SPECIAL TOPIC: Graphene Oxides towards Practical Applications

Unconventional chemical graphitization and functionalization of graphene oxide toward nanocomposites by degradation of ZnSe[DETA]_{0.5} hybrid nanobelts

Liang Xu^{1,2}, Zeng-Wen Hu², Le-Le Wang², Chuanxin He^{1*} and Shu-Hong Yu^{2*}

ABSTRACT The high surface energy of nanomaterials endows them a metastable nature, which greatly limits their application. However, in some cases, the degradation process derived from the poor stability of nanomaterials offers an unconventional approach to design and obtain functional nanomaterials. Herein, based on the poor stability of ZnSe[DETA]_{0.5} hybrid nanobelts, we developed a new strategy to chemically graphitize and functionalize graphene oxide (GO). When ZnSe[DETA]_{0.5} hybrid nanobelts encountered a strong acid, they were attacked by H⁺ cations and could release highly reactive Se²⁻ anions into the reaction solution. Like other common reductants (such as N₂H₄·H₂O), these Se²⁻ anions exhibited an excellent ability to restore the structure of GO. The structural restoration of GO was greatly affected by the reaction time, the volume of HCl, and the mass ratio between GO and ZnSe[DETA]_{0.5} nanobelts. By carefully controlling the reaction process and the post-processing process, we finally obtained several Se-based reduced GO (RGO) nanocomposites (such as ZnSe/Se-RGO, ZnSe-RGO, and Se-RGO) and various selenide/metal-RGO nanocomposites (such as Ag₂Se-RGO, Cu₂Se-RGO, and Pt-RGO). Although the original structure and composition of ZnSe[DETA]_{0.5} nanobelts are destroyed, the procedure presents an unconventional way to chemically graphitize and functionalize GO and thus provides a new material synthesis platform for nanocomposites.

Keywords: stability, degradation, unconventional chemical graphitization, hybrid nanobelt, graphene oxide

INTRODUCTION

Unlike their bulk counterparts, nanomaterials possess high surface energy which causes them to be far from their equilibrium state [1,2], and thus endows them a strong tendency to obtain a lower energy state by reacting with active substances [3]. As a result, many chemical or physical transformations are easily accessible for nanoscale materials. For instance, chemically inert noble metals are resistant to oxidation at the macroscale, while their nanoscale counterparts are chemically unstable and can be easily oxidized [4], such as Au nanoparticles (NPs) [5], Ag NPs [6], and Pt NPs [7–10]. In addition, these noble NPs usually have lower melting points than their bulk counterparts, that is to say, they exhibit low thermostabilities [11]. Except noble metals, other materials also exhibit poor stabilities at nanoscale, which greatly impedes their practical applications. For example, the poor thermostability of noble metal nanocatalysts severely limits their applications in high-temperature catalytic reactions [12]; nanostructured anode materials generally suffer from poor capacity retention due to material pulverization (i.e., poor structural stability) caused by their large deformation during lithiation–delithiation processes [13]; the high sensitivities of halide perovskite nanomaterials to moisture, oxygen and temperature greatly impede their commercialization [14,15].

However, in some cases, the unstable process resulting from the poor stability of nanomaterials can be used as an unconventional approach to design and synthesize func-

¹ College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China

² Division of Nanomaterials & Chemistry, Hefei National Laboratory for Physical Sciences at the Microscale, CAS Center for Excellence in Nanoscience, Institute of Energy, Hefei Comprehensive National Science Center, Department of Chemistry, Institute of Biomimetic Materials & Chemistry, University of Science and Technology of China, Hefei 230026, China

* Corresponding authors (emails: hecx@szu.edu.cn (He C); shyu@ustc.edu.cn (Yu SH))

