Fabrication of Co₃O₄/graphene oxide composites using supercritical fluid and their catalytic application for the decomposition of ammonium perchlorate†

Jian Zhao,*abc Zhensheng Liu,abc Yulei Qinabc and Wenbin Huabc

We report a facile and environmentally benign approach to fabricate Co₃O₄ nanoparticles (NPs)/graphene oxide (G-O) composites by the use of supercritical fluid. With the aid of supercritical carbon dioxide, the ultrafine Co₃O₄ NPs are densely and homogeneously deposited on the supporting G-O sheets. Transmission electron microscope images revealed that the average size of Co₃O₄ NPs in Co₃O₄/G-O composites was 5.9 nm, much smaller than that of bare Co₃O₄ NPs, indicating that the graphene oxide sheets with Co₃O₄ NPs attached could hinder the growth and aggregation of Co₃O₄ crystals during synthesis. The layered graphite oxide sheets are exfoliated by the nucleation and growth of Co₃O₄ NPs. The composites exhibit a special catalytic effect for the thermal decomposition of ammonium perchlorate due to the combination of G-O sheets and Co₃O₄ NPs. This supercritical fluid method could be further extended to synthesize other G-O or graphene-based metal oxide composites using appropriate metal precursors.

Introduction

Graphene, a single-atom-thick sheet of hexagonal arrayed sp²-bonded carbon atoms, has attracted tremendous attention from both academic and industrial communities in recent years due to its unique graphitic basal plane structure, high specific surface area, excellent thermal, mechanical, and electrical properties.1-6 This novel two-dimensional carbon material is revolutionizing interdisciplinary research activities in various fields, such as nanocomposites, fuel cells, nanoelectronics, sensors, supercapacitors and hydrogen storage.5-7 To date, graphene sheets have been produced by several synthesis methods such as mechanical cleavage, rapid thermal expanding of graphite and chemical oxidation of graphite.4-6 Given the facile solution processing, graphene has been commonly prepared by chemical reduction of graphene oxide (GO) in solutions. Because of strong van der Waals interactions, the as-reduced graphene sheets tend to form irreversible aggregates, which is disadvantageous for realizing its potential applications.

Although graphene is chemically inert, graphite oxide, the starting material utilized to prepare graphene, is more active and readily exfoliated into graphene oxide (G-O) in solutions due to the presence of oxygen-containing functional groups (hydroxyl, epoxy, carboxyl and carbonyl groups). Given its ease of manipulation in solutions, large surface area and numerous nucleation centers created by the oxygen-containing functional groups, G-O could be an excellent supporting material to load nanoparticles (NPs) with high content for catalysts. The combination of G-O and nanoparticles could exhibit extraordinary properties that can not be provided with their individual components.

Ammonium perchlorate (AP) is one of the main constituents used in various modern composite propellants.13 The combustion behavior of the composite propellants is often evaluated by the thermal decomposition characteristics of AP. The lower pyrolysis temperature and more exothermic heat are important for the utilization of AP. Conventionally transition metal oxides are demonstrated to play an important role in the catalysis of AP decomposition to realize a higher combustion rate and better performance of the propellants.13,14 Spinel Co₃O₄ is an important magnetic p-type semiconductor with interesting physical properties, which has
been widely used in a wide variety of scientific and technological applications such as catalysts (AP decomposition is an example), sensors, pigments, magnets and nanodevices.\textsuperscript{15,16} To promote its intrinsic properties and broaden the horizons for its use, attention is focused on the preparation of the Co$_3$O$_4$ with nanostructures.\textsuperscript{17–20} In recent years, considerable methods for the synthesis of graphene/Co$_3$O$_4$ nanoparticle composites have been developed successfully.\textsuperscript{21–26} However, the particle size of the supported Co$_3$O$_4$ nanoparticles prepared by conventional solution methods is relatively large (at least several tens of nanometers in most cases). Moreover, the investigations for the employment of G-O as a supporting material are limited. Developing a simple and efficient route for fabricating highly dispersed Co$_3$O$_4$/GO hybrids is desirable. Also, direct deposition of Co$_3$O$_4$ NPs on G-O sheets would be interesting to enrich the applications of Co$_3$O$_4$. It is expected that G-O/Co$_3$O$_4$ composites can lead to an integration of the properties of the two components (G-O and Co$_3$O$_4$ NPs) in the new composites that will present special features for the catalysis of AP decomposition.

