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# Elemental bismuth-graphene heterostructures for photocatalysis from ultraviolet to infrared light

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**ABSTRACT:** For an optimized use of solar energy, the fabrication of photocatalysts that are sufficiently stable and responsible for harvesting full-spectrum light from ultraviolet to infrared is required to solve environmental issue and water shortage crisis, but remains a great challenge so far. Here, we show that elemental bismuth-graphene heterostructures synthesized by solvothermal method followed by calcination have high photocatalytic activity under not only ultraviolet but visible and even infrared light. These heterostructures are very stable after many photocatalytic cycles, and no leaching of bismuth is observed. Analysis of the morphological structures indicates that the heterostructures remain unchanged after repeated cycling, while displaying no appreciable loss in activity. Furthermore, the experimental and theoretical results demonstrate that the heterostructures have the sufficient band gap energy for simultaneously absorbing across the whole solar spectrum and producing photogenerated electrons which can be shuttled across elemental bismuth-graphene interface, ultimately turning out to be responsible for the degradation reaction. These findings may help the development of elemental photocatalysts with compatible activities from ultraviolet to infrared regions and hence enable solar energy conversion.

#### INTRODUCTION

Motivated by the problem that is inadequate access to safe water and sanitation, design and development of suitable heterostructured materials for photocatalytic solar-energy conversion systems has evoked great interest in decontaminating water from source to point-of-use at lower cost and with less energy.1-3 For full utilization of solar energy, one key requirement is that nanomaterials would combine an ability to efficiently degrade pollutants in wastewater, having an optimal bandgap that absorbs light in the wavelength region of not only ultraviolet (<400 nm, ~5%), but visible (400-800 nm, ~45%) and even infrared (>800 nm, ~50%), and to remain stable during a long-term photocatalytic reaction (Figure S1). Over the past decade, pioneer work has developed various pure and modified inorganic semiconductors as the efficient photocatalysts for water purification.<sup>4-9</sup> For example, TiO2 and ZnO doping with metal impurities were proven to show photodegradation capability under ultraviolet and visible light.<sup>10,11</sup> Nevertheless, the large-scale commercial application still strongly suffers from the basic limitations, including i) the bandgaps of oxide-based semiconductors are typically too large for infrared and most of the visible (>600 nm) light to be utilized, and ii) the defectsites can act as recombination centers and trap photocarriers before reaching to the reaction surface, thus decreasing quantum yield.<sup>12</sup> Indeed, the development of coupled

semiconductor systems can efficiently facilitate the interfacial electron transfer and tentatively extend photoresponse into infrared region.<sup>13-18</sup> However, the photocatalytic activities of the as-made photocatalysts are not sufficient due to the low photon energy and the strong thermoeffect. Moreover, most of them are incompatible to harvest full-spectrum solar light.<sup>19</sup> For these reasons, the search for photocatalysts with compatible activity from ultraviolet to infrared region and excellent stability attracts significant attention and becomes an important pursuit towards enabling a continual economy.

In addition to compound semiconductors, primary element-based nanomaterials such as silicon have emerged as an interesting type of photocatalytic system for organic contaminant degradation and hydrogen generation due to their suitable band structures.<sup>20-22</sup> For example, there was report of red phosphorus for photocatalytic hydrogen production from water under visible light irradiation.<sup>23</sup> Alternatively, significant attempts have been focused on understanding their unusual electronic properties and designing bismuth photocatalysts capable of using the less abundant but more energetic ultraviolet light.<sup>24,25</sup> For example, bismuth nanoparticles were found to be very efficient in the degradation of dyes under ultraviolet<sup>26</sup> and visible irradiation<sup>27-30</sup>, but not under infrared light. Benefitting from their size/shape dependent plasmonic effects<sup>31-33</sup> (0.45-2.63 eV), we predict that the photocatalytic response of elemental bismuth-based photocatalysts can be extended to infrared region via enhancing the electrical coupling between elemental bismuth and active materials, which should overcome the challenge in simultaneously achieving a) sufficient ultraviolet, visible and infrared-light response, b) suitable energy levels of conduction and valence bands, and c) effective interfacial separation of photogenerated electron. To demonstrate this, using graphene as the active material, we fabricate the heterostructures of elemental bismuth and graphene, and then explore their photocatalytic activity from ultraviolet to infrared region for the degradation of pollutants (Scheme 1 and Supporting Information). First, elemental bismuth nanoparticles were grown on the surface of graphene oxide (GO, Figure S2) by solvothermal reduction of bismuth acetate at 180 °C (named as BGHs). Subsequently, the dried BGHs were calcined at 500 °C in argon to ensure molecular-level mixing of graphene with elemental bismuth and then create the high-quality heterostructures with intimate interfacial contact (named as c-BGHs). As a comparison, pure bismuth nanoparticles were also synthesized using the similar protocol except the absence of GO (named as BNPs and c-BNPs for products before and after calcination).



