Synthesis of a zinc oxide/graphene hybrid material by the direct thermal decomposition of oxalate

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Abstract

Hybrid materials of zinc (II) oxide (ZnO) nanocrystals and graphene are of current interest due to their cheap, Earth-abundant composition, low toxicity, and varied applications in photocatalysis, sensing, and electronics among others. We have developed a novel methodology for the synthesis of such materials utilizing the thermal decomposition of zinc (II) oxalate in solid-state solution with graphene nanoplatelets. Although the procedure simply involves precursor mixing and heating, electronic interaction between the ZnO and graphitic phases is spectroscopically observed in the hybrid material—beyond that of a homogeneous mixture of ZnO and graphene—via powder XRD, XPS, and ATR-IR spectroscopy. The synthetic method employed can be easily tuned for the desired hybrid product stoichiometry, and is easily industrially scalable with minimal chemical waste products.

Introduction

Hybrid—or composite—materials of zinc (II) oxide (ZnO) and graphene (or, often, reduced graphene oxide) are currently of great interest in the materials science community because they are inexpensive, non-toxic, and boast a spectrum of useful applications [1–3]. Creating strong electronic interaction between nanoscale graphene and ZnO in a composite can significantly modify the ZnO band structure, leading to an array of exciting new properties for the bulk material. For example, they have seen use as photocatalysts [4–10], sensors [11–14], capacitors [15–20], and as transparent conductive thin-films [21] to name just a few. Equally as diverse as their applications are the methods of synthesizing ZnO/graphene hybrid materials. By far, the most popular fabrication methods involve either solvothermal or sol-gel techniques [4, 9, 14, 16, 20, 22–27], however there have been a fair number of studies involving either electrodeposition of the material [7, 11, 21, 28], or solution-based synthesis involving pH manipulation of a Zn\(^{2+}\) ion precursor [15, 29, 30].

In the interest of developing a synthesis that is as simple, safe, and cost-effective as possible, a solid-state thermal method is preferred due to the minimal equipment requirements, and straight-forward industrial scalability. Nearly all solid-state methods involve the synthesis of pure, nanocrystalline ZnO first, which is then sintered with graphene or graphene oxide, resulting in a material with two clear, distinct phases rather than a cohesive mixture with a more uniform band structure [6, 31]. To achieve a more cohesive composite, a methodology involving the thermal decomposition of a zinc-containing precursor in a solid-state solution of graphene, or reduced graphene oxide is preferred. Synthesis of ZnO by thermal decomposition typically employs zinc (II) acetate dihydrate (Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O) as a precursor [8, 32–34], however, Hong \textit{et al in} 2015 reported that synthesis of a ZnO/graphene composite from a mixture of graphene and Zn(CH\(_3\)COO)\(_2\) resulted in the formation of amorphous carbon as a byproduct [35]. Amorphous carbon is an impurity in the...
finished product that is difficult to remove, so it is desirable to begin with a zinc compound that will thermally decompose into only ZnO and other gaseous byproducts.

The decomposition of zinc oxalate dihydrate (ZnC$_2$O$_4$ · 2H$_2$O) has been demonstrated to occur in two stages: the dehydration of the complex, followed by decomposition to ZnO, carbon monoxide (CO), and carbon dioxide (CO$_2$), as shown in equations (1) and (2) [36, 37]. Malecka et al showed the temperature dependence of product formation in these processes using thermal gravimetric analysis, differential thermal analysis, and mass spectrometry all in tandem [36]. They determined that the rate of decomposition is determined by nucleation and growth of the ZnO phase. It has also been shown that under an aerobic environment, the overall process becomes exothermic as there is a secondary oxidation of the CO product to CO$_2$ catalyzed by the newly formed ZnO sites [37]. (equation (3)) Thus, when heated in air, ZnO, H$_2$O, and CO$_2$ are the only products of the decomposition reaction.

\[
\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{T>90 \degree C} \text{ZnC}_2\text{O}_4 + 2\text{H}_2\text{O} \tag{1}
\]

\[
\text{ZnC}_2\text{O}_4 \xrightarrow{T>300 \degree C} \text{ZnO} + \text{CO} + \text{CO}_2 \tag{2}
\]