Supercritical fluids (SCFs) technology has been widely used in the field of materials science due to the unique properties of SCFs such as low viscosity, high diffusivity, near-zero surface tension and pressure-dependent density.\textsuperscript{27,28} Among SCFs, supercritical CO$_2$ (SC CO$_2$) is particularly attractive for a wide variety of applications because of its unique properties. SC CO$_2$ ($T_c = 31.1$ °C, $P_c = 73.8$ bar) has been considered as a green reactive medium because of its nontoxic, inexpensive, nonflammable, natural abundance and environmentally benign merits. Thus SC CO$_2$ may replace organic solvents for its use, attention is focused on the preparation of the G-O/Co$_3$O$_4$ composites, 10 mg of graphite oxide dispersed in a 5 mL ethanol solution of cobalt nitrate hexahydrate (10 mg mL$^{-1}$) was sonicated for about 30 min. After the mixture was loaded into a 25 mL high-pressure stainless vessel, the vessel was placed in a constant oil bath of 35 °C. Then CO$_2$ was charged into the vessel with a pressure up to 9.0 MPa. The vessel was heated to a temperature of 150 °C and maintained for about 24 h, allowing cobalt nitrate hexahydrate to decompose completely. Carbon dioxide was slowly vented when the vessel was cooled down to ambient temperature. The collected precipitates were ultrasonically dispersed in ethanol, rinsed and filtered with an excessive amount of ethanol to remove the unreacted precursors and impurities. The products were dried in a vacuum oven at 60 °C for 24 h.

XRD patterns were obtained using a D-MAX 2500/PC operated at 40 kV and 100 mA with Cu K$_\alpha$ radiation ($\lambda = 0.15418$ nm). The data was collected from 2$\theta = 5$–80° at a scan rate of 0.02° s$^{-1}$. Morphology and structure of the composites were examined by TEM on a JEM 2100 transmission electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS). TGA were recorded on a TG209F1 (Netzsch, Germany) in a temperature range of 50 to 800 °C at a heating rate of 5 °C min$^{-1}$ in an air flow. DSC was performed on a DSC204F1 (Netzsch, Germany) from 100 to 500 °C at a heating rate of 10 °C min$^{-1}$ under a nitrogen flow.

Results and discussion

X-ray diffraction analysis is used to determine the chemical composition and crystalline structure of the G-O/Co$_3$O$_4$ composites. Fig. 1 shows XRD patterns of pristine GO and
G-O/Co$_3$O$_4$ composites. As shown in Fig. 1a, the most intense peak at around $2\theta = 11.1^\circ$ corresponds to the (002) reflection of GO. The interlayer spacing (0.80 nm) is larger than that of pristine graphite (0.34 nm) due to the introduction of oxygen-containing groups (hydroxyl, epoxy, carboxyl and carbonyl groups). As can be seen in Fig. 1b, the (002) reflection peak of layered graphite oxide disappears, indicating that the regular lamellar structure of graphite oxide sheets has been destroyed during the preparation process of the composite. The diffraction peaks are similar to those of pure spinel Co$_3$O$_4$ (JCPDS no.80-1542). No obvious peaks corresponding to cobalt nitrate hydrate or other cobalt oxides are observed in the powder pattern. Under the experimental conditions, the conversion of Co(NO$_3$)$_2$$\cdot$6H$_2$O is efficient and the presence of crystalline Co$_3$O$_4$ is confirmed by the well-resolved diffraction peaks.

The TEM images of GO–Co$_3$O$_4$ composites are displayed in Fig. 2a and b. It could be clearly seen that the crumpled G-O sheets were densely and uniformly decorated by highly dispersed Co$_3$O$_4$ NPs with a size distribution of 3.2–8.8 nm. The average size of Co$_3$O$_4$ NPs is 5.9 nm (Fig. 2c), significantly smaller than that of Co$_3$O$_4$ particles (usually at least tens of nanometers) prepared by conventional solution methods. The resulting composites were treated with long term ultrasonication (more than 1 h), and the Co$_3$O$_4$ NPs were still decorated on the G-O sheets. This indicates a strong interaction between G-O sheets and Co$_3$O$_4$ NPs. By serving as “spacers”, these in situ formed particles, caused the exfoliation of the lamellar graphite oxide. Previous studies indicated that graphite oxide sheets were mostly modified with epoxy and hydroxyl groups on the basal planes, with carboxyl and carbonyl groups at the edges. These oxygen-containing groups can act as anchoring sites, allowing the nucleation and growth of Co$_3$O$_4$ NPs on G-O sheets. Without the support of G-O sheets, much larger aggregates of Co$_3$O$_4$ particles were
observed (Fig. S1 in ESI†). G-O sheets play a critical role in inhibiting severe aggregation of nanoparticles. The composition of the composites was confirmed by the EDS spectrum as shown in Fig. 2d. The presence of Co, C and O is illustrated on the surface of GO sheets and no N is detectable, suggesting that the precursor is completely converted to cobalt oxide under the experimental conditions.

