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ARTICLE TYPE

High photocatalytic performance by engineering Bi_2WO_6 nanoneedles onto graphene sheets

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A facile sonochemical method was developed in this study to engineer Bi_2WO_6 (BWO) nanoneedles onto graphene sheets, producing a graphene/BWO composite. BWO was *in situ* formed on reduced graphene oxide during ultrasonic processing, and the subsequent thermal treatment produced BWO nanoneedles that were homogeneously dispersed on the surface of graphene sheets; these needles, with a cross section size of ~450 nm at the bottom and an average length 2500 nm, grew nearly vertically on the sheets. When used as a photocatalyst, the composite produced a high quantity 23.61 μmol h^{-1} of O_2 from water, 4.79 times higher than that by neat BWO powder; it also created H_2 at 234.83 μmol h^{-1}. It was found that the reduction of graphene oxide plays a key role in fabricating nanoneedles and ultrasonication can promote the interaction between graphene and BWO. Thus, the strategy provides an efficient approach for the fabrication of graphene composites containing nanoneedles.

Introduction

The photocatalytic production of hydrogen and oxygen from water is vital to energy and environment because of its great potential in converting solar energy to chemical energy. Since the pioneering work of photocatalytic splitting of water by TiO_2 electrodes in 1972[1], extensive studies have been conducted on binary metal oxides, such as TiO_2[2-4], ZnO[5, 6] and Bi_2O_3[7,8]. Many binary metal oxides are disadvantaged by their valence bands typically consisting of O 2p[9], which limits their applications in O_2 production. They are also ineffective in visible absorption which occupies ~43% the solar radiation energy. To solve the problem, scientists have turned to ternary metal oxides such as $BiVO_4$[10, 11] and Bi_2WO_6[12, 13] owing to their visible light adsorption abilities. The bands of ternary metal oxides are formed by atomic orbitals from more than one element, and thus the modulation of element ratios can finely tune the valence potentials and the conduction bands as well as the band energy, which makes them promising for visible-light-active photocatalysts. Of all these oxides, Bi_2WO_6 has attracted particular interest due to its band gap 2.75 eV corresponding to a photo-absorption light region up to 450 nm[12]. Nevertheless, the photocatalytic activity of pure Bi_2WO_6 is limited by the poor rates of charge separation and transfer. Two major methods have been explored to address these limitations: high specific surface area is reported effective in improving the photocatalytic performance[2, 10]; and doping Bi_2WO_6 with other elements, such as C, Ag, Fe, is proved effective either in extending the photo-response region or maximizing the separation efficiency or increasing the oxidation power of photogenerated carriers[14-16]. However, it is a formidable challenge to find a single material which demonstrates all these functions with no doping.

Fortunately, coupling the metal oxides with graphene appears promising to address this challenge[17, 18]. Graphene could enhance the transport of electrons photo-generated in semiconductor particles owing to the abundance of delocalized electrons from the conjugated sp2-bonded carbon network[4, 19, 20]. Meanwhile, its large surface area in theory can provide sufficient active sites, increasing the efficiency of water splitting[21]. In addition, the introduction of graphene darkens the composites hence extending their absorption in almost the entire visible light region. Graphene-based metal or semiconductor composites are generally synthesized using graphene oxide (GO) as the precursor, because GO is rich in functional groups like hydroxyl and epoxide groups on the basal planes and carboxyl groups at the edges[12, 22]. The presence of oxygen functionalities allows interactions with cations and thus provides reactive sites for the nucleation and growth of nanoparticles. This makes GO suitable to engineer nano-entities of metals and semiconductors. It was found that the morphology of semiconductors on GO plays a key point in photocatalytic performance, such as needle-like morphology showing higher performance than particulate morphology[23].

Herein, we report for the first time the synthesis of a composite consisting of Bi_2WO_6 (BWO) nanoneedles engineered onto graphene sheets. The composite shows a markedly enhanced performance of producing H_2 and O_2 from water when used as a photocatalyst under visible light irradiation. A mechanism for the formation of BWO nanoneedles on graphene sheets is also proposed based on the results.

