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High thermal conductivity and temperature probing of copper nanowire/upconversion nanoparticles/epoxy composite

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ABSTRACT

Epoxy resin has been intensively used as an electronic packaging material for its good mechanical strength and electrical insulativity. However, the low thermal conductivity of epoxy resin limits its applications. Inorganic fillers with a high loading fraction (>30 vol%) is typically used to enhance the thermal conductivity. But the high loading fraction could degrade the mechanical property and challenge the processing. In this work, we develop a new class of epoxy composites comprising very long (up to tens of micrometers) single-crystalline copper nanowires (a diameter of ~20 nm and a length of up to ~40 μm) as filler. A high thermal conductivity of 2.59 W/mK was obtained at a very low loading fraction of Cu nanowires at 0.12 vol%, corresponding to an 8-fold enhancement in thermal conductivity of plain epoxy resins. We also demonstrate that ytterbium and erbium codoped sodium yttrium tetra-fluoride ($NaYF_4$:Yb/Er) upconversion nanoparticles can be concomitantly incorporated into the epoxy composite, providing an accurate temperature of the composite. The dual functionality should render the epoxy composite an attractive candidate in electronic device.

1. Introduction

Thermal conducting materials are essential components in electronic devices such as electronic packaging and thermal interfacing [1]. For use in packaging and encapsulating, a thermal conducting material should have high thermal conductivity and electrical insulativity as well as high chemical and mechanical stability. The needs are unlikely to be fully satisfied by traditional thermal conducting materials such as metals and ceramics. In this regard, polymer composites composed of a polymer matrix incorporated with thermally conductive fillers, including metals, ceramics, and carbon-based materials, have been developed as an emerging class of thermal conducting materials [2,3].

Phonon transport is the main mechanism of heat conduction in most polymers, which transfer heat through the interactions between the subatomic particles [4]. Therefore, the lattice imperfections such as dislocations, voids, and impurities can introduce anharmonicities to lead phonon scattering. In a multi-phase system, the phonon scattering usually occurs when phonons propagate through a phase boundary. Incorporation of filler in polymers to form a composite is a common approach to improve the thermal conductivity. Composite thermal conducting materials primarily take advantage of the mechanical robustness and the electrical insulating property of the polymer matrix, while the inorganic or organic fillers are responsible for improving the thermal conductivities. The fillers in most studies are 0-demensional nanoparticles that are readily available in precisely controllable composition, size, morphology, and surface coating. Silicon carbide [5], silicon dioxide [6], aluminum nitride [7], barium titanate [8] are reported for enhancing the thermal conductivity of polymer. Usually, a high loading fraction (>30 vol%) of the fillers are typically required to achieve an appropriate level of thermal conductivity [9,10], resulting in degraded mechanical properties and processing challenge of the composites [11]. Meanwhile, high concentration of filler has adverse effect on the transmittance of the composite thus limiting their application in electronic devices [12].

To alleviate the problems associated with nanoparticle fillers, current researches are directed to the use of 1- and 2-dimensional nanofillers, such as nanowires and nanosheets that show high continuity and low percolation threshold [13]. For example, carbon nanotubes and graphene nanosheets have been used as fillers that show markedly improved performance with low filler

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concentration [11]. However, high cost of the materials hampers practical applications of these systems. Hexagonal boron nitride (BN) was reported extensively as filler material for thermal conducting applications due to its high thermal conductivity, great mechanical properties, high chemical and thermal stabilities [14,15]. Adding Born nitride nanotubes (BNNTs) into the polyvinyl butyral (PVB), polystyrene (PS), and polyethylene vinyl alcohol (PVA), the values of thermal conductivity can be improved 20.1, 21.1 and 14.7 times, respectively [16]. W-L Song et al. incorporated exfoliated BN sheets into PVA matrix and the resulting composite material exhibits high thermal conductivity value up to 30 W m^{-1} K^{-1} at 50 vol% BN loading fraction, which is close to 15% of the thermal conductivity of aluminum metal [17]. Y. Xu et al. reported silane surface modified BN can greatly improve the thermal conductivity of epoxy composite by up to 97%. At 57 vol % BN, the thermal conductivity reached 10.3 W/m K [18].

Similar to BN, AlN with silane modified can achieve high thermal conductivity up to 11.0 W/m K at 60 vol% [18]. AlN wiskers and AlN particles as filler at 60 vol%, the thermal conductivity of polyvinylidene fluoride (PVDF) can reach a high thermal conductivity of 11.5 W/m K [19]. Apart from polymer filled with boron nitride and aluminum nitride one-dimensional SiC nanowires/polyimide (PI) composites showed high thermal conductivity and retained electrical insulation property at the same time. The maximum value of thermal conductivity of PI composite was 0.577 W m^{-1} K^{-1} with 7 wt% SiC nanowires, which was 138% times of that of pure PI polymer [20].