Scheme 1. Process for preparation of c-BGHs through a solvothermal route followed by further calcination at 500 °C for 2 h.

#### **EXPERIMENTAL SECTION**

Reagents and Chemicals. Graphite (99%), bismuth(III) acetate ( $Bi(CH_3COO)_3$ , 99%), dimethyl sulfoxide ( $C_2H_4OS$ , DMSO, 99.9%), methyl orange (C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S, MO), 1,5diphenylcarbazide (C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O, >97%), titanium(IV) oxide (TiO<sub>2</sub>, P25, 99.9%), and potassium dichromate ( $K_2Cr_2O_7$ ) 99%) were purchased from Alfa Aesar. Concentrated sulfuric acid  $(H_2SO_4, 98\%)$ , potassium permanganate (KMnO<sub>4</sub>), hydrochloric acid (HCl, 37% w/w aq.), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 35% w/w aq.), sodium hydrosulfite  $(Na_2S_2O_8)$ , sodium oxalate  $(Na_2C_2O_4)$ , 2-propanol, and ethanol were obtained from Beijing Chemical Reagent Co. Ultra-high purity argon (>99.999%) was supplied by Beiwen Special Gases Factory. All the chemicals were used as received without further purification and all experiments were performed at room temperature unless otherwise indicated. Furthermore, fresh deionized (DI) water (arium<sup> $^{\circ}</sup> Lab Water Systems, 18.2 M\Omega cm) was required for the</sup>$ whole experiment.

**Fabrication of elemental bismuth-graphene heterostructures.** Elemental bismuth-graphene nanostructures were prepared via a general two-step method. Typically,

Bi(CH<sub>3</sub>COO)<sub>3</sub> (0.2000 g) was dispersed in 30 mL of DMSO. After vigorous stirring, to the resulting solution was added 0.5 mL of GO (~4 mg mL<sup>-1</sup>). According to the electrostatic interactions, Bi<sup>III</sup> ions would deposit on the surface of GO nanosheets during vigorously stirring at room temperature. Then the mixture was transferred into a 45-mL Teflon-lined stainless steel autoclave and heated at 180 °C for 4 h. The obtained product (named as BGHs) was collected by centrifugation, washed extensively with ethanol and water several times, and dried in a freezer dryer under vacuum. At last, the dried BGHs were calcined at 500 °C for 2 h under an argon atmosphere to form heterojunctions. For comparison, bismuth particles without graphene were also received using the similar protocol but without the addition of GO (named as BNPs and c-BNPs for products before and after calcination) and pure graphene nanosheets were synthesized in the absence of bismuth(III) acetate (named as rGO and c-GO for products before and after calcination).