tional nanomaterials that are inaccessible *via* direct synthesis methods [3,16]. For instance, the low melting points of nanomaterials allow them to undergo thermal treatment at very low temperatures, which is beneficial to their processing, such as the welding of metal nanowires [17] and the fusing of different metal oxide NPs [18]. Moreover, although the enhanced surface oxidation of nanomaterials degrades their practical performance in the application processes [3,19], oxidation at nanoscale is not always a disadvantage. For metal oxide nanomaterials with different oxidation states, their oxidation–reduction phase equilibria shift to favor the phases that have lower surface energies [20,21]. Thus, some unstable phases at macroscale may become more stable at nanoscale. For example, nano- Co_3O_4 exhibits a more durable catalytic activity than bulk Co_3O_4 for the oxidation of CO [21,22]. In addition, oxidation etching at nanoscale is an efficient way to process nanomaterials. Single quintuplet Bi_2Te_3 layers could be successfully obtained by layer-by-layer corrosion of layered-crystalline-structured Bi_2Te_3 nanoplates with suitable oxidizing agents [23]. The unstable processes of nanomaterials can be used to assemble and reconstruct nanomaterials as well. Xu *et al.* [24] found that CdTe/CdSe NPs became unstable after depleting some of the stabilizers (i.e., surface ligands) on their surfaces, and these destabilized NPs could spontaneously assemble into one dimensional (1D) [25,26], two-dimensional (2D) [27], or other complex nanostructures [28], which are difficult to obtain through conventional methods. In a similar way, when the structural stabilizers (i.e., organic components) in inorganic–organic hybrid nanomaterials are released from the hybrids, the lamellar structures of these hybrid materials are destroyed, thus causing their deformation, reconstruction, or degradation. Yu *et al.* [29] reported the transformations of inorganic–organic hybrids into advanced nanomaterials by removing organic components of the hybrids *via* ion exchange reactions [30,31], interfacial reactions [32,33], and redox reactions [34]. Very recently, our group found that stabilizer-depleted ZnSe layers, which were obtained by acidification of ZnSe –amine lamellar hybrids, were unstable and can be easily oxidized into porous Se nanosheets [35]. Obviously, the poor stability of nanomaterials can be adopted for design and synthesis of functional nanomaterials.

Herein, a new approach has been developed to chemically graphitize and functionalize graphene oxide (GO) at room temperature based on the poor stability of $\text{ZnSe}[\text{DETA}]_{0.5}$ hybrid nanobelts (DETA = diethylenetriamine). We found that the acidification of ZnSe –

$[\text{DETA}]_{0.5}$ would release Se^{2-} into the solution when a small amount of HCl was added into the mixed solution of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts and GO. The Se^{2-} has a very low redox potential (-0.924 V), which gives its ability to reduce GO. The structural restoration of GO was greatly affected by the reaction time, the volume of HCl, and the mass ratio between GO and $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts. More interestingly, we found that the obtained reduced GO (RGO) was Se-doped. In addition, we prepared several Se-based RGO nanocomposites, such as ZnSe/Se-RGO , ZnSe-RGO , and Se-RGO . Among them, Se-RGO nanocomposite exhibits a high chemical reactivity but a poor structural stability. Based on this, $\text{Ag}_2\text{Se-RGO}$, $\text{Cu}_2\text{Se-RGO}$, Pt-RGO , and even Se nanowire-RGO nanocomposites can also be easily prepared with Se-RGO as precursor. Thus, Se-RGO nanocomposite provides a new platform for the synthesis of various functional selenide/metal-RGO nanocomposites.

EXPERIMENTAL SECTION

Materials

Na_2SeO_3 , HCl, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, DETA, hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) (85 wt%), ethylene glycol (EG), AgNO_3 , $\text{Cu}(\text{NO}_3)_2$, and H_2PtCl_6 were purchased from Shanghai Chemical Reagents Co., Ltd. GO was obtained from Shanghai Ashine Technology Development Co., Ltd. All of the chemical reagents were used as received without further purification.

Synthesis of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts

$\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts were synthesized according to a hydrothermal reaction previously developed by our group [35,36]. Typically, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (6 mmol) and Na_2SeO_3 (6 mmol) were dissolved in a mixed solution (70 mL) with a volume ratio of $V_{\text{H}_2\text{O}}/V_{\text{DETA}}/V_{\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}} = 16:14:5$ under magnetic stirring. Subsequently, the mixed solution was transferred into a 100-mL Teflon-lined autoclave and then maintained at 140°C for 12 h. The obtained white floccules were washed several times with deionized water (DIW) and ethanol.