Experimental section

1. Preparation of RGO

1 g of GO (prepared by the Hummer's method) was added to 2000 mL of water and stirred at ambient temperature for 2 h,

followed by sonication at room temperature for 3 h using a high-intensity ultrasonic probe (Ti horn, 20 kHz, 75 W/cm^2). Then 32 mL of hydrazine (85%) was added under magnetic stirring, and the mixture was continuously stirred at 60 °C for 12 h to obtain reduced graphene oxide (RGO).

2. Preparation of RGO-BWO and RGO-BWO-T

2.5 g of Bi $(NO_3)_3 \cdot 5H_2O$ was added to 25 mL of water, which produced white suspension caused by $Bi(OH)_3$ precipitate. 2.5ml of 65% HNO_3 was dropped into the suspension under vigorous magnetic stirring at ambient temperature. When the mixture appeared transparent, 0.6 g RGO was added to the above solution, with stirring at ambient temperature for 3 h. The mixture gradually became pasty, and turned black.

1.31 g of $(NH_4)_{10}W_{12}O_{41}$ was added to 10 mL water to obtain transparent solution which was added to the aforementioned RGO mixture with the pH tuned to 7. The mixture was continuously stirred at 50 °C for 2 h, followed by sonication at room temperature for 3 h using a high-intensity ultrasonic probe (Ti horn, 20 kHz, 100 W/cm^2). The mixture was centrifuged and rinsed with ethanol and H_2O several times, followed by drying under vacuum at 60 °C, to obtain a composite (RGO-BWO) containing Bi_2WO_6 and RGO. After calcination at 450 °C for 3 h under nitrogen, a black crystalline composite (GR-BWO-T) was obtained.

3. Preparation of BWO and BWO-T

As a bench mark, pure Bi_2WO_6 powders were also prepared by a similar procedure without adding RGO precursor. The sample dried under vacuum is denoted BWO. After calcination at 450°C, pale yellow crystalline powders (BWO-T) were obtained.

4. Photocatalytic water splitting experiments

Photocatalytic oxygen reactions were conducted at 20 ºC in a Lab Solar gas photocatalysis system with external light irradiation. The light source was a Xenon lamp (300 W, PLS-SXE300/300UV, China) equipped with a cut-off filter L42 ($\lambda >$ 420 nm). Prior to testing, oxygen dissolved in 60 mL of ultra-pure water was removed by degassing when the water was thermally treated. In O_2 production, 0.03 g of the photocatalysts (BWO-T, physically mixed BWO-T/GR (77 % graphene+23 % BWO-T), and GR-BWO-T) and 10 mL of 16.0 mmol/L $Fe_2(SO_4)_3$ were added to the reactor in tandem under vigorous magnetic stirring to ensure the particles suspending all the time. In H_2 production, 0.03 g of the photocatalyst (GR, GR-BWO-T, and physically mixed BWO-T/GR) and 15 mL of methyl alcohol were added to the reactor successively under vigorous magnetic stirring to ensure the particles suspending similarly. During the experiment, the temperature was controlled at 20 °C by using tap water. The amount of gas produced was determined using gas chromatography **(GC7890II, thermal conductivity detector, nitrogen carrier gas)**

5. Characterization

The synthesized samples were characterized by X-ray diffraction (XRD) using a RigakuD/max2550VL/PC system operated at 40 kV and 40 mA with Cu-K α radiation (λ = 1.5406 A°), at a scan rate of 5° min^{-1} and a step size of 0.050° in 2θ. Nitrogen adsorption measurements at 77 K were performed using an ASAP2020 volumetric adsorption analyser, after the samples had been outgassed for 8 h in the degas port of the adsorption apparatus. Field-emission scanning electron microscopy (FESEM) was performed on a JEOL JSM-6360LV field emission microscope at an accelerating voltage of 15kV. Transmission electron microscopy (TEM) was carried out on a JEOL 2010 microscope at 200kV. TEM specimens were prepared by grinding the synthesized samples into powder with a mortar and pestle and the powder was dispersed in pure ethanol and picked up with holey carbon supporting films on copper grids. A Dilor LABRAM-1B microspectrometer with 633 nm laser excitation was used to record the Raman spectrum of the samples. Fourier transform-infrared measurements (FT-IR) were recorded on KBr pellets with a PE Paragon 1000 spectrophotometer. Thermal gravimetric analysis (TGA) was conducted on a PETGA-7 instrument with a heating rate of 20 °C min^{-1}. Diffuse reflectance electronic spectra (DRS) were measured with a Perkin–Elmer 330 spectrophotometer equipped with a 60 mm Hitachi integrating sphere accessory.