Physical characterizations. Morphologies of samples were characterized using electron microscopes with an energy-dispersive X-ray (EDX) analyzer including filedemission scanning electron microscope (FE-SEM, S-4800, an acceleration voltage of 10 kV, Hitachi Hightechnologies, Japan) and transmission electron microscope (TEM, Tecnai G<sup>2</sup> 20 S-TWIN, an acceleration voltage of 200 kV, FEI Company, USA). X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance X-ray diffractometer (Bruker, USA) with  $Cu-K_{\alpha}$  radiation  $(\lambda = 1.5406 \text{ Å})$  at a scanning rate of 5° min<sup>-1</sup> and a scanning range from 10° to 90°. X-ray photoelectron spectroscopy (XPS) measurements and the element valence states were performed with an ESCALab220i-XL spectrometer using a twin-anode Al- $K_{\alpha}$  X-ray source (1486.6 eV). Micro-Raman spectra were acquired with a Raman Spectroscope (Renishaw inVia plus, United Kingdom) under ambient conditions with 514 nm excitation from an argon ion laser. Ultraviolet-visible (UV-vis) data were obtained with a U-3900 spectrophotometer (Hitachi, Ltd., Japan). Diffuse reflectance ultraviolet-visible-infrared (UV-vis-IR) spectra in the reflectance mode were recorded using an Agilent Cary 500 UV-vis-IR Spectrometer equipped with an integrating sphere at room temperature using BaSO<sub>4</sub> as a reference. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed with an unfiltered He I gas discharge lamp (21.22 eV). Fourier transform infrared (FT-IR) spectra were recorded on an infrared microscope (iN10-IZ10, Thermo Fisher). Atomic force microscope (AFM) measurements were conducted with a Bruker Multimode 8 AFM (Bruker, USA) in ScanAnalyst mode with cantilevers with spring constant of 0.35 N m<sup>-1</sup> and a frequency of 65 kHz. The photoluminescence properties were studied using a Horiba Jobin Yvon FluoroLog3 spectrometer. The photocurrents were corrected on a Keithley 4200 station with the computer-controlled four-probe technique.

**Experimental set up for photodegradation of MO under direct sunshine.** The photocatalytic activity of c-BGHs was further evaluated by the degradation of MO

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59 60 under direct sunshine. The experiments were carried out on the sunny day (14th Feb 2015) at Beijing city between 12 p.m. and 2 p.m. where the intensity fluctuation of sunshine was minimal (outside temperature 2-5 °C). The solar power density (as well as other light sources) was measured at 0.039-0.048 W cm<sup>-2</sup> by an Optical Power Meter (PM100D, Thorlabs Inc., USA). In such case, 15 mg of c-BGHs was dispersed in 15 mL of acidic aqueous solution of MO (pH 2.00, 60 µg mL-1). After the adsorption/desorption equilibrium was reached, 30 mL of  $C_2 O_4^{2}$ solution was added to the above suspension. Finally, the samples were analyzed by UV-vis spectrophotometer after centrifugation. Similarly, the control experiments were also conducted under solar light with P25 to compare the photocatalytic activity of each other and without catalyst to measure any possible direct photolysis of the dyes.

**Calculation of highest occupied molecular orbitals and lowest unoccupied molecular orbitals.** In this work, the Gaussian o3 program was applied to perform the computations in the gas phase. B3LYP and MP2 approaches were used to calculate the frontier molecular orbitals of MO molecules, including highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs).

#### **RESULTS AND DISCUSSION**

Characterization of c-BGHs by SEM shows that bismuth nanoparticles retain their size at the nanoscale (~300 nm) after calcination and are wrapped intimately by graphene nanosheets (Figure 1a and Figure S3). Compared with BGHs, there are inappreciable changes in size and morphology of bismuth nanoparticles except the creation of more nanoscale wrinkles in graphene. This is in contrast to the morphology of c-BNPs (Figure S4) and suggests the presence of strong interfacial interaction of bismuth nanoparticles with graphene sheets (Figure S5).<sup>34</sup> A highresolution TEM image indicates that the surface of bismuth nanoparticles is covered by a layer of ~4 nm in thickness (Figure 1b). Together with the result from energy dispersive X-ray spectroscopy (Figure 1d, inset), we infer that this layer is most like an oxide of bismuth.



**Figure 1.** (a) SEM image of c-BGHs. (b) High-resolution TEM image of c-BGHs. Inset: EDS analysis of the corresponding bismuth nanoparticle. (c) Comparison between the XRD data of BGHs and c-BGHs. (d,e) XPS core-level spectra and deconvolution into Bi4f (d) and Ois. (e) Contributions for c-BGHs. (f) Schematic structure of c-BGHs.

