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The effect of metal oxide decorated graphene hybrids on the improved thermal stability and the reduced smoke toxicity in epoxy resins

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HIGHLIGHTS

- Adding metal oxide–graphene hybrids improved thermal stability of EP significantly.
- The barrier effect of graphene is the crucial factor for enhanced thermal stability.
- The organic volatiles and toxic CO are decreased during pyrolysis of the composite.
- The catalysis and adsorption effect of metal oxide/graphene are the mechanism of the smoke suppression.

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ABSTRACT

Metal oxide decorated graphene hybrid materials, Co_3O_4–graphene and SnO_2–graphene, were synthesized for improving the thermal stability and suppressing the smoke in combustion for epoxy resins. Incorporation of metal oxide/graphene hybrids leads to significant thermal stabilization: a 37 and 27 °C increment in the temperature of 5% mass loss is observed for SnO_2–graphene/EP and Co_3O_4–graphene/EP, respectively, compared to that of pure EP. The barrier effect of graphene and the restricted mobility of the polymer chains by metal oxide are believed to be the crucial factor for improving the thermal stability. TG-FTIR analysis shows that the amount of organic volatiles of EP is significantly reduced and the toxic CO is suppressed after incorporating SnO_2–graphene or Co_3O_4–graphene, impling the reduced fire hazards. The synergism between the catalysis effect of metal oxide and the adsorption effect of graphene is the possible mechanism for the smoke suppression.

1. Introduction

Epoxy resin (EP), as a very important thermosetting polymer, has been widely used to manufacture high-performance composites in many fields such as aerospace structure materials, electronic laminate materials, and insulation materials due to its excellent adhesion, mechanical strength and solvent resistance [1–3]. However, like many synthetic polymers, there is one obvious disadvantage related to the high flammability of EP. The combustion of EP generates a large amount of heat and toxic smoke. Fire fatalities are usually reported as resulting from the lethal atmosphere generated by fires. Carbon monoxide concentrations measured in real fires can reach up to 7500 ppm [4], which would probably result in a loss of consciousness in 4 min [5]. A statistical study covering almost 5000 fatalities showed that the vast majority of fire deaths are attributable to carbon monoxide poisoning [6]. Therefore, it is of significant importance to improve the thermal stability and reduce the smoke toxicity of EP.

Graphene, a one-atom-thick carbon sheet with unique electronic and geometric properties, has been demonstrated to be one of the most promising candidates for the next generation of polymer nanocomposites. Small fraction of the graphene can lead to a significant improvement in thermal stability of polymers: the onset degradation temperature (T_{onset}) of the graphene/polystyrene is increased by approximately 60 °C at 0.19 vol% of graphene loading [7]; the addition of as low as 0.04 vol% graphene sheets leads to a 54 °C increase of T_{onset} for polyethylene [8]. Recently, graphene has been extensively investigated as a support for heterogeneous catalysts due to the ultrahigh aspect ratio for catalytic reaction [9]. Metal oxide/graphene hybrid materials are widely

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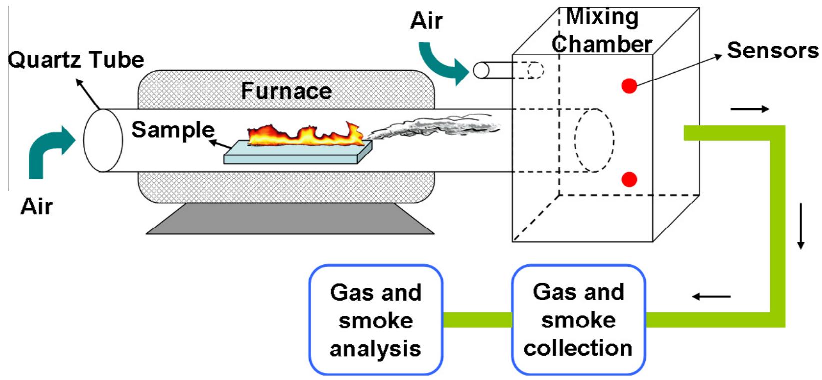

Scheme 1. The diagrammatic illustration of the steady state tube furnace.