Results and discussion

The phase structures of as prepared samples were characterized by X-ray diffraction patterns (XRD). In Fig. 1, the main diffraction patterns of graphene/Bi_2WO_6 composite after thermal treatment (GR-BWO-T) are similar to those of pure Bi_2WO_6 powders (BWO) fabricated by a similar process but without reduced graphite oxide (RGO), characteristic of orthorhombic BWO (JCPDS card no. 39-0256). The observed five major diffractions match well with the (131), (200), (222), (331) and (262) crystal planes of orthorhombic BWO, respectively. A careful comparison identified a small diffraction at 2θ = 26° in pattern of GR-BWO-T but not in the Bi_2WO_6 after thermal treatment (BWO-T), indicating the existence of RGO in the GR-BWO-T composite. Moreover, a few sharp peaks emerged in GR-BWO-T while not in BWO-T, can be ascribed to (060), (202), and (123) planes of BWO. This is caused by the emerging of some different exposed facets in GR-BWO-T from that in BWO-T.

The BWO fraction in the composite was determined by performing thermo-gravimetric analysis (TGA) in air at 40 –900 °C (as shown in Fig. 2). A severe mass loss is seen at around 200°C due to the decomposition of oxygen-containing groups of GO in air. A significant mass loss was observed at temperatures from 510 to 700 °C for all the samples due to the destruction of the carbon skeleton (carbonyl/double bond) of graphene. The weight loss of GR–BWO–T was stabilized at 23% between 700 and 900 °C, implying a BWO fraction of 23 wt%.

The morphologies of BWO-T and GR-BWO-T were analyzed by scanning electron microscopy (SEM) (in Fig. 3). It is observed that BWO (a, b in Fig.3) mainly displays rectangle morphology (~110×1600×2300 nm), but rods (with a length of 600-800 nm) are also observed taking less quantity. Regarding GR-BWO-T (c, d in Fig. 3), BWO nanoneedles are uniformly dispersed on graphene sheets and they appear to grow on the graphene sheets, suggesting that BWO needles might interact with graphene. These nanoneedles have a cross-section size of around 450 nm at the bottom, and a length of ~2500 nm. It is worth noting that the nanoneedles grow nearly vertically on the sheets, which prevents the graphene sheets stacking and thus provides space for access to water molecules and light during the photocatalytic reaction, resulting in a significant improvement in the photocatalytic efficiency. Thus, SEM observation provides direct evidence for the fabrication of BWO nanoneedles on the graphene sheets.

The Raman spectrum of GR-BWO-T (Fig. 4) displays two prominent peaks at around 1350 (D band) and 1601 cm^{-1} (G band), suggesting the existence of graphene in the composites. Similarly, two prominent peaks appear at 1340 and 1582 cm^{-1} in GO; by contrast, the GO spectra after thermal processing displays two peaks at 1343 and 1594 cm^{-1}. It is worth noting that GR-BWO-T shows an obvious G band up-shift compared with those of GO and GR, solid evidence for the chemical bonding between BWO and graphene, as supported by previous studies[12, 24, 25]. It is known that the *n*-type doping of graphene causes a downshift of G band, while the *p*-type doping results in an up-shift[26, 27]. In this study, the Raman shift of the G band for GR-BWO-T provides strong evidence for the accelerated charge transfer between GR and BWO-T. Furthermore, the 2D band in GR-BWO-T shift to higher wavenumbers compared with GO and GR, which may be ascribed to the disordered and randomly arranged GRs, indicating that the RGO in RGO-BWO-T has been further deoxygenated and reduced thermally[28]. Moreover，a higher D/G intensity ratio (1.163) is found in GR-BWO-T in comparison with those in neat GR (1.086) and in GO (0.906), thus indicating a likely higher structural integrity of graphene resulting from the fabrication[29].