Further insights into the structural information were obtained by XRD analysis. XRD patterns before and after calcination exhibit similar diffraction peaks. The distinct reflections typically associate with the rhombohedral bismuth crystals (JCPDS no. 44-1246),<sup>35</sup> in accordance with the result from TEM measurement (Figure 1c and Figure S6a). The absence of the stacking-related (002) diffraction peak (at ~26° for graphite and ~13° for graphite oxide) indicates that the dispersion of graphene is probably close to the single-sheet level.<sup>34</sup> Remarkably, the weak peak at ~27.92° which is assigned to diffraction from the (201) plane of bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>, JCPDS no. 27-0050) can be found in c-BNPs (Figure S6b).<sup>36</sup> This is not surprising because bismuth is easily oxidized under oxygen atmosphere.<sup>26</sup> However, this peak shifts to 28.08° after calcination, in accordance with the (101) plane of bismuth suboxide (BiO, JCPDS no. 27-0054).37 This indicates that the additional structures are developed during calcination with the assistance of graphene. The change in the chemical states is further demonstrated by XPS (Figure S7,8). In Figure 1d, the two peaks of c-BGHs located at 156.8 and 162.1 eV, respectively, attributed to the binding energies of Bi4f7/2 and Bi4f5/2 in metallic bismuth, are nearly identical to those of BGHs; however, other doublet shift down to 158.6 and 163.9 eV, respectively, corresponding to a 1.8 eV shift relative to the peaks of metallic bismuth. This chemical shift is less than that obtained for Bi<sup>III</sup>, evidencing the formation of suboxide species on the surface of bismuth nanoparticles.<sup>38,39</sup> Most interestingly, in comparison of the evolution of O1s spectra, O=C-O peak shifts towards higher binding energy after calcination due to the decrease of the total charge density (Figure 1e). Coupled with the result of density functional calculations (Figure S9), it is indicative of O=C-O groups bonding with Bi<sup>II</sup> at the hetero-interface, forming thermodynamically stable four-membered-ring.40 This is also confirmed by the results of Fourier transform infrared and Raman spectroscopy (Figure S10,11). Ideally, the ring structure can serve as a "bridge" which makes bismuth nanoparticles and graphene cross-linked but not physical mixed nor isolated (Figure 1f), permitting the interaction between electronic states at the graphene-bismuth interface and thus leading to extend the absorption into infrared region and promote interfacial charge transfer.41,42

Then, we performed the photocatalytic experiments with c-BGHs under visible, infrared, ultraviolet light as well as full-spectrum light (Figure 2,3, Figure S12, Table S1, and Supporting Information). Their photocatalytic activities were evaluated by investigating the degradation rates of methyl orange (MO, an azo dye) and chromium (VI)  $(Cr^{VI})$ , a heavy metal ion) in acidic water (pH<3.00). As expected, c-BGHs show a high photocatalytic activity under visible and infrared light, far higher than that of commercial TiO<sub>2</sub> (P<sub>25</sub>): we obtained more than 95% (under visible light) and 60% (under infrared light) photodegradation of MO after a 40-min irradiation, while no degradation was obtained with P25 (Figure 2a,b). In particular, to identify the infrared photocatalytic activity, we conducted the photodegradation test under monochromatic light of wavelength of 808 nm. They achieved a degradation rate of 95% within 40 min, demonstrating that their photocatalytic activity indeed originated from infrared light (Figure S13). Besides, c-BGHs display good photocatalytic activity under ultraviolet light: an 85% degradation rate of MO was reached in 40 min irradiation (Figure 2c). Similar trends are observed for the photocatalytic degradation of Cr<sup>VI</sup>: c-BGHs produced degradation rates of 80% and 60% after 40-min irradiation by visible and infrared light, respectively, but no reaction was observed with P25 control (Figure 3a,b). The degradation rate under ultraviolet light was 80%, which was somewhat lower than that of P25 (Figure 3c).



**Figure 2.** (a-d) Photocatalytic degradation of MO under visible (a), infrared (b), ultraviolet (c) and full-spectrum (d) light irradiation. (e) Illustration of the time evolution of MO photodegradation using c-BGHs under infrared light.