Synthesis of ZnSe/Se-RGO nanocomposite

First, 3 mL of HCl was injected into 150 mL of DIW, and 150 mg of GO was dispersed in 50 mL of DIW, and 3 mmol of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts was dispersed in 50 mL of DIW. Then, these solutions were mixed together under vigorous stirring. Finally, the reagent bottle was sealed by Parafilm to isolate oxygen, and the mixture

was kept stirring for 12 h at room temperature. The obtained black floccules were collected and washed several times with DIW and ethanol.

Synthesis of Se-RGO nanocomposite

The obtained ZnSe/Se-RGO nanocomposites were dispersed in 50 mL of DIW, and 0.5 mL of HCl was rapidly injected into this solution under moderate stirring. Then, the conical flask was opened to air, and the solution was kept stirring for 24 h at room temperature. The obtained black floccules were collected and washed several times with DIW and ethanol.

Synthesis of ZnSe-RGO nanocomposite

The obtained ZnSe/Se-RGO nanocomposites were heated up to 600°C with a heating rate of 5°C min⁻¹ in nitrogen atmosphere and kept at 600°C for 3 h. Then the obtained black solids were collected.

Synthesis of Ag₂Se-RGO nanocomposite

A small amount of Se-RGO nanocomposite was redispersed in 30 mL of EG. Then, an AgNO₃ solution (0.1 g in 5 mL EG) was added into the suspension of Se-RGO nanocomposite with vigorous magnetic stirring for 2 h at room temperature. The products were collected and washed several times with DIW and ethanol.

Synthesis of Cu₂Se-RGO nanocomposite

A small amount of Se-RGO nanocomposite was redispersed in 25 mL of DIW. Then, 0.8 mL of Cu(NO₃)₂ solution (0.5 mmol mL⁻¹) and 0.5 mL of ascorbic acid solution (1 mmol mL⁻¹) were added into the suspension of Se-RGO nanocomposite with vigorous magnetic stirring for 2 h at room temperature. The products were collected and washed several times with DIW and ethanol.

Synthesis of Pt-RGO nanocomposite

A small amount of Se-RGO nanocomposite was redispersed in 30 mL of EG. Then, 1 mL of H₂PtCl₆ solution (77 mmol L⁻¹) was added into the suspension of Se-RGO nanocomposite. The mixture was kept at 60°C for 24 h with vigorous magnetic stirring. The products were collected and washed several times with DIW and ethanol.

Stability of Se-RGO nanocomposite

A small amount of Se-RGO nanocomposite was redispersed in 30 mL of EG/DIW. Then, the solution was kept at room temperature for 48 h with mild magnetic stirring. The products were collected and washed several times

with DIW and ethanol.

Material characterizations

The obtained samples were characterized with various analytical techniques. The sample morphology was observed with a Zeiss Supra 40 scanning electron microscope (SEM) operating at 5 kV and a Hitachi H7650 transmission electron microscope (TEM) operating at 120 kV. Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) elemental mapping was carried out on a JEOL-2100F instrument. X-ray diffraction (XRD) patterns were recorded on a Phillips X'Pert Pro Super X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALab MKII X-ray photoelectron spectrometer with an X-ray source (Mg K α $h\nu = 1253.6 \text{ eV}$). Raman scattering spectra were obtained with a Renishaw System 2000 spectrometer using a 514.5-nm argon ion laser. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under a nitrogen flow using a TA STD Q600 thermal analyzer at a heating rate of 10°C min⁻¹. Fourier transform infrared (FTIR) spectra (KBr) were obtained on a Nicolet 8700 instrument.

RESULTS AND DISCUSSION

Previous study illustrated that the degradation of ZnSe-[DETA]_{0.5} nanobelts could release Se²⁻ into the solution [35]. In view of the low redox potential of Se²⁻/Se (-0.924 V) and the fascinating properties of graphene [37–39], we chose Se²⁻ to chemically restore GO to form RGO nanocomposites. The degradation of ZnSe-[DETA]_{0.5} nanobelts in a GO solution may be a good way to realize the chemical graphitization and functionalization of GO. Fig. 1a–d present the typical TEM and SEM images of the nanocomposites obtained by acidification of ZnSe[DETA]_{0.5} nanobelts in a GO solution. Compared with the thickness of pristine ZnSe[DETA]_{0.5} nanobelts (35–50 nm) (Supplementary information Fig. S1), the nanobelts flatly attached on the RGO after acidification (Fig. S2) are much thinner (approximately 18 nm) and very flexible (Fig. 1d), due to the depletion of DETA stabilizers and the partial dissolution of ZnSe [35]. The partial dissolution of ZnSe caused by acidification released Se²⁻ and Zn²⁺ into the solution. On one hand, these Se²⁻ anions enabled the chemical reduction of GO in the solution, and thus simultaneously doped Se into the RGO. On the other hand, the dissolved oxygen in the reaction solution could also react with Se²⁻, resulting in the formation of Se. Therefore, the system was carefully

