Materials Research Express

PAPER

TiN-based organic-inorganic composite films with dual functions of solar control and low-emission for energy-saving coatings

Yachao Ma¹, Daoyuan Yang, Qiao Jiang, Kai Zhu, Huiyu Yuan, Junyan Cui and Lin Yuan

¹ School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, Henan, People’s Republic of China
² Ruitai Technology Co., Ltd, People’s Republic of China
E-mail: yangdaoyuan@zzu.edu.cn

Keywords: titanium nitride, organic-inorganic composites film, optical property, thermal insulation, energy-saving

Abstract

With the fast development of modern intelligent buildings, the demand for a comfortable environment and ‘low carbon’ technologies, for example, energy-saving buildings, becomes more intense. Thermal insulation coatings as one of the most promising routes to alleviate the energy consumption of buildings attract extensive attention in recent years. In this work, titanium nitride-based organic-inorganic composite films (TiN O₁/films) were introduced as the thermal insulation coatings to window glass via blade coating method. Additionally, two different synthesis methods were adopted to prepare the inorganic TiN nanoparticle and its effect on the optical property of the coatings was studied detailedly via the ultraviolet-visible-near-infrared (UV–vis–IR) spectrophotometer and Fourier transform infrared spectrometer characterizations. In addition, the thermal insulation properties of the films were characterized by a system that simulates the natural environment. Various characterizations show that the synthesized TiN O₁/films can not only pass through the visible light but also has high reflectance at the mid-infrared range, that is with the functions of solar control and low emission, well satisfying the requirements of the energy-saving coatings for window glass. These results demonstrated the good feasibility of TiN O₁/films in thermal insulation coatings, and also provide a direction for the development of more novel thermal insulation materials with large-scale.

1. Introduction

In recent years, large windows and glass curtain walls are widely used in the architecture field. However, the severe energy consumption of buildings due to the poor thermal insulation property of glass leads to large-cost and uncomfortable feelings for people [1, 2]. In order to improve energy efficiency and reduce energy consumption, thermal insulation coatings have been applied to the glass as one of the energy-saving and emission reduction approaches [3]. At present, there are two kinds of thermal insulation coatings [4]. One is the solar control film, which can reflect the near-infrared solar radiation (which occupies about 50% of the total solar radiation) while allowing natural light to pass through, therefore it can be applied to hot summer areas [5]. Another is the low-emission film, which has high reflectivity in the mid-far infrared region (the infrared radiation of object at room temperature is in this range) and limits infrared radiation absorption of glass to reduce the emission of mid-far infrared radiation [6]. Therefore, it can be used as a thermal insulation coating in the cold climate-areas. Additionally, to meeting the requirements of thermal insulation coatings used for all weather conditions, multilayer films are explored and applied [4, 7]. However, such multilayer films are complex and high-cost. Hence, the development of novel energy-saving films, especially single-layer film, with dual functions of solar control and low-emission that can be used for both hot summer and cold winter areas is highly urgent [8–10].

Over the past few years, TiN film has attracted more and more attention in the field of energy conservation [11–13]. Primarily, TiN has good electrical conductivity and low-emission properties due to its special electronic structure [14–16]. Additionally, TiN exhibits good optical transmittance in the visible region, well meeting the requirements of the novel energy-saving film in optical theory. Therefore, TiN-based material can be regarded as