**Figure 3.** (a-d) Photocatalytic degradation of  $Cr^{VI}$  under visible (a), infrared (b), ultraviolet (c) and full-spectrum (d) light irradiation. The concentration of various photocatalysts in acidic water was 1 mg mL<sup>-1</sup>.

To further attest the correlation between photocatalytic degradation and heterostructures, we carried out pollutant degradation experiments in the presence of BNPs, c-BNPs and a mixture of calcined graphene oxide (c-GO) and c-BNPs (Figure 2,3 and Figure S14). We found that BNPs displayed rather limited photocatalytic activity under visible, infrared and ultraviolet irradiation (Table S2), and almost no pollutant degradation was obtained with c-BNPs. Even the mixture of c-GO and c-BNPs showed only a slight decomposition of pollutants under the same conditions. We also measured the kinetic rate constants for each of the above photocatalytic events using pseudofirst-order kinetic model (i.e. Langmuir-Hinshelwood model, Supporting Information),<sup>43,44</sup>

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where  $C_0$  and  $C_t$  are the concentrations of pollutant in solution at time 0 and t, respectively, and  $k_{app}$  is the apparent rate constant. Especially, for MO degradation by c-BGHs, the rate of adsorption equilibrium is comparable to that of degradation reaction. Therefore, the Langmuir-Hinshelwood model is no longer applicable. To extract the degradation rates of MO, we fitted these data to the following formula, which assumed the light absorbance proportional to the concentrations of MO both in solution and on the surface of c-BGHs,

$$A = a \exp(-k_{-1}t) + b \exp(-k_{2}t)$$
(2)

where  $k_{-1}$  is the desorption rate constant and  $k_2$  is the rate constant. Good fits were obtained for the above model, confirming that the light absorbance was assuredly proportional to the total MO concentration in the solution (Figure S15). The estimates of kinetic rate constants from above models are summarized in Table S3,4. Together with the process efficiency and catalytic efficiency (Table S5-8), these calculations give the values to quantify the photocatalytic activity and consistently suggest that the heterostructures have the fastest reaction rates.

To understand the origin of photocatalytic activities of c-BGHs under ultraviolet, visible and infrared light, we then investigated their electronic band structures. As shown in Figure 4a, DRS results suggest that the optical absorption edge of c-BGHs is extended to infrared region over both BNPs and BGHs due to the strong interfacial interaction between graphene and bismuth nanoparticles (Supporting Information).<sup>45</sup> The optical energy bandgap  $(E_a)$  of c-BGHs is determined to be 1.38 eV from the extrapolation of the Tauc plot (Figure 4b), suggesting that c-BGHs can be activated by light from ultraviolet to infrared region. This is mainly due to the hybrid surface layer consisting of bismuth suboxide and graphene, whose absorption is superimposed to a "background" absorption from the bismuth core of the heterostructure. For characterizing the energy levels of conduction and valence bands, UPS was used to determine the ionization potential (equivalent to the valence band energy,  $E_{VB}$ ) of c-BGHs. The  $E_{VB}$  is determined to be 1.65 eV by subtracting the width of the He I UPS spectrum form the excitation energy and then converting to electrochemical energy potential in Volts (vs. reversible hydrogen electrode (RHE)) (Figure 4c). The conduction band energy  $E_{CB}$  is thus estimated at 0.47 eV (vs. RHE) from  $E_{VB} - E_g$ . The Fermi level is given (1.34 eV vs. RHE) by the formula for  $E_{VB} - \Delta E_{VB}$ , where  $\Delta E_{VB}$  is the energy position of the valence band with respect to the Fermi level (Figure S16). Furthermore, the bandgap of MO in neutral (MO°) and acidic (MO<sup>+</sup>) conditions were evaluated by Guassian program (Supporting Information). Depending on the alignment of the energy levels, the Fermi level for c-BGHs is well positioned in the middle of the bandgap of MO° and MO<sup>+</sup> after adsorption equilibrium. This ascertains that the degradation of MO and Cr<sup>VI</sup> is energetically possible under acidic condition (mostly industrial wastewater), but not under neutral condition (Figure S17). The conduction band energy level for c-BGHs is located above the top of the lowest unoccupied molecular orbital (LUMO) level for  $MO^+$  and the reduction level for  $Cr^{VI}$ , which permits transfer of electrons. These results indicate that c-BGHs are capable of degrading  $MO^+$  and  $Cr^{VI}$  under visible, infrared and ultraviolet light via reduction process (Figure 4d). Moreover, based on the results of electrospray ionization mass spectrometry (Figure S18), the possible pathway of reduction is further proposed in Figure S19.

