Journal of Alloys and Compounds 751 (2018) 215–223

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Tunable infrared radiation properties of hybrid films co-assembled with semiconductor quantum chips and exfoliated ultra-thin LDH nanosheets

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ARTICLE INFO

Article history:
Received 15 December 2017
Received in revised form
24 March 2018
Accepted 6 April 2018
Available online 11 April 2018

Keywords:
Tunable surface radiation
Layer-by-Layer assembly
Semiconductor quantum chip
Exfoliated LDH nanosheets

ABSTRACT

The controllability of glass surface radiation is of great significance on regulating temperature for applications in energy conservation in residential buildings. In this work, nano-scale hybrid films with tunable surface radiation are successfully prepared via layer-by-layer assembly of exfoliated layered double hydroxide (LDH) nanosheets with In_2O_3 quantum chips covering the surface of glass substrates. In this hybrid system, the ultra-thin LDH nanosheets are exfoliated from hexagonal plate-like particles of Mg-Al-NO_3^- LDH nanosheets after anion-exchange of Mg-Al-CO_3^{2-} LDH nanosheets. And In_2O_3 semiconductor quantum chips are obtained after an annealing treatment from $In(OH)_3$ nanosheets which are prepared in sodium oleate/indium chloride hydrothermal system. The prepared LDH nanosheets and In_2O_3 quantum chips are assembled layer-by-layer onto glass substrates to form the multilayer films. Morphological and structural evolution of the hybrid films is investigated by X-ray diffraction (XRD) and UV–vis absorption spectra. The characterization results show that the hybrid films exhibit ordered tunable structures, which predicts that the infrared emissivity can be adjusted throughout the infrared spectrum. The surface radiation properties of the hybrid films are studied, and the results show that the number of the layers has a significance influence on the surface radiation properties of the films. Attractively, the hybrid films possess thickness-dependent surface radiation properties with the lowest infrared emissivity of 0.420. The nano-scale hybrid films obtained in this work show great tunability on infrared emission and illustrate to be good candidates for saving energy in the field of energy conservation buildings and smart windows.

1. Introduction

In the recent years, the energy consumption is increasing rapidly due to the high-speed development of the world economy. The high energy consumption leads to the shortage of the fossil fuel reserves, excessive greenhouse gas emissions and further disturbs the climate balance, causes global warming and extreme weather [1,2]. Numerous efforts are being made to save fossil energy by developing renewable energy such as solar, wind, ocean, hydrogen, and carbon-neutral fuel [3,4]. Among these energy sources, solar radiation shows great advantages due to its natural clean energy source with no need for energy conversion. In contrast to the common energy conversion methods that require energy and sources to transfer energy, solar radiation is a passive enhancement of Earth's natural method [5]. Most radiative heat from solar radiation is concentrated in the infrared band at 8–14 µm. Until now, the control of surface radiation of materials at infrared band has remained a great challenge [6].

Nowadays, smart windows, comprised of functional films and glass substrates, have been applied for energy saving due to their ability to adjust the throughput of the sunlight and solar heat into the building [7]. Generally, these windows operate by blocking a large fraction of the sunlight on hot days, while transmitting solar

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https://doi.org/10.1016/j.jallcom.2018.04.073

energy in cold weather [8–10]. Through temperature -responsive solar energy modulation, windows with tunable infrared radiation films exhibits extraordinary effects in green building field [11–13]. These kinds of film show controllability on the emissivity of infrared radiation energy by modulating thermal radiation in the far infrared and microwave region in order to control the heating passed through [14]. Because of their tunability in infrared radiation and passive influence ability of energy, tunable infrared radiation films have great advantages in environmentally friendly fields and sustainable development fields [15]. Extensive works on the development of tunable infrared radiation films in this field have been reported, organic materials and inorganic materials are two kinds of important materials which show great potential in energy saving field. Organic polymers possess unique properties including light weight, corrosion-resistant, tractability and adjustable structures which can provide the possibility of tuning the infrared emissivity according to our need [16,17]. Yang et al. [18–20] prepared optically active polyurethanes (PUs) based on different enantiomeric excesses of isocyanate-phenols derived from tyrosine. Bu et al. [21,22] designed and synthesized a series novel optically active helical polyacetylenes derived from chiral phenylalanine and serine. However, organic polymers containing highly absorptive chemical bonds, e.g. C-H, C=O, N-H, etc., result in relatively high emissivity, which limit their applications in tunable infrared emissivity field [23]. Organic polymers also show poor thermal stability and opacity which is not applicable for tunable infrared radiation materials. In this way, inorganic materials show significant advantage in the infrared regulatory field due to its easily adjustable structure and transparency towards sunlight [24]. Lu et al. [25] have prepared the ferrite-based amorphous coatings with high infrared radiation properties on the surface of carbon steel substrate by plasma spraying process. Ye et al. [26]reported the preparation of “sandwich” core-shell composites via chemical deposition and seed-growth under ultrasonic irradiation. Although the core-shell composites achieved obvious emissivity variation from 0.785 to 0.424 by doping different metallic oxides, it lacks regulatory mechanism on infrared emissivity. These inorganic coatings (or metal materials) with smooth surfaces may have higher reflectance and lower absorptance resulting in low infrared radiation [27]. The compositions and microstructures of most of inorganic coatings have significant influence on infrared radiation [28]. However, it has been challenging to have the inorganic coatings applied in the tunable infrared areas due to uncontrollable compositions, microstructures and low emissivity character.