© 2020 The Author(s). Published by IOP Publishing Ltd
an ideal candidate for the single-layer energy-saving film on the glass that combines the function of solar control and low-emission [12, 13]. Currently, TiN films have been prepared by various methods, such as reactive magnetron sputtering, laser ablation, ion beam deposition and plasma-assisted chemical vapor deposition [4, 17, 18]. However, the methods mentioned above are complicated in operation, demanding in conditions and inapplicable to the preparation of energy-saving coatings on buildings with large-scale. Therefore, there is an urgent demand for a simple and efficient method to prepare the TiN energy-saving film. Blade coating method is simple, and the operation is convenient, which makes it possible for the preparation of thin films with large-scale. The properties of the composite film are not only related to the inorganic functional powder itself, but also to the dispersion of the powder in the film-forming agent. The better the dispersion of the slurry, the better the performance of the film. Generally, after the surface modification of the inorganic functional powder, it can be mixed evenly with the organic film-forming agents through a simple bead milling method to prepare a composite slurry for blade coating. After that, the composite slurry is dropped on the substrate, and the blade is pushed at a uniform speed to form a flat coating on the substrate surface; The final organic/inorganic (O/I) composite films are thus obtained via subsequent treatment like drying or ultraviolet irradiation. Besides, by adjusting the gap between the blade and the substrate, the thickness of the film can be adjusted simply and conveniently. This method can combine the functionality of inorganic nanoparticles with the flexibility of organic polymer matrices, being considered to be an ideal method for preparing architecture energy-saving coatings.

In this paper, TiN powder was synthesized by two different methods, namely hydrolytic sol-gel method (HSG) and non-hydrolytic sol-gel method (NHSG) respectively. After surface modification, it was dispersed into acrylic resin to prepare the composite slurry. Finally, a smooth slurry layer was evenly scraped on the glass substrate by blade coating. After a short period of ultraviolet irradiation, a uniform TiN O/I composite film can be obtained. The feasibility of the prepared TiN O/I film as a novel energy-saving film was studied, and the effects of TiN powder synthesized by HSG or NHSG methods on the optical and thermal properties of the film were discussed. The results show that the synthesized TiN O/I films exhibit good optical and thermal features, well satisfying the requirements for thermal insulation coatings on the glass.

2. Experiment

2.1. Materials

Titanium butyrate (TBOT), polyvinylpyrrolidone (PVP) and acetic acid (AcOH) were utilized as starting materials to prepare TiN powder. γ-methacryloxypropyl trimethoxy silane (KH570) was used to modify TiN. These chemicals were purchased from China National Medicines Co., and are analytical reagent grade without further purification. The acrylic resin (homemade) was used as the organic matrix, Phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (purchased from Aladdin Industrial Corporation) was used as the photoinitiator of acrylic resin.

2.2. Preparation of TiN nanoparticles

The preparation of TiN precursor via HSG: Firstly, a certain amount of PVP was dissolved in the aqueous solution of ethanol with magnetic stirring at 30 °C. Subsequently, AcOH was added to the solution and stirred for tens of minutes to make the mixed solution uniform. With continuously vigorous stirred, TBOT was dropwise added into the solution and the temperature was kept at 30 °C (the weight ratios of TBOT: AcOH: H2O: PVP were 10: 13.3: 8.3: 6.5). During the whole stirring process, the color of the solution changed from transparent to yellowish at the beginning of adding TBOT and then turned to transparent golden yellow after a few minutes of stirring. This phenomenon indicates the hydrolysis and condensation process of TBOT. After several hours of continuous stirring, a homogeneous sol was obtained.

The preparation of TiN precursor via NHSG: Firstly, take an appropriate amount of PVP dissolved in absolute ethanol. Then AcOH was added to the solution and stirred for tens of minutes to make the mixed solution uniform. Finally, TBOT was dropwise added into the solution with continuously vigorous stirred, the solution will gradually change from the transparent light-yellow to transparent golden-yellow (the weight ratios of TBOT: AcOH: EtOH: PVP were 10: 13.3: 16: 6.5). After several hours of continuous stirring, a homogeneous sol was obtained.

Both of the sol was dried at 60 °C for 24 h. With the evaporation of the solvent and other organic liquid phases, sol turned into gel and became xerogel in the end. The xerogel was ground to powders in a mortar prior to calcination. The precursor powders were placed into an Al2O3 crucible. Afterward, the carbothermal reduction and nitration were carried out at 1300 °C with a heating rate of 5 °C min−1 and maintained at the maximum temperature for 3 h. Samples were taken out after the furnace cooled down to room temperature.
normally. All reduction experiments were conducted in a nitrogen environment with a flow rate of 120 ml min\(^{-1}\).