Figure 1 Characterizations of ZnSe/Se-RGO nanocomposite. (a, c) TEM and (b, d) SEM images of ZnSe/Se-RGO nanocomposite; (e) EDS elemental mapping images of ZnSe/Se-RGO nanocomposite; (f) TGA of ZnSe/Se-RGO nanocomposite; (g) XPS spectra in the C 1s region of ZnSe/Se-RGO and GO; (h) FTIR spectra of ZnSe[DETA]_{0.5}, ZnSe/Se-RGO, and GO. Insets in panel (f) are the photographs of the reaction solution before/after adding HCl.

sealed by Parafilm during the reaction to prevent the diffusion of oxygen and improve the reaction between Se^{2-} and GO. The chemical composition of the obtained nanocomposite was investigated by EDS elemental mapping and TGA. Fig. 1e exhibits the Se, Zn, and C elements in the obtained nanocomposite. The more extensive distribution of Zn may be caused by the adsorption of the released Zn^{2+} on the RGO. In addition, the quantitative calculation from the EDS elemental mapping indicates that the stoichiometric ratio of Se and Zn is 3.5:1 in the obtained nanocomposite. Thus, the obtained nanocomposite is rich in Se, and XPS analyses confirm that Se shows three bonding characteristics: $-\text{C}-\text{Se}-\text{C}-$ (56.13 eV) (i.e., doped Se in RGO), Se^0 (55.22 eV), and Se^{2-} (54.13 eV) (i.e., ZnSe) (Fig. S3). TGA was used to further reveal the existence of Se^0 and ZnSe in the obtained nanocomposite, showing two regions of weight loss (Fig. 1f): the first weight loss, which occurred from room temperature to 500°C, resulted from the removal of adsorbed water and Se, while the second weight loss be-

tween 850 and 1150°C was ascribed to the removal of ZnSe. The insets in Fig. 1f show that the color of the nanocomposite solution changes from yellow to black after adding HCl into the reaction solution, which is an obvious visible characteristic of the reduction of GO. The reduction of GO can also be demonstrated by XPS and FTIR spectra (Fig. 1g, h). The C 1s spectrum of GO has two peaks: one at 284.82 eV for sp^2 carbon in graphite [40] and the other at 286.83 eV assigned to C-OH, C=O, and O=C-OH species [41]. However, the obtained nanocomposites show only one C-C peak at 284.82 eV and exhibit two broad peaks at 1564 and 1168 cm^{-1} , resulting from the aromatic C=C stretching and C-O stretching vibrations, respectively [42]. Thus, after the degradation of ZnSe[DETA]_{0.5} nanobelts, the major oxygen-containing groups in GO were eliminated, and the obtained nanocomposite was composed of Se, ZnSe, and RGO, named as ZnSe/Se-RGO nanocomposite.

Raman spectroscopy, as one of the most sensitive and informative tools to characterize disorder in sp^2 carbon

