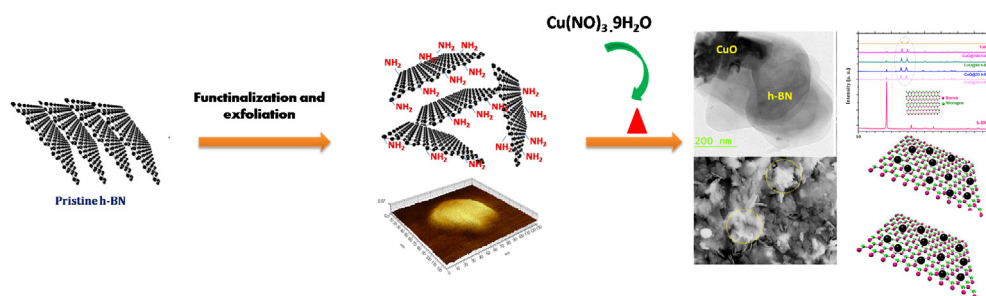Regular Article

Functionalized white graphene – Copper oxide nanocomposite: Synthesis, characterization and application as catalyst for thermal decomposition of ammonium perchlorate

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GRAPHICAL ABSTRACT

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ABSTRACT

Reactivity is of great importance for metal oxide nanoparticles (MONP) used as catalysts and advanced materials, but seeking for higher reactivity seems to be conflict with high chemical stability required for MONP. There is direct balance between reactivity and stability of these MONP. This could be acheived for metal oxide by dispersing them in a substrate. Here, we report a simple, efficient and high-yield process for the production of copper oxide (CuO) nanoparticles dispersed on a chemically inert material, few-layer hexagonal boron nitride (h-BN) with a thickness around 1.7 nm and lateral dimensions mostly below 200 nm. The mechano-chemical reaction which take place at atmospheric pressure and room temperature involves a urea assisted exfoliation of pristine boron nitride. Copper oxide nanoparticles dispersed on the surface of these few layered h-BN reduced its tendency for aggregation. The optimum concentration of CuO:h-BN was found to be 2:1 which shows highest catalytic activity for the thermal decomposition of ammonium perchlorate. The high catalytic activity of the in situ synthesized CuO-h-BN composite may be attributed to uniform distribution of CuO nanoparticles on the few layered h-BN which in turn provide a number of active sites on the surface due to non aggregation.

1. Introduction

Metal oxide nanoparticles (MONP) have been widely used in various fields including photonics, electronics, biomedicine, and chemistry because of their fascinating properties [1–4]. Most of the investigations on MONP focus on their size, shape, and composition rather than their stability and reactivity [5,6]. However, both stability and reactivity are two critical factors for them to ensure their subsequent characterization and application. When the dimensions of metal oxide particles tend to be at the nanometer scale, they become more reactive and unstable. This is because of their high surface energy and large surface-to-volume ratio as the size become in the nanometer range [7]. As a result, both

stability and reactivity seem to be contradictory and very difficult to achieve simultaneously in a synthetic process [8–10].

Among these MONPs, copper oxide (CuO) nanoparticles attract great interest due to their outstanding and distinct features in electronics, catalysis, and photonics [11–14]. However, these are also very easy to get aggregated and thereby effecting their chemical and physical properties (e.g. catalytic activity) [15]. To avoid aggregation, these nanoparticles are dispersed on a substrate which acts as an anti–agglomerating agent. From the viewpoint of materials science and technology, distributing these sensitive MONP over the surface of an inert material would be an effective and alternative strategy. Interestingly, several such substrate materials have been recently found, like Al_2O_3, carbon nitride, TiO_2, SiO_2, etc. [16–18]. Moreover, dispersed nanoparticles not only acquire remarkable stability but also promote physicochemical performances, which are so attractive and fascinating that they extend the breadth of practical applications of these nanoparticles [19,20]. Sanoop et al. has studied the effect of graphite oxide support on the distribution and catalytic activity of Fe_2O_3 nanoparticles and concluded that dispersing iron oxide nanoparticles on graphite oxide surface not only decrease the tendency for aggregation of iron oxide but also increase its catalytic activity [21].

In recent times, great efforts have been given to the functionalization of hexagonal boron nitride (h-BN) nanosheets to achieve better dispersion in solvents [22]. Zhi has employed organic solvents such as N,N-dimethylformamide for exfoliation and stabilization of h-BN nanosheets, by taking advantage of polar–polar interactions between the functional groups and the h-BN surface during sonication–centrifugation technique [23]. Lie et al. have reported that ball-milled h-BN can be functionalized with a long alkyl chain amine via Lewis acid–base interactions due to its increased number of defects. They also reported that water dispersion of h-BN nanosheets can be achieved directly by edge functionalization [24]. In recent times, Sainsbury et al. obtained hydroxyl-terminated h-BN nanosheets by the oxidation of exfoliated h-BN nanosheets [25]. However, even after long periods of intense ultrasonication, the concentration of the h-BN dispersions was typically below 2 mg ml^{-1}. Therefore, the development of a high-yield process to achieve highly dispersed h-BN nonmaterial in water remains as a challenge.