2.3. Preparation of TiN-acrylic resin composite slurry
A certain mass of coupling agent KH570 was pre-dispersed in the aqueous solution of ethanol (the weight ratios of ethanol: deionized water were 9: 1), then adjusted the pH value of solution to 4 with AcOH. Afterward, TiN powder was well dispersed into the KH570 pre-dispersing solution with the assistant of ultrasonic (the weight ratios of KH570: TiN were 1: 5). The mixed solution was refluxed at 75 °C for 3 h. After the reaction, the TiN powder modified by KH570 (M-TiN) was separated using centrifugation, washed with absolute ethanol and then dried at 60 °C for 24 h in a vacuum oven.

Subsequently, 1.0 wt% M-TiN powder and 1.0 wt% photoinitiator were added into acrylic resin away from light. After bead milling for 4 h, TiN-acrylic resin composite slurry can be obtained.

2.4. Preparation of TiN O/I composite film
Finally, the slurry was evenly coated on a glass substrate with a blade coater (SLT-A,) and irradiated under ultraviolet light for 15 s, the TiN O/I film with a thickness of 40 μm can be obtained. The thickness of the film can be adjusted by adjusting the height between the coater and the glass substrate.

The preparation process of TiN O/I composite film and the sample pictures of each stage are shown in figure 1.

2.5. Characterization
The infrared spectrum of the precursor powder was characterized by Fourier transform infrared spectrometer (FTIR, Tensor II). The crystal phases of the final products were identified by x-ray diffractometer (XRD, Panalytical Empyrean Range) with Cu Kα radiation (λ = 0.1541 nm) at 40 kV and 30 mA. The morphology of the TiN powder was observed by scanning electron microscopy (SEM, Auriga FIB-SEM). The existence of KH570 on the surface of TiN nanoparticle was also investigated by FTIR. At the same time, the particle size distribution of the particles in the slurry is tested by laser particle sizes analyzer (Zetasizer Nano-zs90). Finally, the transmission measurements of the composite films were conducted at wavelengths ranging from 300 to 2500 nm on a UV-vis-NIR spectrophotometer (Agilent Cary 5000). Infrared reflectance in the range of 2.5–20 μm was measured by Fourier transform infrared spectrometer equipped with an integration sphere.
2.6. Thermal insulation performance test

The thermal insulation performance of the TiN O/1 composite film was evaluated by a system that simulates the natural environment. As shown in figure 2(a), the model house was constructed with a 2.0 cm thick polystyrene foam board, and one side window was covered with ordinary glass (ordinary model house) or glass coated with the synthesized TiN O/1 film (TiN model house). An infrared lamp (PHILIPS, 250W) was used as the heat source to simulate solar radiation, and the temperature sensor was employed to measure the temperature of the model house [19]. Figure 2(b) is the partially enlarged view of TiN coated glass and its theoretical optical diagram in the ideal case.

3. Results and discussion

3.1. Characterization of TiN powder

Figure 3(a) is the FTIR spectrum of the precursor powder, and 3(b) is the partially enlarged spectrum of 3(a). It can be seen from 3(b) that the absorption peak of the –C=O in PVP is located at 1666.23 cm\(^{-1}\), while the absorption peak in the HSG-TiN and NHSG-TiN precursors has red-shifted. This indicates that during the preparation of the precursor, PVP has undergone a complexation reaction with TBOT to form a stable
coordination compound; the more the peak shift, the more sufficient the reaction and the more coordination compounds are generated. Besides, comparing the FTIR spectra of the precursor powders of HSG-TiN and NHSG-TiN in 3(a), it can be found that the absorption peak of NHSG-TiN near 660 cm\(^{-1}\) (–Ti–O) is weakened, indicating that the hydrolysis of TBOT is suppressed without the participation of water in the reaction, the formation of –Ti–O–Ti– is reduced, so the reaction with PVP is enhanced, the red-shifted of –C=O absorption peak is more obvious \[20–22\].