materials [43], was conducted to illustrate the chemical structural changes of GO during the degradation process of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts. Generally, the Raman spectra of GO/RGO have four main peaks: D peak ($1330\text{--}1340\text{ cm}^{-1}$); G peak ($1580\text{--}1600\text{ cm}^{-1}$); 2D peak (2700 cm^{-1}); and D+D' peak (2940 cm^{-1}) [43,44]. The intensity ratio (I_D/I_G) of D peak and G peak commonly increases after the chemical reduction of GO due to the restoration of sp^2 carbon and the decrease in the average size of the sp^2 domains [45,46]. As shown in Fig. 2a, b, with increasing reaction time and HCl volume, the I_D/I_G of ZnSe/Se-RGO nanocomposite dramatically increases, demonstrating that the structure of the initial GO is well restored. Prolonging reaction time allows the reaction between GO and Se^{2-} to proceed more thoroughly, while the larger volume of HCl leads to more Se^{2-} , thus improving their reaction with GO. Concerning the mass of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts, when the mass ratio between GO and the $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts exceeded 1:2, the I_D/I_G of ZnSe/Se-RGO nanocomposite remained almost constant (Fig. 2c). Thus, the structural restoration of GO was weakly dependent on the amount of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts. These parameters also affected the final morphology of the obtained ZnSe/Se-RGO nanocomposite. Compared with the reaction time and the HCl volume, the effect of the mass of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts on the morphology of ZnSe in the obtained nanocomposite was significant (Figs S4, S5). The excess amount of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts was beneficial for maintaining the belt-like structure of ZnSe in the final nanocomposite (Figs S4c, S5c). $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts could also well keep their original belt-like structure if no HCl added (Fig. S6), but the chemical structure of the initial GO was poorly restored (Fig. S7). In addition, Raman spectra of all samples have a strong band with a maximum at 250 cm^{-1} , which can be attributed to Se and ZnSe

(Fig. S8).

The reaction mechanism between GO and $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts was investigated by using an *in situ* reaction equipment to monitor the change of pH and conductivity of the reaction solution (Fig. 3 and Fig. S9). A precise low temperature thermostat was used to maintain the reaction temperature at 303.15 K for providing stable reaction/monitoring conditions. Firstly, the reaction solution was saturated by N_2 to eliminate dissolved oxygen (Fig. 4), which can cause the oxidation of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts and Se^{2-} . Then, as shown in Fig. 3a–c, the solutions of HCl, GO and $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts were sequentially added into the N_2 -saturated reaction solution to trigger the interactions between GO, $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts, and HCl. After adding HCl, the pH value of the reaction solution dramatically decreased due to the increase of the concentration of H^+ , while the conductivity quickly increased because of the increase of ions in the solution (Fig. 4). Unlike HCl, the addition of GO did not heavily affect the pH value and the conductivity of the reaction solution, but slightly increased the dissolved oxygen concentration (Fig. 4), due to the dissolved oxygen in GO solution. When $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelt solution was added into the reaction solution, the color of the reaction solution changed into khaki, a mixed color of yellow (the color of GO) and white (the color of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts) (Fig. 3b, c). Meanwhile, the conductivity of the reaction solution decreased to some extent (Fig. 4) because of the strong interactions between HCl and $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts, such as acidolysis of ZnSe and protonation of DETA [35], which resulted in the destabilization of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts. These destabilized $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts released highly reactive Se^{2-} into the solution, which triggered the reduction of GO. Thus, the addition of acid is extremely important for the interaction between ZnSe-

Figure 2 Effects of different parameters on the structural restoration of GO. Raman spectra of RGO obtained by changing (a) the reaction time; (b) the volume of HCl; and (c) the mass ratio between GO and $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts.

Figure 3 Photographs of the *in situ* reaction equipment for monitoring the reaction between GO and ZnSe[DETA]_{0.5} nanobelts during different reaction stages.

Figure 4 Evolution of oxygen saturation, pH value, and conductivity of the reaction solution.

[DETA]_{0.5} nanobelts and GO nanosheets. As the reaction proceeded, the color of the reaction solution changed from yellow to black (Fig. 3d–f). In addition, the obtained ZnSe/Se-RGO nanocomposite exhibited poor dispersibility (Fig. 3g, h), indicating that the hydrophilic oxygen-containing groups of GO were eliminated and the structure of the initial GO was well restored (Fig. S10).