To further determine the chemical composition of Co3O4/G-O composite, X-ray photoelectron spectroscopy (XPS) measurements were carried out in the region of 0–1100 eV (Fig. 3a).

Fig. 3  (a) XPS survey spectra of Co3O4/GO, (b) C1s XPS spectra of Co3O4/G-O, (c) Co2p XPS spectra of Co3O4/G-O, (d) O1s XPS spectra of Co3O4/G-O, (e) C1s XPS spectra of GO.
The binding energies obtained in the XPS analyses were corrected for specimen charging by referencing the C 1s peak to 284.60 eV. The C 1s XPS spectrum of the Co3O4/G-O composite are shown in Fig. 3b (discussed below). The Co 2p XPS spectra of the composite exhibit two peaks at 795.7 and 780.1 eV, corresponding to the Co 2p1/2 and Co 2p3/2 spin–orbit peaks of Co3O4 (Fig. 3c). The presence of Co3O4 can be further confirmed by O 1s XPS peak close to 530 eV, which corresponds to the oxygen species in the Co3O4 phase for Co3O4/G-O as shown in Fig. 1d. Groups of O correspond to Co–O at 530 eV, C(O)OH at 531.6 eV, C═O at 532.5 eV and C–OH at 533.9 eV on G-O, respectively.

The C 1s XPS spectrum of GO (Fig. 3e) clearly indicates a considerable degree of oxidation with three components that correspond to carbon atoms in different functional groups: the nonoxygenated ring C, the C in C–O bonds, the carbonyl C(C═O) and the carboxylate carbon (HO–C═O). Although the C 1s XPS spectrum of the Co3O4/G-O composite (Fig. 3b) also exhibits these oxygen-containing functionalities, their peak intensities are a little smaller than those in GO, confirming that some epoxide, hydroxyl, and carboxyl functional groups are removed. It is noted that the C/O ratio for G-O in the composite was estimated to be 2.9 after subtracting the oxygen species involved in O–Co chemical bonds of Co3O4 in the composite, which is higher than that (C/O = 2.2) of the as-prepared GO. This indicates that G-O was slightly reduced.

A possible formation mechanism can be proposed based on our experimental results. A simple scheme for such an in situ formation process is illustrated in Fig. 4. It is well-known that SCFs possess unique properties including low viscosity, rapid diffusion and near-zero surface tension. GO was first suspended in an ethanol solution of Co(NO3)2·6H2O. Then CO2 was charged into the vessel up to 9 MPa at a temperature of 35 °C, resulting in a mixed supercritical fluid containing ethanol and CO2 to dissolve Co(NO3)2·6H2O. The surface of graphite oxide could be wetted easily by cobalt nitrate hexahydrate in the fluid as a result of zero surface tension of the SCF. It consequently facilitates Co(NO3)2 to reach and be adsorbed on the surfaces of the graphite oxide where epoxy and hydroxyl groups were decorated on the surfaces with carboxyl and carbonyl groups at the edge of the sheets. Graphite oxide was negatively charged so that the positive cobalt ions in the fluid can be adsorbed onto the surfaces of graphite oxide, followed by interlamination into graphite oxide sheets due to electrostatic attraction and the special features of SCFs such as low viscosity, rapid diffusion and near-zero surface tension. At a higher temperature, the absorbed Co(NO3)2 was decomposed to form Co3O4. The aforementioned oxygenated functional groups were utilized as nucleation sites. Co3O4 preferably nucleated on the surfaces of graphite oxide and grew into nanoparticles, forming NP-containing composites. These in situ formed particles in

![Fig. 4](image)

A scheme shows a proposed formation route of anchoring metal oxide NPs onto the surfaces of graphene oxide sheets.
return destroyed the regular layer restacking, leading to the exfoliation of lamellar graphite oxide (and thus forming graphene oxide). SC CO$_2$ plays an important role in the uniform dispersion of the ultrafine Co$_3$O$_4$ nanoparticles on G-O. To prove the function of SC CO$_2$, we also synthesized GO/Co$_3$O$_4$ composites in the absence of CO$_2$. Uneven particle distribution is notable as can be seen in Fig. S2 (see ESI†). Large aggregates with a particle size distribution of tens to hundreds of nanometers are found.

