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In situ loading ultra-small Cu_2O nanoparticles on 2D hierarchical TiO_2-graphene oxide dual-nanosheets: Towards reducing fire hazards of unsaturated polyester resin

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HIGHLIGHTS

- We have synthesized and characterized the hierarchical Cu_2O—TiO_2—GO nanosheets.
- The influence of Cu_2O—TiO_2—GO nanosheets on fire hazards of UPR was investigated.
- TG-IR-MS results was used to reveal thermal degradation of UPR nanocomposites.
- Toxic volatiles originated from thermal degradation were clearly identified.

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ABSTRACT

Fire hazards have seriously hindered the commercial application of unsaturated polyester resin (UPR), and polymer inorganic nanosheet nanocomposites hold great promise in improving their flame-retardant properties. Herein, the hierarchical structured Cu_2O—TiO_2—GO nanosheets were synthesized and characterized by XRD, Raman, TEM and XPS. Then Cu_2O—TiO_2—GO nanosheets were incorporated into UPR matrix to obtain flame-retardant UPR nanocomposite. Incorporation of 2 wt% Cu_2O—TiO_2—GO nanosheets into UPR matrix resulted in an obvious reduction in PHRR and THR by 29.7 and 19.1%. TG-IR-MS results revealed that toxic pyrolysis gas such as benzene, CO and aromatic compounds greatly were decreased. In addition, RIIR spectra demonstrated the limited influence of Cu_2O—TiO_2—GO nanosheets on thermal degradation of UPR matrix, and SEM images of char residues showed that Cu_2O—TiO_2—GO nanosheets could improve their compactness. Based on the analysis of gaseous and condensed phase, a plausible flame-retardant mechanism was hypothesized to elaborate how Cu_2O—TiO_2—GO nanosheets work inside the flaming UPR nanocomposite. This innovative idea may be expanded to other polymer system and open a new door to develop polymeric nanocomposites with high performance.

1. Introduction

Unsaturated polyester resin (UPR), an economical thermoset material with prominent properties and good processability, has been extensively applied in fiber-reinforced composites industry in recent decades [1]. However, the high inflammability of UPR tremendously restricts its application. Moreover, a large amount of dense smoke combined with toxic effluent escapes when burning, which seriously threatens the health and lives of human trapped in fire scene. Over the past years, great effort such as developing new flame retardant has been dedicated to improve the flame retardance of UPR [2,3]. Notably, inorganic nanometer flame retardants have attracted more and more attention, due to the flame retardant efficiency and non-toxicity [4,5].

Graphene, an emerging monolayer of carbon atoms arrayed in honeycomb network, has showed exceptional superiorities over traditional materials in many potential fields such as sensors [6,7], electronics [8,9], hydrogen storage [10] and supercapacitors [11,12]. Considering the unique two-dimension layered structure and large specific surface area of graphene, it could act as a

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nano-barrier to slow down heat release, inhibit the transfer of inflammable gas into the flame zone as well as energy feedback, and retard the escape of toxic effluent [13]. Furthermore, the ability of graphene surface to capture free radicals during the combustion would slow down the flaming spread and catalyze carbonization [14,15]. Unfortunately, the flame retardant efficiency of graphene alone remains limited.

As is well-known, metal oxides including SiO_2, Co_3O_4, Sb_2O_3, Bi_2O_3, SnO_2 and so on have been usually utilized to improve the flame retardance of polymer in industrial application [16–18]. These metal oxides catalyze the formation of char residue, increase the strength of char residue and improve the graphitization of char residue during the combustion of polymer. Many works have proved Copper and copper oxides were excellent smoke suppressants for inflammable polymer [19,20]. In particular, Previous literature has reported Cu_2O nanoparticles exhibited excellent catalytic activity toward CO oxidation in $CO/O_2/N_2$ mixture [21]. As is well-known, the most of the dead are die of CO in fire accident. Up to now, our team has detailedly demonstrated that TiO_2 nanotube could reduce heat release and toxic smoke of burning polymer via absorbing free radicals, smoke particles and gaseous effluent [22,23]. Considering the boom of two-dimensional structure, the application of TiO_2 nanosheet in flame retardant polymer deserves exploring. To our knowledge, the relevant researches have not been reported until now.

In the paper, for the first time, we successfully in-situ loaded ultra-small Cu_2O nanoparticles onto hierarchical TiO_2—GO nanosheets through a one-pot hydrothermal reaction. Subsequently, hierarchical Cu_2O—TiO_2—GO nanosheets were added into UPR matrix and its flame-retardant behavior was investigated. Meanwhile, the analysis of gaseous and condensed phase were utilized to gain insight into the flame-retardant mechanism of Cu_2O—TiO_2—GO/UPR.