Metal nanowires, like silver and copper nanowires also reported for enhance the thermal conductivity of the polymer. Silver nanowires were reported to enhance the thermal conductivity of silicone [21], polycarbonate [22], epoxy [23]. Compared to silver nanowires, copper nanowires have relative low cost and similar thermal and electrical conductivity. Copper nanowires/CNTs/Epoxy composites with 57.5 wt% filler (50 wt% multi-walled carbon nanotubes mixed with 50 wt% copper nanowires) can reach thermal conductivity up to 2.83 W m^{-1} K^{-1}, as reported by Y. Xing et al. [24]. The maximum thermal conductivity was 10.1 times of that of neat epoxy. Wang et al. [25] prepared a composite material through in-situ polymerization of acrylate in presence of Cu nanowires. They demonstrated that a small amount of copper nanowires could increase thermal conductivity of the polymer matrix by more than 10 folds, highlighting the feasibility to construct cost-effective thermally conductive composite materials. TiO_2-coated copper nanowires/epoxy composites exhibited higher thermal conductivity than copper nanowires/epoxy composites [26]. The improvement was contributed by the removal of air voids in the interface of copper nanowires and epoxy. Dense arrays of vertically aligned copper nanowires synthesized by templated electrodeposition method were reported to have the thermal conductivity as high as 70 W m^{-1} K^{-1} [27]. The lateral thermal conductivity was found to be only 1–2 W m^{-1} K^{-1}. Copper nanowire with high thermal conductivity as well as high light transmittance has been reported recently for preparing transparent conducting films [28]. Besides, copper nanowires also can be applied to electromagnetic interference material [29], electrical conductivity filler [30].

When heat is applied, polymeric materials undergo both physical and chemical changes and result in undesirable changes to the properties of the materials. Traditionally method, e.g. thermometer was not suitable as it can not be connected to the matrix, especially the inner space of the material. Encapsulating the temperature sensor in the polymeric composite was a better choice. There are few reports about composite for temperature probing. Two laminae of continuous carbon fibers in a crossply configuration encapsulated in polymer matrix were found to be a temperature sensor [31]. The contact resistivity of the junction decreased reversibly upon heating, which can be used for temperature sensing. Polyaniline/kaolinite composite can be used as temperature sensing as the resistivity of the composite was increased with increasing temperature [32]. Europium-β-diketonate complexes contained in poly (vinyl methyl ketone) film showed highly temperature dependent between 0 and 70 °C [33]. Co-doping of rare earth ions, erbium (Er) and ytterbium (Yb) to fluoride glass, the two neighboring fluorescence lines of erbium by upconversion could be used as temperature sensor [34]. Herein, we chose $NaYF_4$ for its high upconversion quantum yields.

In this work, we report a general approach to construct transparent high thermal conductivity polymer composite by using commercially available epoxy resin as polymer matrix in conjunction with very long (tens of micrometers) copper nanowires as fillers. We show that a high thermal conductivity (2.59 W/mK) can be realized at an appreciably low loading faction (0.07 vol%). This also allows us to incorporate second fillers composed of lanthanide-doped upconversion nanoparticles without suffering from loss of integrity of the composites, providing an additional capability to probe the operating temperature by ratiometric means [35].

2. Experimental section

2.1. Materials

$CuCl_2$, and $Ni(NO_3)_2 \cdot 6H_2O$, were purchased from Acros Organics. $Y(C_2H_3O_2)_3 \cdot xH_2O \cdot$, $Er(C_2H_3O_2)_3 \cdot xH_2O$, $Yb(C_2H_3O_2)_3 \cdot xH_2O$, NaOH, NH_4F, Oleylamine (80–90%), and 4,4′-methylenebis (2-methylcyclohexylamine) (curing agent), were purchased from Sigma Aldrich. Graphite was purchased from Qingdao Jinrilai graphite Co., Ltd. Epoxy (EP 4100) was purchased from ADEKA Corporation. All chemicals were used as received without further purification. PDMS (Polydimethysiloxane), Sylgard®184 was purchased from Dow Corning Company.

2.2. Preparation of Cu nanowires

The long Cu nanowires were prepared according to a literature method [36]. The Nickel salt was used as catalyst for the synthesis of copper nanowires. Briefly, 8 mmol $CuCl_2$ and 4 mmol $Ni(NO_3)_2 \cdot 6H_2O$ were mixed with 100 mL oleylamine under strong stirring in an argon atmosphere. To fully dissolve the metal salt, the solution was kept at 80 °C for 20 min. Thereafter, the solution was heated to 180 °C for 10 h. The product was collected by centrifugation and washed three times with hexane and toluene. Finally, the Cu nanowires were kept under vacuum for further experiment.

2.3. Preparation of upconversion nanoparticles

Upconversion, an anti-Stokes emission is a process of sequentially absorbing two or more photons to lead to the emission of light at shorter wavelength than excitation wavelength. Lanthanide-doped nanocrystals can convert near-infrared light to visible light to achieve upconversion emission. $NaYF_4$:Yb/Er upconversion nanoparticles were synthesized through coprecipitation in a binary solvent mixture of oleic acid and 1-octadecene [35]. Typically, 1.2 mL water solution of $Y(CH_3CO_2)_3$, 0.76 mL water solution of $Yb(CH_3CO_2)_3$, 0.04 mL water solution of $Er(CH_3CO_2)_3$ were added to a 50 mL flask with 4 mL of oleic acid and 6 mL of 1-octadecene. The mixture was heated from room temperature to 150 °C for 40 min while stirring to form the rare earth-OA complex. The solution was then cooled down to room temperature and added with 5 mL methanol solution of NH_4F (1.5 mmol) and NaOH (1 mmol). The resultant mixture was stirred for 30 min. After the methanol was