Figure 5 shows the nitrogen adsorption/desorption isotherms for BWO-T, RGO and GR-BWO-T. The BET (Brunauer, Emmett and Teller) surface area of GR-BWO-T increases from 5.6 (pure BWO-T sample) to 20.7 m^2 g^{-1}, far lower than that of RGO (49.12 m^2 g^{-1}). A larger specific surface area of photocatalysts can supply more surface active sites and make charge carriers' transport more available, leading to an enhancement of the photocatalytic performance. The behavior of the isotherm for GR-BWO–T was similar to that of RGO, indicating the presence of open pores. The P/P_0 position of the inflection points is related to the size of mesopores, and the sharpness of these steps indicates the uniformity of pore size[30]. As the relative pressure increases, the isotherms of both RGO and GR–BWO–T exhibit sharp inflections when the P/P_0 ranges 0.4–0.6, a characteristic of capillary condensation within a uniform interlayer spacing. In comparison, neat BWO-T shows an isotherm of type III, indicating the presence of large macropores, because the hysteresis loops of macropores are associated with slit-like pores formed by the aggregations of plate-like particles; both GO and GR-BWO-T have isotherms of type IV, suggesting the presence of mesopores. In other words, it appears that the prepared nanocomposite is composed of sheet-like graphene decorated with BWO nanoneedles.

The FT-IR spectra of GO, RGO and GR-BWO-T are shown in Fig. 6. The representative absorptions of GO are at 3400 cm^{-1} (O–H stretching vibration), 1736 cm^{-1} (C=O stretching vibration of COOH groups), 1396 cm^{-1} (tertiary C–OH stretching vibration), and 1072 cm^{-1} (C–O stretching vibration)[31]. In comparison, RGO and GR-BWO-T show absorptions at the same wavelength but with far lower absorption intensity, indicating the reduction of GO. The absorption band appearing at 1572 cm^{-1} clearly shows the graphene skeletal vibration (C=C), indicating its formation in GR and GR-BWO-T. New absorptions appear between 500 and 1200 cm^{-1}, which can be attributed to stretching vibration of Bi–O and W–O[32, 33]. Especially two new absorptions at 728 and 830 cm^{-1} are associated with the formation of W–O–C bonds and apical O–W–O bonds, respectively, which will be confirmed by XPS analysis (in Fig. 8).

The light-absorbance property of the samples was studied with a *UV–vis* spectrophotometer, and Fig.6 contains the measured UV–visible diffuse reflectance electronic spectra. All samples display photo absorption from a UV to visible light rang (below 450 nm). BWO-T displays photo absorption properties from the UV light region to the visible light absorption shorter than 470 nm, which is attributed to the transition from the hybrid orbital of O 2p and Bi 6s to the W 5d orbital[34]. While the GR-BWO-T shows an intense, broad background absorption in the visible light region, which was similar with that of RGO. The increase of absorption in the visible light region is due to the reintroduction of black body properties typical of graphite-like materials, indicating the existence of graphene in GR-BWO-T. The big difference could also be seen from the color difference, where the BWO-T was yellow, the RGO and GR-BWO-T samples were both black. Because of the increased absorbance, a more efficient utilization of the solar energy can be obtained. Therefore, we can infer that the introduction of graphene in BWO-T nanoneedles is effective for the visible-light response of the composite. Similar phenolmenon has been reported in CdS-Cluster-Decorated graphene nanosheets, where the samples with 40%'s graphene content showed excellent photocatalytic performance .

X-ray photoelectron spectroscopy (XPS) was used to confirm the formation of bond between graphene and BWO during the sonochemical process. As shown in Fig. 7a, the sample contains Bi, W, O and C elements and a trace amount of nitrogen. While C and N are ascribed to the residual from the precursor solution and also the adventitious carbon from XPS instrument itself. Two peaks with binding energies around 467.5 and 443.2 eV can be clearly seen in Fig. 7a, which can be ascribed to the signals of Bi $4d_{3/2}$ and Bi $4d_{5/2}$[35]. The peaks at 38.0 and 35.7 eV in GR-BWO-T correspond to $W4f_{5/2}$ and $W4f_{7/2}$, respectively, both of which can be assigned to a W^{6+} oxidation state[14]. Compared with BWO-T, these peaks were shifted up by 0.2 and 0.1 eV respectively, suggesting the formation of chemical bonding between the BWO and C elements in GR-BWO-T. It is obvious that Bi4f consists of two peaks with binding energies ~159.4 and 164.7 eV, corresponding to the signals from doublets of Bi $4f_{7/2}$ and Bi $4f_{5/2}$ in the trivalent oxidation state. Fig. 8b shows the XPS spectra of GR–BWO–T and BWO-T in the binding energy range 280–290 eV (C 1s). The two peaks at 287 and 285 eV for BWO indicate a low quantity of oxidation of graphite which was introduced as impurities during testing. The binding energy of 285 eV is due to non-oxygenated ring C (284.3 eV), and 287 eV is due to the C in C–O bonds (285.2 eV), the carbonyl C (C=O, 287.4 eV) and carboxyl C(COOH, 289.1 eV) respectively. The C 1s in both