Figure 4 shows the XRD patterns of TiN powder synthesized by two different methods, together with the standard diffraction profile of TiN as reference (JCPDS No.87-0628). All of the diffraction peaks could be indexed to the standard TiN pattern, and no impurity peaks are identified, indicating that the powder with high purity has been synthesized. However, comparing with the XRD pattern of TiN synthesized by HSG (HSG-TiN), it was found that the peak of TiN synthesized by NHSG (NHSG-TiN) is broader, which means that TiN particles produced by this method are finer. Commonly the grain size of the powder can be calculated by the Debye–Scherrer equation:

\[
D = \frac{k\lambda}{B \cos \theta}
\]

Where D is the average crystal size, \(k\) is a dimensionless shape factor, with a typical value of 0.89. \(\lambda\) is the x-ray wavelength (Cu K\(\alpha\) = 0.1541 nm), B is the line broadening at half the maximum intensity (FWHM), \(\theta\) is the Bragg angle (in degrees). Taking (200) peak for calculation, the grain size of HSG-TiN is 26.3 nm, and NHSG-TiN is 20.2 nm, respectively. Comparing the data of the two groups, it is preliminarily deduced that NHSG-TiN powder exhibits a smaller particle size.

Figures 5(a) and (b) show the SEM images of HSG-TiN and NHSG-TiN, respectively. It can be seen from figure 5(a) that there is a significant agglomeration of HSG-TiN and the particle size of some agglomerates is close to micron-scale, while the agglomeration of NHSG-TiN is lighter, having a size of 100–300 nm shown in figure 5(b). As is known that, TBOT is prone to hydrolysis in the presence of water. Meanwhile, the condensation of hydrolysate takes place to form a –Ti–O–Ti– three-dimensional network. And this three-dimensional network will cause the agglomeration of nanoparticles during subsequent sintering procedure. According to the infrared spectrum of the precursor, it can be seen that in the NHSG-TiN precursor, the formation of the –Ti–O–Ti– is suppressed, thus reducing severe agglomeration during the subsequent calcination process. Figures 5(c) and (d) are SEM images of HSG-TiN and NHSG-TiN with higher magnification, and it can be seen that both the agglomerates are composed of small particles with 20–30 nm.

### 3.2. Characterization of the composite slurry performance

An important factor that affects the homogeneous distribution of the slurry used for blade coating is the interfacial bonding between the inorganic nanoparticles and polymer matrix. Generally, nano-inorganic powder has a strong tendency to agglomerate due to its high surface energy and has a weak binding force with the polymer matrix because of the inert surface. Therefore, it is necessary to conduct some surface modification on the inorganic powder so that it can be well dispersed in the polymer matrix, for example, the utilization of a silane coupling agent. Figure 6 gives the reaction mechanism of silane coupling agent KH570 in the preparation
Figure 5. SEM images of HSG-TiN (a), (c) and NHSG-TiN (b), (d).

Figure 6. Reaction mechanism of KH570 in preparation of the modified TiN nanoparticle.
of modified TiN nanoparticle. The specific surface area of the TiN nanoparticle is large, and a large number of hydroxyl groups (–OH) will adsorb on the surface. In the process of heating and stirring, the silanol groups (–Si–OCH₃) of the KH570 hydrolyzed to form silanol bonds (–Si–OH), which can react with the –OH groups of TiN, forming a layer of organic compounds on the surface of TiN particles. The organic chains R of KH570 can not only cause a steric hindrance that prevents the TiN nanoparticle from agglomeration but also combine inorganic particles with the organic matrix, thus improving the homogeneous dispersion of the slurry.