Here we report a simple, efficient and one-step method for the functionalization of few-layer h-BN by solid-state ball milling of commercially available h-BN and urea powder under atmospheric condition and preparation of a copper oxide-h-BN nanocomposite. Though, the exfoliation of boron nitride using urea under inert atmosphere was reported by W. Lei et al. [24] our method has several advantages, such as low cost, high yield, lack of organic solvents, substrates or vacuum systems and specially lack of inert atmosphere. The dispersibility of as produced few layer functionalized h-BN in water was studied in detail to produce highly stable colloidal suspensions. This exfoliated and functionalized few layered h-BN was used as a dispersing agent for the insitu synthesized copper oxide nanoparticles. Physical and chemical properties of copper oxide-h-BN composites were well characterized by various analytical techniques and these properties were correlated with its catalytic activity on the thermal decomposition of ammonium perchlorate, a well known oxidizer for composite solid propellants used in missiles and launch vehicles.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were of analytical grade and used without further purification. Analytical grade reagents viz., Cupric nitrate trihydrate (Merck, India) h-BN (Sigma-Aldrich, India), Urea (Sigma-Aldrich, India) were used for the synthesis of catalysts. Ammonium perchlorate made in house with purity >99% was used for studying the catalytic activity.

2.2. Synthesis

2.2.1. Preparation of h-BN

h-BN used in this work was exfoliated as per the previously reported method with some modification [24]. In a typical synthesis, h-BN and urea were mixed together at different h-BN:urea weight ratio from 1:20 to 1:60 inside a steel milling container having zirconia balls using a planetary ball mill (Sintex VFD-L) at a rotation of 600 rpm for 22 h at room temperature under air atmosphere. The high rotation speed provides effective exfoliation of h-BN on a large scale. The urea not only assists the exfoliation but also protects the h-BN from excessive mechanical damage, preventing an extensive formation of lattice defects. After ball milling, the obtained powder was washed with deionized water to remove urea. Aqueous dispersions thus obtained were then centrifuged at 4000 rpm and the residue was dried at 100 °C to obtain exfoliated h-BN powder. The size and thickness of the few-layer h-BN particles were reduced to lowest when the h-BN:urea weight ratio become 1:60. Thus in this study, the weight ratio of h-BN:urea and milling time were fixed at 1:60 and 22 h, respectively, to get h-BN sheets with suitable size and thickness for the preparation of CuO@h-BN composites.

2.2.2. Preparation of CuO nanoparticles-h-BN composite

A series of four CuO@h-BN composites were prepared with CuO to few layered h-BN weight percentage of 100, 50, 33 and 25. In a typical synthesis (CuO@h-BN of 100%) 1 g of h-BN in 15 ml of deionized water and 3 g of cupric nitrate 20 ml of deionized water was stirred for 15 and 5 min respectively. The solutions were then mixed and magnetically stirred for another 30 min. The product was dried in a vacuum oven at 90 °C for 24 h. The resulting mixture was then heated from room temperature to 400 °C in an air atmosphere at a heating rate of 5 °C min^{-1} and kept at that temperature for 60 min. The other composites were also prepared by the same procedure, by changing the concentration of cupric nitrate. The compositions of CuO-h-BN composites are shown in Table 1.

2.3. Characterization

Powder X-ray diffraction data of samples was collected on a Bruker D8-Discover powder X-ray diffractometer in a Bragg-Brentano configuration with a CuKα radiation (1.5418 Å) at a scan rate of 2.5 deg min^{-1}. Crystalline phases were identified by comparing the experimental diffraction patterns to Joint Committee on Powder Diffraction Standards (JCPDS). Perkin-Elmer GX FTIR spectrometer was used for FTIR analysis. Field emission scanning electron microscopy (FESEM) observations were performed to examine the morphology of the samples using Carl Zeiss, Supra 55 model field emission scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDX). Nano structure was evaluated using FEI Tecnai G2 30 S-TWIN, High Resolution Transmission Electron microscope with an accelerating voltage of

Table 1
Weight percentage of h-BN and CuO in the composites.

Sample	Weight percentage of h-BN	Weight percentage of CuO
CuO@100 h-BN	100	100
CuO@50 h-BN	50	100
CuO@33 h-BN	33	100
CuO@20 h-BN	25	100