Due to the temperature-dependent decomposition behavior of ZnSe/Se-RGO nanocomposite (Fig. 1f), the

ZnSe-RGO nanocomposite was prepared by annealing the ZnSe/Se-RGO nanocomposite at 600°C for 3 h to remove Se⁰. As shown in Fig. 5a, after annealing, the TGA curve of the obtained ZnSe-RGO nanocomposite only exhibits one region of weight loss (from 850 to 1150°C), which corresponds to the removal of ZnSe, while the region of weight loss for Se⁰ does not appear. Thus, Se⁰ in the ZnSe/Se-RGO nanocomposite was completely removed after annealing, and pure ZnSe-RGO nanocomposite was obtained. However, ZnSe in the obtained ZnSe-RGO nanocomposite did not retain its initial morphology (i.e., as a nanobelt) but evolved into small NPs due to the ripening caused by heating (Fig. 5a). The annealing process improved the crystallization of ZnSe in the obtained ZnSe-RGO nanocomposite, and sharp and strong characteristic peaks of hexagonal ZnSe (JCPDS 15-0105) were observed in the XRD pattern of the ZnSe-RGO nanocomposite (Fig. 5b). In addition, compared with ZnSe/Se-RGO nanocomposite, the I_D/I_G of the ZnSe-RGO nanocomposite is almost unchanged after annealing (Fig. 5c). The XPS spectrum of the ZnSe-RGO nanocomposite was also determined, and the single C–C peak at 284.82 eV indicated the chemical structure of GO was well restored (Fig. S11). The fine XPS spectrum of Se is depicted in Fig. 5d. Similar to ZnSe/Se-RGO nano-

Figure 5 Characterizations of the ZnSe-RGO nanocomposite. (a) TGA curve and TEM image (inset) of the ZnSe-RGO nanocomposite; (b) XRD patterns of the ZnSe/Se-RGO and ZnSe-RGO nanocomposites; (c) Raman spectra of GO, ZnSe/Se-RGO, and ZnSe-RGO nanocomposites; and (d) high-resolution Se 3d spectra of the ZnSe-RGO nanocomposite.

composite, the ZnSe-RGO nanocomposite also contained three forms of Se (i.e., $-C-Se-C-$, Se^0 , and Se^{2-}). The large peak area of the fitting peak of Se^{2-} means that ZnSe represents the main surface composition, and the fitting peak of Se^0 is attributed to the surface oxidation of ZnSe [47].

The Se-RGO nanocomposite can be obtained by further acidification of the ZnSe/Se-GO nanocomposite in air in a HCl solution with a high concentration for another 24 h. Finally, we obtained Se-RGO nanocomposite, and all ZnSe nanobelts in ZnSe/Se-RGO nanocomposite were oxidized to Se NPs (Fig. 6a, b). The TGA curve of the obtained Se-RGO nanocomposite exhibited only one region of weight loss (from 300 to 500°C), which corresponded to the removal of Se, while the region of weight loss for ZnSe did not appear (Fig. 6c). Thus, Se^0 was the dominant form of Se in the Se-RGO nanocomposite. Fig. S12 shows the TEM images of the Se-RGO nanocomposite after annealing at 600°C for 3 h. All Se NPs were removed, and we did not observe any other NPs except for Se-doped RGO nanosheets, meaning that all ZnSe in the ZnSe/Se-RGO nanocomposite were transformed into Se NPs. As a result, unlike ZnSe/Se-RGO

nanocomposite, the Se-RGO nanocomposite contained only two forms of Se (i.e., $-C-Se-C-$ and Se^0) (Fig. 6d). The C-C peak (at 284.82 eV) indicated that GO nanosheets were well reduced (Fig. S11).

Furthermore, the Se NPs of Se-RGO nanocomposite exhibited a high chemical reactivity, which endowed the Se-RGO nanocomposite as an excellent precursor for the synthesis of various RGO nanocomposites. Fig. 7a, b show the TEM images of Ag_2Se -RGO and Cu_2Se -RGO nanocomposites, which were obtained by simply adding $AgNO_3$ and $Cu(NO_3)_2$ into the Se-RGO nanocomposite solution at room temperature, and the sizes of Ag_2Se / Cu_2Se NPs are 30–200 nm (Fig. S13). Similar to the Se NPs in Se-RGO nanocomposite, all Ag_2Se and Cu_2Se NPs attached on RGO sheets (Fig. S14). The XRD patterns of the as-synthesized nanocomposites, as shown in Fig. 7f, indicate that the products are Ag_2Se (JCPDS Card, No. 24-1041) and Cu_2Se (JCPDS Card, No. 88-2043). In addition to the Ag_2Se - and Cu_2Se -RGO nanocomposites demonstrated here, we believe that various selenide-RGO nanocomposites can be easily obtained by using Se-RGO nanocomposite as chemical precursor or using Ag_2Se - and Cu_2Se -RGO nanocomposites as ion-exchange tem-

Figure 6 Characterizations of the Se-RGO nanocomposite. (a) TEM and (b) SEM images; (c) TGA curve and (d) high-resolution Se 3d spectra of the Se-RGO nanocomposite.