To investigate whether KH570 was successfully grafted on the surface of TiN, the structural characterization of M-TiN was investigated by FTIR analysis. As shown in figures 7(a)–(c) represent the FTIR spectra of KH570, NHSG-TiN and KH570 modified NHSG-TiN (M-NHSG-TiN). Compared with NHSG-TiN, the spectrum of M-NHSG-TiN has two weak absorption peaks at 2946 cm⁻¹ and 2842 cm⁻¹, corresponding to the vibration absorption of -CH₃ and -CH₂ respectively [23]. Further, the absorption peaks at 1720 cm⁻¹ and 1637 cm⁻¹ correspond to C=O vibration adsorption and C=C vibration adsorption [24], respectively. And the –Si–O–C vibration absorption peak is located in the region of 1000–1200 cm⁻¹ [25]. All the absorption peaks mentioned above originate from KH570, demonstrating that KH570 was successfully grafted on the surface of TiN.

In order to investigate the effect of KH570 on particle size, TiN powder and acrylic resin were mixed and ball milled for 4h, and then the particle size distribution of the powder in the composite slurry was tested. Figure 8 shows the particle size distributions of HSG-TiN (a), KH570 modified HSG-TiN (M-HSG-TiN) (b), NHSG-TiN (c) and M-NHSG-TiN (d), respectively. Compared with HSG-TiN, it can be seen that the particle size of M-HSG-TiN is smaller in the acrylic resin, D₅₀ is 99.17 nm. Meanwhile, the standard deviation also becomes smaller (σ decreased from 36.45 to 27.64) meaning that the particle distribution is more concentrated. The same trend has been shown in NHSG-TiN. It is because that the KH570 can graft on the surface of the nano-TiN, causing the mutual exclusion and the steric hindrance effects, therefore agglomeration is controlled. Furthermore, compared with M-HSG-TiN, the particle size of M-NHSG-TiN is smaller in acrylic resin, and the particle distribution is more concentrated.

The sedimentation stability of slurry is another important property for the composite slurry, which reflects the dispersion performance of inorganic particles in an organic matrix. This performance can be tested by ultraviolet-visible spectrophotometer. A part of the slurry used for the particle size distribution test was centrifuged at 10000 r min⁻¹ for 10 min, and then the supernatant was used for the transmittance test to characterize the sedimentation stability of the TiN-acrylic resin slurry (the lower transmittance, the better sedimentation stability). As can be seen from figure 9, the transmittance of M-NHSG-TiN slurry and NHSG-TiN slurry at 550 nm are 28.34% and 17.52% respectively, indicating that the stability of the slurry is improved after modification. On the one hand, the agglomeration of TiN is significantly reduced after modification, the smaller particle size, the better dispersion performance. On the other hand, there is an organic group (R) on the surface of M-TiN, which has favorable adhesion and compatibility with acrylic resin. Therefore, the dispersion of TiN powder in acrylic resin was improved and the slurry became more stable after KH570 modification.
3.3. Film optical performance test

Figure 10 shows the transmittance spectra of M-HSG-TiN O/I film and M-NHSG-TiN O/I film. The background shows the solar radiation spectrum distribution of AM 1.5 (corresponding to the Sun standing 37° above the horizon). Both TiN O/I films have transmittance peaks located at 471 nm in the visible region, meanwhile, the transmittance in the near-infrared region is relatively low. The transmittance of TiN O/I composite film in the

---

**Figure 8.** Particle size distributions of HSG-TiN (a), M-HSG-TiN (b), NHSG-TiN (c) and M-NHSG-TiN (d) in acrylic resin.

**Figure 9.** UV–vis spectrophotometer of NHSG-TiN O/I slurry.
visible range is comparable to that of the TiN film prepared by reactive magnetron sputtering. Wu [26] prepared the TiN film by reactive magnetron sputtering, when the sputtering time is 1 min, the transmittance of the TiN film in the visible light range is about 30%, meeting the National Standards of the People’s Republic of China for coated glass (GB/T 18915–2013) and performance films for glass in building (GB/T 29061–2012) (the transmittance of Sun-E film in the visible light range should be greater than 30%, and the infrared reflectivity should be greater than 50%). That means the TiN O/I film can maintain good visible light transmission while blocking heat from infrared light, therefore, it can be used as a solar control film. Comparing the transmittance of two films, we can found the visible light transmittance of M-NHSG-TiN O/I film is slightly higher than that of M-HSG-TiN O/I film, while the transmittance in the near-infrared range is lower. Therefore, it can be inferred that M-NHSG-TiN O/I film has a better solar control ability compared with M-HSG-TiN O/I film.