2. Experimental

2.1. Synthesis of Cu_2O—TiO_2—GO nanosheets

Hierarchical structured Cu_2O—TiO_2—GO nanosheets were synthesized through a one-pot hydrothermal reaction. 0.1 g graphene oxide (GO, homemade in the lab by Hummers' method [24]) dissolved in 25 mL tetrabutyl titanate liquid under mechanical stirring and ultrasonication for 6 h to get the wheat solution. Afterwards, 0.5 g $Cu(Ac)_2$ was added into the above solution under mild stirring for 24 h to obtain the homogenous mixture. Then the 3 mL hydrofluoric acid was dropped to the above mixture under strong stirring for 2 h until it turn into gel. The gel was incorporated to a 50 mL dried Teflon autoclave at 190 °C for 22 h. After that, the gray powder were centrifuged and washed with purified water and ethanol several times. To obtain HF-free hierarchical structured Cu_2O—TiO_2—GO nanosheets, the powder was immersed into 1 M NaOH and stirred for 12 h. Then it was filtered, washed with purified water and ethanol to neutral and dried in vacuum oven at 70 °C overnight. Obviously, pure TiO_2, Cu_2O—TiO_2 and TiO_2—GO nanosheets were synthesized through the same route.

2.2. Preparation of Cu_2O-TiO_2-GO/UPR nanocomposite

The preparative route of 2 wt% Cu_2O—TiO_2—GO/UPR nanocomposite was performed as follows: the calculated amount of Cu_2O—TiO_2—GO powder was incorporated into 60 g UPR matrix and stirred under ultrasonication for 24 h to get the homogenous mixture. A certain amount of benzoyl peroxide (BPO) was added into the above mixture and stirred under ultrasonication for 1 h. Then it was poured in the 100 × 100 mm teflon mould, degassed until bubbles disappeared, cured at 70 °C under vacuum for 3 h and post-cured at 120 °C for 4 h. To prevent the oxidation of Cu_2O nanoparticles during the preparation process, vacuum bag was used to seal teflon mould and degassed until interior air disappeared. For comparison, pure UPR, TiO_2/UPR, TiO_2—GO/UPR, Cu_2O—TiO_2/UPR and TiO_2—GO/UPR nanocomposites were prepared through the same route.

2.3. Characterization

Transmission electron microscopy (TEM) (JEM-2100F, Japan Electron Optics Laboratory Co., Ltd.) was applied to investigate the morphology of. X-ray diffraction (XRD) measurements were implemented on a Japan Rigaku D Max-Ra rotating anode X-ray diffractometer. The scanning speed and range were 4°/min and 10–80° respectively. X-ray photoelectron spectrometer (XPS) spectra were recorded using a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al Kα X-ray source ($h\nu$ = 1486.6 eV). Laser Raman spectroscopy measurements were performed using a SPEX-1403 laser Raman spectrometer (SPEX Co., USA) with excitation provided in back-scattering geometry by a 514.5 nm argon laser line. Thermogravimetric analysis (TGA) was carried out using a Q5000 thermoanalyzer instrument (TA Instruments Inc., New Castle, DE) under an air flow of 20 mL min^{-1}. The temperature was increased from room temperature to 800 °C at a linear heating

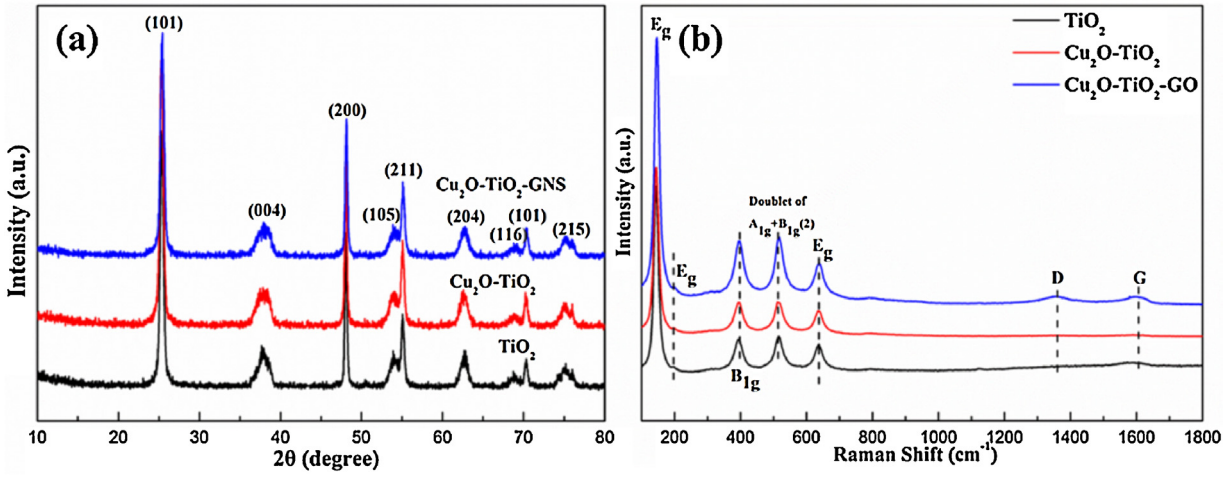

Fig. 1. XRD patterns (a) and Raman spectra (b) of TiO_2, Cu_2O—TiO_2 and Cu_2O—TiO_2—GO nanosheets.