Figure 7 Characterizations of various selenide/metal-RGO nanocomposites. TEM images of (a) Ag_2Se -RGO nanocomposite, (b) Cu_2Se -RGO nanocomposite, and (c) Pt-RGO nanocomposite; SEM images of Se-RGO nanocomposites stored in (d) DIW and (e) EG for 48 h; and (f) XRD patterns of various selenide/metal-RGO nanocomposites.

plates. We further investigated the first-order solid–solid phase transition of the obtained Ag_2Se -RGO nanocomposite. The DSC cycle of Ag_2Se -RGO nanocomposite shows an endothermic peak (at 104.54°C , β to α structure transition) during heating and an exothermic peak (at

87.17°C , α to β structure transition) during cooling (Fig. S15), indicating that the crystal structure of Ag_2Se -RGO nanocomposite undergoes a reversible phase transition. Remarkably, the transition temperatures of Ag_2Se -RGO nanocomposite are much lower than the reported

values [48]. In addition, we also used Se-RGO nanocomposite to synthesize Pt-RGO nanocomposite by reacting Se-RGO nanocomposite with H_2PtCl_6 at 60°C . As shown in Fig. 7c, unlike larger Se, Ag_2Se , and Cu_2Se NPs, Pt NPs are very small (about 9.4 nm) and evenly distributed on the RGO sheets (Figs S13 and S16). As shown in Fig. 7f, XRD pattern of these Pt NPs is in good agreement with the standard literature data (JCPDS Card, No. 87-0646). In a similar way, we believe that the nanocomposites of other noble metals (such as Au, Pt, or multiple alloys) and RGO can also be prepared. Thus, the Se-RGO nanocomposite provides a new platform for the synthesis of various functional RGO nanocomposites. The Se NPs of Se-RGO nanocomposite also exhibit a poor structural stability. When Se-RGO nanocomposite was stored in EG for 48 h, the Se NPs of Se-RGO nanocomposite evolved into Se nanowires (Fig. 7e and Fig. S17a). Unlike attached Se NPs, these Se nanowires were partially independent and had a good crystallinity (JCPDS Card, No. 73-0465) (Fig. 7f). However, when the Se-RGO nanocomposite was stored in DIW for 48 h, the Se NPs of Se-RGO nanocomposite maintained their original morphology (Fig. 7d and Fig. S17b) and crystallinity (Fig. 7f). Remarkably, the morphology of Se NPs could remain for more than 3 months, when the Se-RGO nanocomposite was stored in water at 4°C (Fig. S18), meaning that the Se NPs of Se-RGO nanocomposite had a good structural stability in water.

CONCLUSIONS

In summary, the degradation of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts under acidic conditions can easily release highly reductive Se^{2-} into the reaction solution; the Se^{2-} has a very low redox potential (-0.924 V), thus enabling the chemical graphitization and functionalization of GO at room temperature. The structural restoration of GO heavily depends on the concentration of the released Se^{2-} in the reaction solution, which is determined by several factors, including the reaction time, the volume of HCl, and the mass ratio between GO and the $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts. Several Se-based RGO nanocomposites ($\text{ZnSe}/\text{Se-RGO}$, ZnSe-RGO , and Se-RGO) can be prepared by modulating the degradation process of $\text{ZnSe}[\text{DETA}]_{0.5}$ nanobelts. Among these nanocomposites, the Se-RGO nanocomposite can be used as a versatile precursor to synthesize various functional RGO-based nanocomposites, such as $\text{Ag}_2\text{Se-RGO}$, $\text{Cu}_2\text{Se-RGO}$, Pt-RGO , and even Se nanowire-RGO nanocomposites. This study opens an unconventional avenue to graphitize and functionalize GO under mild conditions based on the poor stability of

