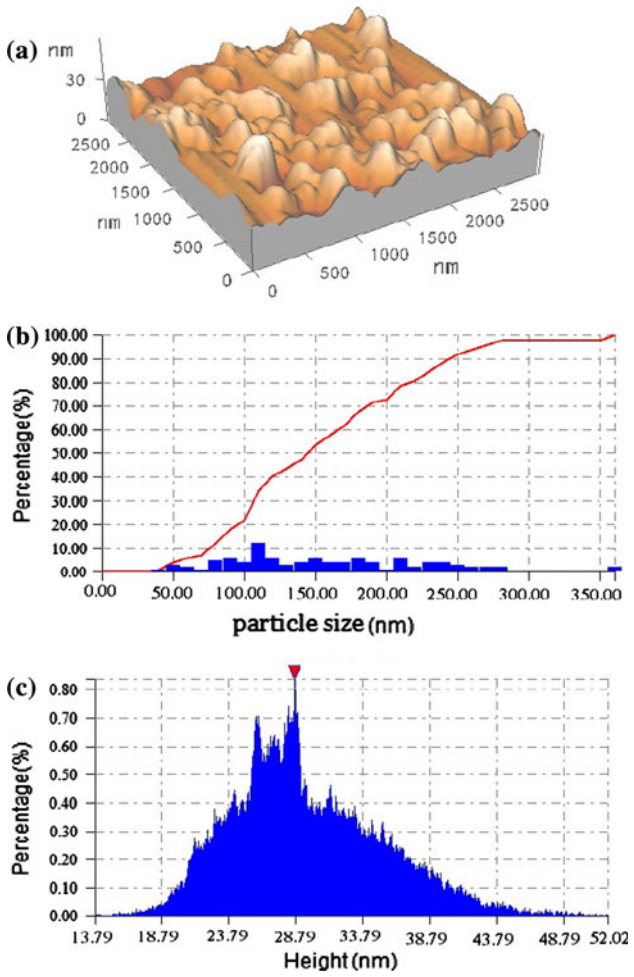

Fig. 9 The micro-surface topography of hybrid silica film by AFM

of 153.3 nm. Compared to the particle size in Fig. 3, this particle size of the silica film is smaller than the particle size of SiO_2/pigment hybrid sol, which might be due to the dynamic light scattering technology of the Zetasizer. Generally speaking, smaller nanoparticles have a higher moving speed based on Brownian Motion in solution [9]. The moving range of the nanoparticles, including the particle size and the thickness of the solvent layer around the nanoparticle, is larger than the actual particle size [28, 29]. From Fig. 9c, the height distribution is similar to the particle size distribution (Fig. 9b). Although the peak value of the height distribution is found between 25.0 and 29.0 nm, the average height is 35.9 nm from the imager analysis software.

4 Conclusions

This study focuses on hybrid silica sol by doped organic pigment disperse solution in the inorganic basic silica. The Zeta potential of the silica sol was −15.8 mV, the particle size of SiO_2/pigment hybrid sol was 220.2 nm and the surface tension of the SiO_2/pigment hybrid sol was 43.6 mN/m. The stability of SiO_2/pigment hybrid sol was relatively good and the maximum absorption wavelength was consistent with that of the pigment disperse solution. The content of organic component in SiO_2/pigment hybrid sol was 7.1% from Thermogravimetric (TG), and was larger 2.2% than that of the silica sol, and this difference is mainly attributes to the weight of pigment and the condensate of OP-10 and KH-560. The atomic force microscopy (AFM) analysis revealed an irregular particle deposition, and the average particle of the deposition was 153.3 nm and the height was 35.9 nm. These analyses of the colloidal and film properties provide important information for the investigations and applications of SiO_2/pigment hybrid sol as an effective coating for fibers, textiles and polymers.

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