As a transparent thermal insulation film on the glass, the particle size has a significant impact on its visible light transmission and near-infrared shielding properties. Firstly, for the transparent thermal insulation film, the particles with sizes far below the wavelength of visible light can effectively suppress light scattering and reduce the coating’s haze so as to ensure the higher visible light transmittance of the film. The loss of transmittance of nanoparticle-filled polymer composites due to scattering can be estimated from the equation below [27–29]:

\[ T = \frac{I}{I_0} \propto \exp \left( -\frac{32\varphi_p x^4 \lambda^4 n_m^4}{\lambda^4} \left( \frac{n_i}{n_m} \right)^2 + 2 \right) \]  

(2)

where \( I \) and \( I_0 \) are the transmitted and incident light intensity, \( r \) is the radius of spherical particles, \( \varphi_p \) is the volume fraction of inorganic particles, \( x \) is the optical path length, \( \lambda \) is the wavelength of incident light, and \( n_i \) and \( n_m \) are the refractive index of particles and polymer matrix, respectively. Equation (2) shows that the smaller particle size and good dispersion of nanoparticles in the polymer matrix can effectively decrease the light scattering. That is the smaller particle size, the higher visible light transmittance. Secondly, decreasing particle size is beneficial to reduce the NIR transmission rate, which can effectively improve the NIR shielding performance.

Figure 11 is the mid-infrared region reflection spectrum of the M-HSG-TiN O/I film and M-NHSG-TiN O/I film. The two spectra are very similar both of them have high mid-infrared reflectivity. As the wavenumber decreases (the wavelength increases), the reflectivity decreases slightly. However, the reflectivity of M-NHSG-TiN film is slightly higher than that of M-HSG-TiN film, and the average reflectance of the two kinds of films is 52.34% and 51.04% respectively. The reflectivity of TiN O/I composite film in the mid-infrared is similar to the TiN film prepared by chemical vapour deposition. Zhao [30] prepared the TiN film by chemical vapor deposition, and the infrared reflectance of the film is close to 50%, meeting the requirements of Sun-E film for infrared reflectance. That means M-NHSG-TiN O/I film can more effectively reduce indoor heat loss in the form of heat radiation, thus it can be used as a low-emission film. Especially, if this coating is applied as the thermal insulation coating.
3.4. Thermal insulation performance test

The model house as shown in figure 2(a) was used to evaluate the thermal insulation performance of the TiN O/I composite film. Figure 12 presents the inner temperature changes of the TiN model house and ordinary model house during the IR heating process and nature cooling process. In the IR heating stage, the temperature quickly increases in the ordinary model house (from 25.8 °C to 53.2 °C in 60 min), while the TiN model house shows a slower rise rate. In particular, the temperature of M-NHSG-TiN model house only increases from 25.5 °C to 46.5 °C in 60 min. The result indicated that most heat radiation is blocked by the TiN O/I composite film. The nature cooling process after heating was also examined. The temperature of ordinary model house shows an overall decrease of 26.8 °C from 53.2 °C to 26.4 °C. By contrast, the temperature of M-HSG-TiN model house drop from 48.2 °C to 27.4 °C (reduced by 20.8 °C), and the M-NHSG-TiN model house drop from 46.5 °C to 27.3 °C (reduced by 19.2 °C). This result indicated that the TiN O/I composite film, especially the M-NHSG-TiN O/I composite film exhibited excellent thermal insulation performance.
4. Conclusions