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \tag{3}
\]

In this work, we take advantage of the relatively simple decomposition pathway of ZnC$_2$O$_4$ to synthesize a ZnO/graphene hybrid structure directly from a mixture of oxalate and graphitic matrix without need for the traditionally utilized sintering process. We confirm that this process nucleates pure ZnO crystallites upon thermal decomposition, and produces a ZnO/graphene hybrid material rather than simply a ZnO/graphene mixture. The slow nucleation of ZnO crystals within the graphitic matrix will allow for electronic interaction between the two phases, which should lead to chemical properties that are different from a mere homogeneous solid-state solution. This method is novel as only the two aforementioned studies have synthesized a ZnO/graphene hybrid material via solid-state thermal decomposition, and in both cases an acetate precursor was utilized.

The synthetic method involved—the thermal decomposition of a metal oxalate/graphene composite—uses only inexpensive materials and is incredibly simple and scalable to perform. It is likely that such a synthesis will be viable for metals other than zinc. The clean decomposition pathways of various metal oxalates have been documented for decades [37, 38]. Utilizing any of these should allow for syntheses of composites with nearly any metal oxide in any stoichiometry [2], allowing for tuning of the band structures of these materials. This is, however, the subject of ongoing research.

Experimental

Synthesis and characterization of zinc oxalate precursor

Zinc oxalate (ZnC$_2$O$_4$) was synthesized by precipitation from near-saturated solutions of ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$, Fisher, ACS) and zinc nitrate hexahydrate (Zn(NO$_3$)$_2$ · 6H$_2$O, Alfa Aesar, 99%). 4.5 g of (NH$_4$)$_2$C$_2$O$_4$ was dissolved in 100 ml of Millipore water, and 8.0 g of Zn(NO$_3$)$_2$ · 6H$_2$O was separately dissolved in 5 ml of Millipore water. The zinc solution was slowly dripped into the oxalate solution using a Pasteur pipette at room temperature. The precipitate was allowed to settle to the bottom of the beaker before decanting most of the solvent, followed by vacuum filtration. The hydrated product, likely ZnC$_2$O$_4$ · 2H$_2$O [36], was pre-dried in a vacuum oven at 80 °C to remove residual solvent. Then, the white powder was heated in a furnace at 200 °C to dehydrate the crystals, resulting in pure ZnC$_2$O$_4$. According to thermogravimetric analysis data for ZnC$_2$O$_4$ [36], 200 °C is hot enough to cause dehydration of the complex without decomposition of the oxalate ion.

The dehydrated ZnC$_2$O$_4$ was characterized using MP-AES to determine the mass percent of Zn. The precursor contained 5.46 mmol Zn for every gram of powder. The ideal amount would be 6.52 mmol, indicating a fair amount of residual water or (NH$_4$)$_2$C$_2$O$_4$ in the product. A key advantage of the decomposition method, however, is that residual water will evaporate and residual (NH$_4$)$_2$C$_2$O$_4$ will decompose into ammonia (NH$_3$) and carbon dioxide (CO$_2$) gasses leaving the desired product. As a result, the precursor was used without further purification, and 5.46 mmol per gram of powder was used as the Zn concentration for stoichiometric calculations.

Synthesis of zinc oxide-graphene hybrid material

Graphene flakes (Graphene nanoplatelets aggregates, sub-microparticles, S.A. 500 m$^2$ g$^{-1}$, Alfa Aesar) were used as purchased as the graphene precursor. Stoichiometric amounts of solid ZnC$_2$O$_4$ and graphene flake precursors were measured using a balance, and then mixed using a mortar and pestle. Samples were mixed to create C:Zn mole ratios of 10:1, 100:1, and 1000:1, and are referred to as ‘10% ZnO’, ‘1% ZnO’, and ‘0.1% ZnO’ respectively in this work. (Technically the graphene portion of the material contains oxygen impurities and these percentages are not strictly correct.) Each of the mixtures was suspended in 15 ml of Millipore water and...
ultrasonicated (Fisher 550 Sonic Disembrator) at 15% power for 30 min. This is to break apart graphene aggregates, which are essentially mesoparticles of graphite [39]. The suspensions were then heated to 100 °C to remove the liquid water, and then to 200 °C to completely dehydrate the powder. Slowly dehydrating in this manner has the unfortunate side-effect of allowing the graphene and ZnC2O4 to separate into discrete layers, so each sample was then removed from the furnace and thoroughly re-mixed using mortar and pestle. The samples were then heated to 450 °C for 6 h to allow for complete precursor decomposition and product annealing [36].