LDH nanosheets are two-dimensional (2D) layer materials consisting of positive charged brucite-like layers with charge balancing anions between the layers. During the past years, LDH films have attracted important attention for preparing low infrared emissivity materials due to their tunable properties and ordered nanostructure [29]. In this regard, Zhu et al. have successfully synthesized small lateral sized lactate intercalated Co-Fe LDH which had a relatively broad span on infrared emissivity [30]. Wang et al. described a facile approach to fabricate DNA/LDHs nanohybrid by co-assembly of exfoliated Ni-In LDH nanosheets with DNA [31], which could reach lower infrared emissivity at 0.528 comparing with bare LDH particles at 0.705. However, the effect of regulating infrared emissivity of these LDH films is not obvious and it lacks regulating on demand, which means that the infrared emissivity of these films could not be modified to meet the real needs. According to these problems, hybrid film is a better choice for smart windows coatings because it can change infrared emissivity by adjusting the thickness of the film. The two-dimensional In_2O_3 nanosheets, so-called quantum chips, are square piece-like nanostructures with a few tens of nanometers in lateral dimension possessing quantum size effect as quantum dots [32]. By controlling the shape, structure and size of the quantum chips, it is possible to easily adjust the size of the energy gap, the size of the exciton binding energy and the energy state of the exciton. With the increase of quantum chip size, the light absorption spectrum of quantum chips appears red shift phenomenon. In_2O_3 quantum chips have broad prospects with applications in the field of membrane assembly comparison as a two-dimensional building blocks due to the similar nanostructures as graphene and carbon nitride.

In this work, ultra-thin exfoliated LDH films was re-assembled with In_2O_3 quantum chips to fabricate 2D hybrid films on glass surface. The infrared radiation properties of hybrid films could be controlled by changing the number of layers of hybrid films because of its effects on the smooth of the surface. This preliminary work discussed the influence on infrared emissivity of the hybrid films by changing the number of the layers, presenting a new approach to the design and preparation of tunable infrared radiation materials. On the other hand, the design of this multi-component ordered assembly nanostructure further expanded the research scope of LDH nanosheets as the building blocks of the matrix assembly system, providing a new method for LDH nanosheets applying in the field of energy.

2. Experimental section

2.1. Chemicals and materials

Several chemicals of hexamethylenetetramine ($C_6H_{12}N_4$), potassium nitrate (KNO_3), nitric acid (HNO_3), formamide ($HCONH_2$), and absolute ethyl alcohol were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China), Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) and indium trichloride ($InCl_3 \cdot 4H_2O$, $\geq$99.90 purity) were obtained from Shanghai chemical reagent general plant. N-hexane (C_6H_{14}) was purchased from Tianjin Kay Tong Chemical Reagent Co., Ltd. Poly sodium-p-styrenesulfonate (PSS) was provided by Shanghai Macklin Biochemical Co., Ltd. All the above reagents were of analytical grade and used as received without further purification. Sodium oleate ($C_{17}H_{33}CO_2Na$) was of chemical grade purchased from Shanghai chemical reagent Co. Ltd. The quartz glass was supplied by Ai Pu optical quartz Co., Ltd, after being washed several times with absolute ethanol and HNO_3, it was cleaned with distilled water followed by drying in air.

2.2. Preparation of In_2O_3 semiconductor quantum chips

In a typical experimental procedure, 822 mg of sodium oleate was added to 120 mL of deionized water and dissolved by magnetic stirring at ambient temperature. To this 264 mg of $InCl_3 \cdot 4H_2O$ was added under continuous stirring. After stirring for 30 min, aforementioned mixture was transferred into a 200 mL Teflon-lined stainless-steel autoclave and kept in an oven at 150 °C for 3 h. After the hydrothermal treatment, the reactor was allowed to cool to room temperature, and the mixture was separated to get precipitation via high-speed centrifugal method. The as-obtained precipitation was washed repeatedly with a mixed solution of ethanol and cyclohexane (vol 4:1) and deionized water respectively, and then calcined in the tube furnace for 3 min under 400 °C after vacuum drying for 48 h under 60 °C. Finally, the In_2O_3 semiconductor quantum chips were obtained.

2.3. Preparation of exfoliated Mg-Al-NO_3^- LDH nanosheets

The procedures for synthesis of exfoliated Mg-Al-LDH nanosheets mainly consisted of three steps: (i) preparation of Mg-Al-CO_3^{2-} LDH nanosheets by coprecipitation method, (ii) anion