In this paper, high purity TiN powders were synthesized by HSG and NHSG, respectively. Compared with HSG-TiN, NHSG-TiN exhibit slightly smaller particle size. In addition, KH570 can successfully graft on the surface of TiN particle, which improves the homogeneous distribution and stable of TiN-acrylic resin slurry. Finally, TiN O/I films were prepared on glass substrates by blade coating method. Both M-HSG-TiN and M-NHSG-TiN O/I composite films have high visible light transmittance, low near-infrared transmittance and high reflectivity in mid-infrared, well meeting the requirements of new energy-saving films on the glass (the transmittance of the new energy-saving film in the visible light range should be greater than 30%, and the infrared reflectance should be greater than 50%). Especially, M-NHSG-TiN O/I film has better optical properties than M-HSG-TiN O/I film and performs better in the thermal insulation performance test. After IR heating the temperature of the M-NHSG-TiN model house increases by 21 °C, which is 6.4 °C lower than the ordinary glass model house. In the nature cooling stage, the temperature of M-NHSG-TiN model house only decreases 19.2 °C, while the ordinary glass model house decreases 26.8 °C. The coating preparation method used in this paper is simple and efficient, which provides a direction for the production of large-scale new thermal insulation coatings.

Acknowledgments

The research was financially supported by the National Key R&D Program of China (2017YFB0310701) and the wisdom gathered in Zhengzhou 1125 talents recruitment program (2060483).

Notes

The authors declare that they have no conflict of interest.