RGO and GR–BWO–T exhibits only a single strong peak at 284.3 eV which is attributed to elemental carbon, with a weak shoulder at 285.4 eV due to the oxygen functionalities (C–O bonds), indicating considerable de-oxygenation by reduction[20]. As shown in Fig. 8c, the observed O1s peak at 532.9 and 530.5 eV can be attributed to the absorbed oxygen and the lattice oxygen in crystalline BWO-T, respectively[14]. Since GR-BWO-T shows higher intensity at 532.9 eV than BWO-T, it is readily inferred that the quantity of absorbed oxygen increases; this means that GR-BWO-T features a higher surface area, corresponding to the foregoing BET analysis (in Fig. 5).

BWO-T, GR-BWO-T and the physically mixed BWO-T/GR were investigated for photocatalytic performance in terms of O_2 creation from water containing electron acceptor Fe^{3+} ions. In Fig 9a, the quantity of O_2 created from H_2O after 8 h was ca.188.93 μmol for GR-BWO-T, 2.1 times higher than the physically mixed BWO-T/GR (ca. 76.03 μmol) and 4.79 times than BWO-T (ca. 39.43 μmol). It should be mentioned that the GR-BWO-T also showed enhanced photocatalytic performance compared with the composites of GR and BWO nanoparticles (164.81μmol)[17]. It is well known that during photocatalysis, light absorption and charge transfer and separation play important roles[36]. E_{VB} (energy of valence band) of BWO-T is more positive than the standard redox potential of H_2O/O_2 (0.10V vs. NHE), suggesting that the photo-generated holes of both BWO-T and GR-BWO-T could theoretically oxidize H_2O to produce O_2. To compare the O_2 creation rate of the samples, the results are calculated based on the quantity of BWO as shown in Fig. 10: the O_2 creation rate by GR-BWO-T (3422.67 μmol/g·h) is 20 times higher than that (164.3μmol/ g·h) by neat BWO-T. The significant difference must be ascribed to (i) increase in the light absorption intensity and range, which can be identified by the result of *UV-vis* diffuse spectra (in Fig. 7), and (ii) reduction of the recombination of electron-hole pairs in BWO due to the presence of graphene sheets (GR) in the composite. GR produced chemical bonding with BWO-T; on the other hand, the nanoneedle morphology of BWO-T helped improve the separation of electrons with their holes, which have been confirmed from the above-mentioned characterizations. Once GR is introduced to the nanoneedles, it can serve as an electron collector and transporter to efficiently separate the photo-generated electron-hole pairs, effectively lengthening the charge carriers' lifetime. Furthermore, the extraordinary surface area of GR allows for photocatalytic reactions to take place not only on the catalyst surface but on the graphene sheet, and this enlarges the reaction space markedly.

The photocatalytic H_2- creation activity was also evaluated under visible-light irradiation using lactic acid as a sacrificial reagent without co-catalyst. It is known that the reduction potential of the photo-generated electrons in BWO-T is not sufficient to reduce H^+ to obtain H_2 due to the position of the conduction band being too positive[12]. As expected, no hydrogen was detected when pure BWO-T was used as a photocatalyst. While a noticeable H_2-creation of 952.38 μmol is seen after 8 h for our neat GR (Fig.9b). It has been reported that the conduction bond (CB) minimum of reduced graphene oxide is composed of anti-bonding π* orbitals, which have a higher energy level than that needed for H_2 generation. Therefore, GR alone with a suitable reduction degree is likely to create H_2 from water. That is why the mixed BWO-T/GR also exhibits a H_2 creation of 687.34 μmol after 8 h. To our surprise, GR-BWO-T displayed a H_2 production of 1878.64 μmol, 170% enhancement over the physically mixed BWO-T/GR. The reason may be inscribed below: Firstly, GR can make BWO photoactive for H_2 generation, according to the report by Erping Gao etc[37]. The electronic interaction between graphene and Bi_2WO_6 might cause a cathodic shift of the E_{VB}, indicating a higher conduction band position and a stronger reductive power which may be involved in the reduction. Secondly, graphene with a two-dimensional conjugated *p* structure and superior electrical conductivity could efficiently transport the photo-generated electrons produced by BWO-T, owing to the bonding between GR and BWO-T as shown in the Raman G shift of GR-BWO-T and the XPS spectra(in Fig. 4 and Fig 8).