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(1)



**Figure 4.** (a) Diffuse reflectance absorption spectrum of BNPs, BGHs and c-BGHs. "I", "II" and "III" represent ultraviolet region, visible and infrared region, respectively. Inset: Photograph of c-BGHs. (b) A plot transformed according to the Kubelka-Munk function versus energy of light. The dashed line is the tangent of the curve. Inset: the Kubelka-Munk transformed spectra of BNPs and BGHs. (c) UPS spectrum of c-BGHs. The dashed red line marks the base line and the tangents of the curve. Inset: UPS spectrum of c-BGHs at high kinetic energy region. (d) Possible photocatalysis mechanism with charge separation in c-BGHs, with electron directly reducing pollutants (MO and  $Cr^{VI}$ ) in acidic water and hole oxidizing water.

Chemically, pollutants except metal ions (including Cr<sup>VI</sup>) are eliminated via oxidation process, in which the photoexcited carriers migrate to the surface and react with oxygen or water to form radical oxygen species, finally degrading and mineralizing organic pollutants (Supporting Information),<sup>46,47</sup>

$$0_2 + e_{CB}^- \to 0_2^- \tag{3}$$

$$h_{VB}^+ + OH^- \text{ (or water)} \rightarrow HO^-$$
 (4)

where  $e_{CB}^-$  is conduction band electrons and  $h_{VB}^+$  is valence band holes. However, unlike the above processes, in c-BGHs the energy levels make reduction reaction thermodynamically favorable, that is, directly transferring  $e_{CB}^-$  to pollutants,

$$Dye + e_{CB}^- \rightarrow Dye_{Red}$$
 (5)

where subscript "Red" represents the reduced form of dye. Remarkably, the advantage of reduction process is that no apparent demand of intermediate states is listed in path and the classic problem caused by low molecular oxygen concentration is avoided.

The photogenerated electrons mobility in c-BGHs was further studied under visible, infrared and ultraviolet light to explore the behavior of excess charge carriers (Figure 5a and Figure S20). We observe the consistent photocurrent responses for each switch-on and -off event, providing evidence that graphene acts as electron sinks, favoring the separation of the photocarriers via the heterostructures while reducing thermoeffect, specially under infrared light irradiation.48 Similar conclusion is also obtained from photoluminescence spectra (Figure S21). The effect of scavengers on the degradation of MO was then examined to confirm the role of the photogenerated electrons (Figure 5b). Trapping experiments were performed upon introduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> scavengers which reacted with electrons to yield SO<sub>4</sub><sup>2-</sup> ions.<sup>49</sup> This reaction competes with reaction (5) and causes the decrease in electrons, which in turn slows down the photodegradation kinetics compared to the control under infrared light irradiation (Table S9).

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**Figure 5.** (a) Photoresponse characteristics of c-BGHs under ultraviolet, visible, infrared and full-spectrum light. After as many as eight cycles, the behavior of c-BGHs remains unchanged. (b) Effects of different scavengers on the degradation of MO in the presence of c-BGHs under infrared light irradiation. (c) Schematic of electron transfer during photocatalytic process.