ORCID iDs

Daoyuan Yang @ https://orcid.org/0000-0001-5617-6169

References

[1] Su X and Zhang X 2010 Environmental performance optimization of window–wall ratio for different window type in hot summer and cold winter zone in China based on life cycle assessment Energy Build. 42 198–202
[2] Yao Y, Zhang L, Chen Z, Cao C, Gao Y and Luo H 2018 Synthesis of Ca3WO4 nanoparticles and their NIR shielding properties Ceram. Int. 44 13469–75
[3] Liu J, Chen B, Fan C, Shi F, Ran S, Yang J, Song X and Liu S-H 2018 Controllable synthesis of small size Ca3WO4 nanorods as transparent heat insulation film additives Crystengcomm 20 1509–19
[4] Lin X, Zhao G, Wu L, Duan G and Han G 2010 TiN thin films for energy-saving application prepared by atmospheric pressure chemical vapor deposition J. Alloys Compd. 502 195–8
[5] Mei S-Q, Ma W-J, Zhang G-L, Wang J-L, Wang J-L, Yang J-H and Li Y-Q 2012 Transparent ATO/epoxy nanocomposite coating with excellent thermal insulation property Micro Nano Lett. 7 12
[6] Huang S, Wang Z, Xu J, Wang L, Lu D and Yuan T 2009 Simulation of the spectra and determination of the optical constants of online low-emission glass from visible to mid-infrared region Thin Solid Films 517 2963–7
[7] Zhao G, Zhao C, Wu L, Duan G, Wang J and Han G 2013 Study on the electrical and optical properties of vanadium doped TiN thin films prepared by atmospheric pressure chemical vapor J. Alloys Compd. 569 1–5
[8] Chang S-C, Hung S-C, Ye C-S, Hsiao Y-J, Lin T-C, Cheng H-Z and Shen Y-I 2018 Thermal stability of SnOx/NiCrOx/Ag/AZO/SnOx glass multilayer films applied in low-emissivity glass J. Chin. Soc. Mech. Eng. 39 427–31
[9] Chen C-N, Wang Z-W, Wu K, Chong H-N, Xu Z-M and Ye H 2018 TiO2–TiN–TiO2 sandwiches for near-infrared plasmonic materials Acs Appl Mater Inter 10 14886–93
[10] Loka C, Park K R and Lee K S 2016 Multi-functional TiO2/Si/Ag(Cr)/TiN coatings for low-emissivity and hydrophilic applications Appl. Surf. Sci. 363 439–44
[11] Hao Q, Li W, Xu H, Wang J and Chu P-K 2018 VO2/TiN plasmonic thermochromic smart coatings for room-temperature applications Adv. Mater. 30 1705421
[12] Smith G B, Ben-David A and Swift P D 2001 A new type of TiN coating combining broad band visible transparency and solar control Renewable Energy 22 79–84
[13] Xiao L, Su Y, Chen H, Liu S, Jiang M, Peng P and Liu S 2011 Solar radiation shielding material for windows TiN studied from first-principles theory Appl. Phys. Lett. 99 061906
[14] Lu L, Luo F, Huang Z, Zhou W and Zhu D 2018 Substrate temperature effects on infrared emissivity of TiNx films Surf. Eng. 35 9–13
[15] Doiron B et al 2019 Quantifying figures of merit for localized surface plasmon resonance applications: a materials survey Acs Photonics 6 240–59
[16] Guler U, G V et al 2012 Performance analysis of nitride alternative plasmonic materials for localized surface plasmon applications Appl. Phys. B-Lasers O 107 7
[17] Meric V V, Molea A, Burnete V N, Neamtu B V and Negrea G 2018 Mater. Res. Proc. ed T F Marinca et al (Millersville: Materials Research Forum Llc) pp 134–42
[18] Chodun R, Nowakowska-Langier K and Zdunek K 2010 Morphology of the TiN coatings obtained by the IPD method with two frequencies of impulse plasma generation Surf. Coat. Technol. 205 528–31
[19] Lu X, Sun Y, Chen Z and Gao Y 2017 A multi-functional textile that combines self-cleaning, water-proofing and VO2-based temperature-responsive thermoregulating Sol. Energ. Mat. Sol. C 159 102–11
[20] Chen X, Fan J and Lu Q 2018 Synthesis and characterization of TiC nanopowders via sol-gel and subsequent carbothermal reduction process J. Solid State Chem. 262 44–52
[21] Liu M, Yan X, Liu H and Yu W 2000 An investigation of the interaction between polyvinylpyrrolidone and metal cations Reactive & Functional Polymers 40 55–64
[22] Giordano C, Erpen C, Yao W, Milke B and Antonietti M 2009 Metal nitride and metal carbide nanoparticles by a soft urea pathway Chem. Mater. 21 5136–44
[23] Yang W, Miao J, Qian J and Zhang Y 2012 On surface modification of nano-TiN with graft copolymer LMPB-g-KH570 J Disper Sci Technol 33 827–34
[24] Cheng G, Qian J, Miao J, Yang B, Xia R and Chen P 2014 The surface modification of TiN nano-particles using macromolecular coupling agents, and their resulting dispersibility Appl. Surf. Sci. 301 79–84
[25] Wang L, Li R, Wang C, Hao B and Shao J 2019 Surface grafting modification of titanium dioxide by silane coupling agent KH570 and its influences on the application of blue light curing ink Dyes Pigm. 163 232–7
[26] Wu J, Murakami R I and Kondo M 2003 Effects of nitrogen gas flow and film thickness on electric properties of TiN thin film deposited at room temperature Int. J. Mod. Phys. B 17 1177–82
[27] Tao P, Viswanath A, Schadler L S, Benicewicz B C and Siegel R W 2011 Preparation and optical properties of indium tin oxide/epoxy nanocomposites with polyglycidyl methacrylate grafted nanoparticles ACS Appl. Mater. Interfaces 3 3638–45
[28] Koziej D, Fischer F, Kranzlin N, Caseri W R and Niederberger M 2009 Nonaqueous TiO2 nanoparticle synthesis: a versatile basis for the fabrication of self-supporting, transparent, and UV-absorbing composite films ACS Appl. Mater. Interfaces 1 1097–104
[29] Caseri W 2008 Inorganic nanoparticles as optically effective additives for polymers Chem. Eng. Commun. 196 549–72
[30] Zhao G, Zhang T, Zhang T, Wang J and Han G 2008 Electrical and optical properties of titanium nitride coatings prepared by atmospheric pressure chemical vapor deposition J. Non-Cryst. Solids 354 1272–5