In this study we developed a sonochemical method for the fabrication of Bi_2WO_6 (BWO) nanoneedles on graphene sheets (GR), which showed excellent photocatalytic performance in the creation of both O_2 and H_2. A mechanism is proposed in Fig. 11. In process I, graphene oxide (GO) is used as a carrier to for BWO nanoparticles followed by thermal treatment, to prepare a sample denoted Gr-BWO-T-I. By contrast, chemically reduced GO (RGO) is used in the process II to produce GR-BWO-T by a similar process. GO has its basal planes mostly decorated with epoxide and hydroxyl groups in addition to a few carboxyl groups. After reduction by hydrazine, the number of these oxygen-containing groups decreased markedly, as outlined in Raman and FT-IR spectra (Fig.4 and Fig.6). When GO and RGO were dispersed in aqueous $Bi(NO_3)_3$ solution (Solution A), adsorption occurred during the stirring: Bi ions adsorbed on graphene oxide (GO) and reduced graphene oxide (RGO) through physisorption, electrostatic binding or charge-transfer interaction, resulting in a uniform dispersion of Bi ions on the surface of GO and RGO. Once $(NH_4)_{10}W_{12}O_{41}$ solution (solution B) was added as elaborated in the Experimental, Solution A reacts with Solution B to produce Bi_2WO_6. Since Bi ions can get attached with oxygen-containing groups, the reaction should occur on the surface of the exfoliated sheets. During the next step, the ultrasonication plays an important role: ultrasound causes acoustic cavitation that leads to the formation, growth and implosive collapse of bubbles in liquid[38]. This prevents the stacking of GO or RGO sheets, resulting in a thin film of amorphous Bi_2WO_6 coating on RGO surface, as clearly shown in SEM and XRD in Fig. S1 and Fig. S2, respectively. However, a thicker film could deposited on GO than RGO because more Bi ions attached to the oxygen-containing groups, as confirmed by the TGA analysis in Fig. S3.

During calcination, the oxygen-containing groups on GO and RGO sheets could work as nucleation sites. More oxygen-containing groups mean more nucleation sites; in other words, there are more nucleation sites on the surface of GO than RGO. Calcination can turn the deposited thin film into nanoparticles or other types of morphology, as supported by a previous work[17], where nanoparticles with size of 30–40 nm were formed on GR sheets through calcination. Due to the less quantity of nucleation sites on the RGO surface, larger nanoneedles with a cross-section size of the bottom around 450 nm and a length of 2500 nm are nearly vertically dispersed on the surface of GR sheets (Fig. 11, Process II). The one-step formation of the GR/Bi_2WO_6 composites under ultrasonic irradiation illustrates the simplicity and efficiency of the sonochemical approach as compared with the commonly used sol–gel procedure limited by complexity and time needed.

Conclusions

A facile sonochemical method has been developed to fabricate ternary BWO nanoneedles on the surface of graphene sheets. The nanoneedles have a cross-section area of ~450 nm at the bottom and a length of 2500 nm, and they formed on the surface of graphene sheets and dispersed homogeneously. When used as photocatalyst, the composite showed high performance in photocatalytic creation both in H_2 (234.83 μmol h^{-1}) and O_2 (23.61 μmol h^{-1}) from water. More interestingly, the oxygen-containing groups showed strong influence on the morphology control of BWO on the surface of graphene sheets. As compared with graphene oxide (GO), reduced graphene oxide (RGO) sheets have less quantity of oxygen-containing groups, providing less sites for both the physisorbtion of Bi ions and the deposition of BWO on the sheets, and this led to the formation of BWO nanoneedles on the sheets after calcination. Untrasonication enables the interaction between GR and BWO. Thus, the strategy provides an efficient approach for the fabrication of graphene-based composites with controlled nanoneedle morphology.

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Notes and references

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