nanomaterials and utilizing the degradation processes of unstable nanomaterials to build up new synthesis platforms for functional nanocomposite materials. Except the case confirmed here, there are many other ways to utilize the unstable process of nanomaterials, such as (i) by combining with “conversion chemistry” (ion exchange, galvanic replacement, and so on) to transform the intermediate nanostructures obtained from the unstable process into target products with expected sizes, shapes, and properties; (ii) by utilizing the dissolution or the etching caused by the unstable process to reshape original nanomaterials into the desired size or morphology; (iii) by utilizing the unstable process to assemble the destabilized nanomaterials into ordered assemblies. Thus, we think that the unstable process of a nanomaterial will be a versatile platform to design and synthesize various functional materials, which cannot be accessible by direct synthesis.

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Author contributions Yu SH and He C conceived and supervised the project. Xu L, Hu ZW and Wang LL conducted the experiments, analyzed the results and wrote the paper. Yu SH and He C revised the manuscript. All authors contributed to the general discussion.

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Supplementary information Supporting data are available in the online version of the paper.

Liang Xu received his Bachelor's degree from Lanzhou University in 2011 and his PhD in 2016 from the University of Science and Technology of China (USTC) under the supervision of Prof. Shu-Hong Yu. Now, he is a postdoctor at Shenzhen University, and his current research focuses on the stability and reactivity of nanomaterials.

Chuanxin He received his PhD in polymer chemistry and physics from USTC in 2010 and now is an Assistant Dean of the College of Chemistry and Environmental Engineering, Shenzhen University. His current research interest is to design and synthesize novel nanostructure materials for fuel cells, water splitting and electrochemical reduction of carbon dioxide.

Shu-Hong Yu completed PhD in inorganic chemistry in 1998 from USTC. Currently, he is leading the Division of Nanomaterials & Chemistry, Hefei National Research center for Physical Sciences at the Microscale, USTC. He was elected as an academician of the Chinese Academy of Sciences in 2019. His research interests include bio-inspired synthesis of nanoscale building blocks, self-assembly and macroscopic assemblies, nanocomposites, and their functions and applications.

基于 $\text{ZnSe}[\text{DETA}]_{0.5}$ 有机无机杂化纳米带的不稳定性实现氧化石墨烯非常规化学石墨化和功能化

徐亮^{1,2}, 胡增文², 汪乐乐², 何传新^{1*}, 俞书宏^{2*}

摘要 与宏观块材不同, 纳米材料高的表面能赋予其亚稳态特性, 使其对外界变化十分敏感. 当纳米颗粒与外界发生强烈相互作用(溶解、酸解等)时, 这些高度不稳定的纳米颗粒将通过一系列持续的调整过程(结构重组、化学转化等)来达到一个新的稳态, 而合理地利用这些调整过程可实现功能纳米材料的非常规设计和制备. 本文基于 $\text{ZnSe}[\text{DETA}]_{0.5}$ 有机无机杂化纳米带的低稳定性提出了一种氧化石墨烯非常规化学石墨化和功能化新策略. 在强酸作用下, H^+ 离子会质子化 $\text{ZnSe}[\text{DETA}]_{0.5}$ 纳米带中的DETA分子, 使得原本被DETA分子所稳定的 ZnSe 无机片层变得极为不稳定, 释放出高还原性的 Se^{2-} 阴离子. 这些高还原性的 Se^{2-} 阴离子与溶液中的氧化石墨烯纳米片相互作用, 在室温条件下即可对其进行非常规化学还原和掺杂. 此外, 由于 Se^{2-}/Se 较低的还原电势(-0.924V), 通过控制 Se^{2-} 阴离子的氧化过程和后处理过程, 可分别得到 $\text{Se}/(\text{Se}+\text{ZnSe})/\text{ZnSe}$ 与还原石墨烯的三种不同复合材料; 其中, Se -还原石墨烯复合材料又可作为前驱体进一步通过物理/化学过程形成 Se 纳米线/ $\text{Cu}_2\text{Se}/\text{Ag}_2\text{Se}/\text{Pt}$ 与还原石墨烯复合材料. 显然, 合理地利用纳米材料的不稳定过程可以为构建各种功能纳米材料提供一个非常规设计和制备平台.