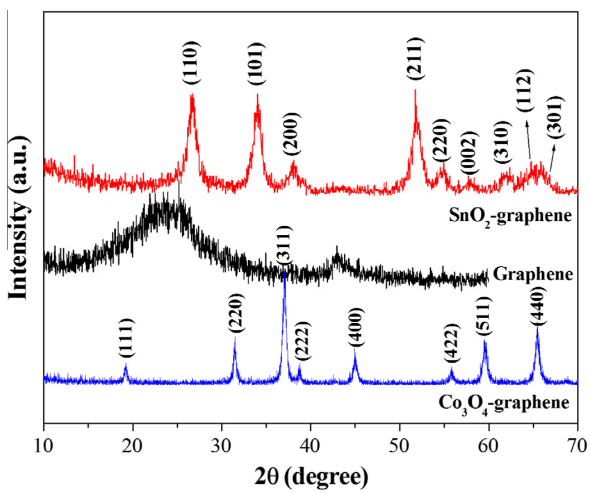

Fig. 1. The XRD patterns of graphene, Co_3O_4–graphene and SnO_2–graphene hybrids.

used for the catalytic oxidation of carbon monoxide, such as CuO-embedded graphene [10], TiO_2-decorated graphene [11,12], Co_3O_4 supported on graphene sheets [13]. Furthermore, metal oxide nanoparticles are usually used in technology as absorbents, ion exchangers and catalysts.

In this work, Co_3O_4 and SnO_2 decorated graphene hybrids were synthesized and incorporated into epoxy matrix. The thermal stability and the smoke suppression of the Co_3O_4–graphene/EP and SnO_2–graphene/EP composites were investigated. The mechanism of the enhanced thermal stability of the composites and the reduced smoke toxicity was proposed. It is anticipated that metal oxide decorated graphene hybrid materials will provide a promising solution to reduce the fire hazards of polymers.

2. Experimental work

2.1. Materials

Graphite oxide (GO) was prepared from graphite using Hummers' method [14]. Cobalt acetate, $SnCl_4$, ethanol, ammonia and 4,4′-diamino diphenyl methane (DDM) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Biphenol A-type epoxy resin was supplied by Hefei Jiangfeng Chemical Industry Co. Ltd (Anhui, China). All the reagents were used as received without further purification. Deionized water was used for all experiments unless otherwise stated.

2.2. Synthesis of Co_3O_4–graphene and SnO_2–graphene hybrids

Co_3O_4–graphene hybrid was synthesized by a simple in situ chemical reduction process [15]. Firstly, 100 mg of GO was added to 400 ml of DI water with the assistance of sonication for 120 min. Then, 350 mg of cobalt acetate and 400 ml of DI water were added dropwise to the above graphene oxide solution. Meanwhile, 4 ml of ammonia was added to reduce cobalt ions and graphene oxide simultaneously. The solution was stirred for 4 h at 100 °C and the resulting precipitates were collected by filtration

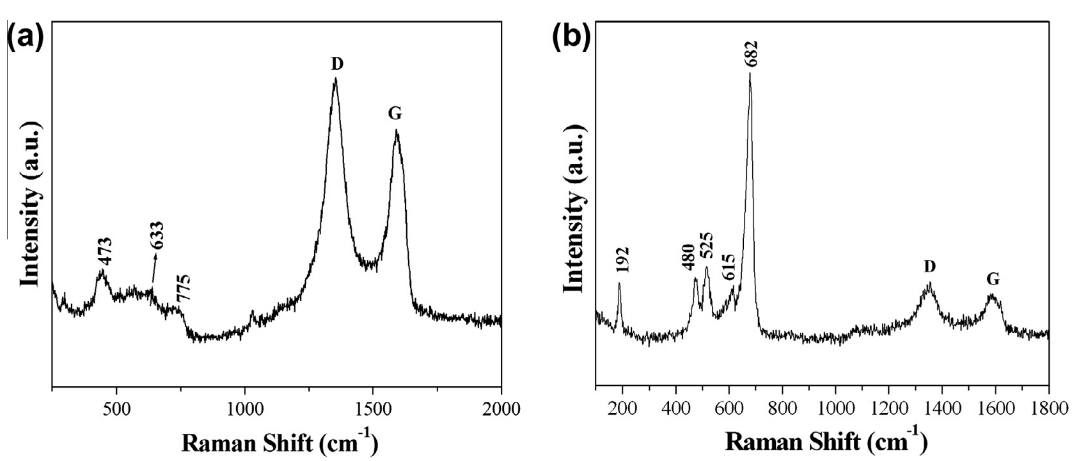

Fig. 2. The Raman spectra of (a) SnO_2–graphene and (b) Co_3O_4–graphene hybrids.