To further evaluate the role of oxygen, MO photodegradation tests were performed under anoxic conditions in which  $0^{-}_{2}$  radical generation was inhibited completely. The result in Figure 4b shows almost no change in the degradation kinetics, confirming the insignificant role of  $0_2^{-}$  in the photocatalytic process, in agreement with the analysis of the conduction band energy level. Nevertheless, when adding external hole scavengers  $(C_2O_4^{2-})$  into the above system we find that the decomposition kinetics are drastically accelerated. This can be attributed to the fact that the introduction of  $C_2 O_4^{2-}$  can suppress the electron-hole recombination via the reaction of  $h_{VB}^+$  with  $C_2 O_4^{2-50}$  These results undoubtedly demonstrate that the degradation process is occurred through the direct transfer of  $e_{CB}^{-}$  to the absorbed MO in which  $C_2 O_4^{2-}$  as the sacrificial donor that can increase electron transfer efficiency. The photocatalytic degradation of MO was further carried out under sunshine in the presence of  $C_2 O_4^{2-}$ . Interestingly, we found that c-BGHs produce a decomposition rate of MO nearly 100% after 25 min compared to 5% photodegradation rate of P25 (Figure 6 and Figure S22-24). This result indicates that the efficient solar photocatalytic activity of c-BGHs is robust for potential application in water purification and wastewater treatment under natural sunlight.



**Figure 6.** Photographs of the photodegradation of MO by c-BGHs in the presence of  $C_2O_4^{2^-}$  before (a) and after (b) sunlight irradiation.

There is no doubt that the photocatalytic activity of c-BGHs essentially originates from the narrow bandgap of elemental bismuth favoring efficient utilization of lowenergy photons. On one hand, graphene as a mechanical clamping layer can dramatically inhibit the agglomeration of bismuth nanoparticles during the calcination process, thus maintaining their intrinsic electronic structures that are unavailable in c-BNPs. On the other hand, when coupling with graphene, in addition to the individual properties of each component, the formed heterostructures facilitate the avoidance of thermoeffect induced by infrared light via promoting the charge separation, while generating the proper energy levels that enable the highly effective electron transfer at graphene/bismuth interfaces.<sup>51-53</sup> Moreover, plenty of active sites for photodegradation are provided due to the enough room originated from graphene for electron extraction by pollutants. Figure 5c summarizes the light absorption by the bismuth core with very small bandgap (few tenths of eV) followed by electron transfer to the surface region, resulting in the enrichment of charge carriers on the surface of graphene under irradiation and then direct transfer to adsorbed MO<sup>+</sup> or Cr<sup>VI</sup> under acidic condition, turning out to be responsible for the degradation of pollutants.

Another important aspect was the stability and recyclability of the photocatalyst, we found that the degradation rates remained almost unchanged even after five cycles and no bismuth ions were released into the solution, suggesting that c-BGHs could be efficiently reused for repeated cycles without appreciable loss of activity and mass (Figure 7a and Figure S25-27). Furthermore, no distinct difference was found, either in the morphology of c-BGHs or in their chemical structures after photocatalytic reactions, as attested by TEM, XRD and Raman characterizations (Figure 7b-d).

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**Figure 7.** (a) Photocatalytic degradation of MO and Cr<sup>VI</sup> in the presence of c-BGHs after up to five cycles measured after visible and infrared light irradiation of duration 10 min. (b) TEM image of c-BGHs after photodegradation of MO under infrared light. Inset: EDX analysis of c-BGHs. (c,d) Raman spectra (c) and XRD patterns (d) of c-BGHs after photodegradation of MO under ultraviolet, visible, infrared and full-spectrum light irradiation.

# CONCLUSIONS

In summary, we present here the heterostructures of elemental bismuth and graphene as an efficient and stable photocatalyst that is able to degrade pollutants in acidic environment under visible, infrared and ultraviolet light. The emerging understanding of the mechanism indicates that these heterostructures can take advantage of the unique catalytic and electronic properties of individual component of the system and extend the photocatalytic activity towards infrared region. The present discovery provides new insights into generalizing the concept of elemental bismuth-graphene heterostructures to other elemental photocatalysts to develop solar-light-efficient photocatalytic applications. Moreover, this work adds to the growing potential of bismuth-based photocatalysts,<sup>54</sup> and is expected to accelerate the pace of the development of new generation photocatalysts with ultrahigh efficacy under full-spectrum solar light.

# ASSOCIATED CONTENT

#### Supporting Information

This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

Additional information about synthesis of GO nanosheets, photocatalytic activity measurements, kinetic modelling of photodecomposition and desorption, calculation of process efficiency and catalytic efficiency, calculation of optical energy bandgap, and physical characterizations, as well as supplementary figures and tables.

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#### **Author Contributions**

All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest

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