TGA was used to determine the content of Co$_3$O$_4$ in the as-prepared composites through oxidative decomposition. The representative TGA curves of GO and G-O/Co$_3$O$_4$ in the air flow are shown in Fig. 5. Three steps can be observed in the TGA curve of graphite oxide in Fig. 3a. Graphite oxide begins to lose mass below 100 °C, which was attributed to dehydration of physisorbed water. The second step at around 217 °C is caused by the evolution of CO and CO$_2$ owing to the removal of oxygen-containing groups on the surface of graphite oxide. At about 580 °C, the loss mass is assigned to the combustion of the carbon skeleton of graphite oxide. At the end, the graphite oxide is completely removed at about 600 °C, while Co$_3$O$_4$ would be stable until 800 °C. Thus the content of Co$_3$O$_4$ could be obtained by using TGA. In comparison, G-O in G-O/Co$_3$O$_4$ composite is decomposed at about 250–350 °C, which is much lower than that of pure graphite oxide. This phenomenon may be attributed to the catalytic role of Co$_3$O$_4$ NPs in the oxidation of carbon materials. About 46.5 wt% of metal oxide is deposited onto the surface of G-O according to the mass loss of G-O in GO–Co$_3$O$_4$ composites.

To explore the potential application of the composites, we investigated the catalytic effect of G-O/Co$_3$O$_4$ on the decomposition of AP which is an important solid rocket propellant. DSC curves of the decomposition of AP and AP with GO, Co$_3$O$_4$ and G-O/Co$_3$O$_4$ composites are shown in Fig. 6. In general, the thermal decomposition of AP takes place in three steps: the endothermic phase transition at 246 °C (ascribed to a phase transition of AP from orthorhombic to cubic), the low-temperature decomposition (LTD) at 338 °C and the high-temperature decomposition (HTD) at 433 °C. The addition of GO increases the exothermic heat (LTD and HTD) as compared to pure AP, which may be attributed to the catalytic effect of GO. When Co$_3$O$_4$ and G-O/Co$_3$O$_4$ were
added, LTD and HTD merged into one step, the decomposition temperature of AP decreased and more exothermic heat was released. For the application of AP, how to increase the exothermic heat and lower the temperature is important. G-O can increase the exothermic heat of AP, and Co$_3$O$_4$ makes two steps blend almost into one process and decreases the temperature of decomposition at the same time. The decomposition temperature of AP with 2% G-O/Co$_3$O$_4$ (297 °C) is lower than that of Co$_3$O$_4$ (308 °C). It is also noted that the exothermic heat of the former (1591 J g$^{-1}$) is higher than that of the latter (1448 J g$^{-1}$). Because of the combination of the individual components for the catalysis of AP decomposition, G-O/Co$_3$O$_4$ not only lowers the decomposition temperature and the use of Co$_3$O$_4$, but also enhances the exothermic heat of AP, which could not be achieved by the individual component alone. Given that 46.5 wt% Co$_3$O$_4$ is contained in the composite, the enhancement of the exothermic heat for the composite is significant. We also demonstrate that the catalysis of GO and Co$_3$O$_4$ (46.5 wt%) mixed by simply mechanical stirring is not as effective as that of the in situ synthesized nanocomposite (Fig. S3 in ESI†). In this case, GO sheets might not be fully exfoliated or uniformly mixed with Co$_3$O$_4$ particles.

Conclusions

In summary, we report a facile and effective supercritical fluid approach to load Co$_3$O$_4$ nanoparticles on G-O sheets. The unique properties of SCFs facilitate the direct deposition of metal oxide on the G-O surface with nanostructure and uniformity. The results show that G-O sheets were densely decorated with highly dispersed Co$_3$O$_4$ NPs with an average size of 5.9 nm and the lamellar structure of graphite oxide was destroyed. The as-prepared composites show an excellent catalysis effect on the decomposition of AP. This simple environmentally benign SCF method can be readily extended to fabricate other graphite oxide-based functional composites with desired properties.

Acknowledgements

The work was partially funded by the National Natural Science Foundation of China (no. 51373088 and 51073082), the National Basic Research Program of China (No. 2012CB722606). The Scientific Research Foundation for the Returned Overseas Chinese Scholars, Qingdao Municipal Science and Technology Program, Basic Research Project (12-1-4-3-(7)-jch and 12-1-4-3-(25)-jch), Chongqing Key Laboratory of Micro/Nano Materials Engineering and Technology (open project KFJJ1202), MOE Key Laboratory of Special Functional Aggregated Materials (Shandong University), Ministry of Education of China (open project) (Shandong University), State Key Laboratory of Chemical Resource Engineering (open project CRE-2012-C-204) (Beijing University of Chemical Engineering), State Key Laboratory of Molecular Engineering of Polymers (open project K2013-20 Fudan University), and the natural science foundation of Shandong Province (ZR2012EMM003).

References