Synthesis of controls

Both ‘0% ZnO’ and ‘100% ZnO’ controls were synthesized using almost exactly the same method as described above. However, in the former no ZnC2O4 precursor was added to the mixture, and in the latter no graphene flakes precursor was added. They were still heated in the furnace in two stages, and ground with mortar and pestle in between.

Additionally, a ‘10% mixture’ control was created simply by mixing 0.060 g of the ‘0% ZnO’ control with 0.039 g of the ‘100% ZnO’ control using mortar and pestle, but not any additional heating. This was to reflect the ‘10% ZnO’ product stoichiometry.

Instrumentation

MP-AES was conducted using an Agilent 4100 MP-AES. Scanning Electron Microscopy (SEM) images were recorded using a Zeiss EVO-HD instrument employing a Brüker Energy Dispersive Spectroscopy (EDS) accessory for elemental analysis. Powder x-ray diffraction (XRD) was conducted using Siemens D500 x-ray Diffractometer. X-ray photoelectron spectra of the products were obtained with a Phi 5100 XPS system using an Al anode. Attenuated total reflectance infrared (ATR-IR) spectroscopy employed a Thermo Scientific iS50 ATR.

Results and discussion

The mole percentages of carbon (C), oxygen (O), and zinc (Zn) in each of the samples were identified using EDS, and the results are shown in table 1. EDS only provides a relatively rough idea of elemental stoichiometry, though it is evident that the product Zn concentrations were slightly higher than anticipated, particularly in the ‘1% ZnO’ sample. There is typically carbon impurity on the order of 1%–2% in all EDS spectra due to atmospheric carbon (dust) incorporating into the sample [40]. It is likely in this case, however, that there was a small amount of un-decomposed oxalate still present in the ‘100% ZnO’ sample, leading to an atomic percentage of 6.5% carbon. Elemental mapping was used to get an idea of the distribution of C, O, and Zn in each sample as well. Figure 1 shows an example of individual elemental signals mapped onto an SEM image of the ‘10% ZnO’ sample. (Maps and SEM images of the other samples are shown in Supplementary Information). It is evident from elemental mapping that the ZnO domains and graphitic domains are homogeneously distributed through the hybrid material.

Powder XRD spectra of each of the samples and controls is shown in figure 2. From a first-order comparison of figure 2(a), the spectrum of ‘100% ZnO’ perfectly matches JCPDS data for ZnO, and the spectrum of ‘0% ZnO’ reflects reported spectra for graphene aggregates (essentially mesoparticles of graphite) [41]. The single, sharp peak at 26.5° in the ‘0% ZnO’ spectrum is indicative of the graphite (002) reflection, and the broad background peaks indicate an overall structure that is amorphous—the expected result for graphene platelets. Figure 2(a) shows that the intensity of the graphite (002) peak decreases and the intensities of the ZnO peaks at 31.8°, 34.4°, 36.2°, and 47.5° all increase when comparing ‘0.1% ZnO’ to ‘1% ZnO’ to ‘10% ZnO’, following the relative concentrations of graphene and ZnO respectively.

Figure 2(b) allows for comparison of the ‘10% ZnO’ sample and the ‘10% mixture’ control. A first-order comparison here shows that the normalized intensity of the graphene (002) peak at 26.5° for ‘10% mixture’ is larger than that of ‘10% ZnO’, despite the stoichiometry of the samples being approximately the same. Upon

| Sample       | C/\% | O/\% | Zn/\% |
|--------------|------|------|-------|
| ‘0% ZnO’     | 98.3 | 1.7  | 0.0   |
| ‘0.1% ZnO’   | 97.8 | 1.9  | 0.3   |
| ‘1% ZnO’     | 93.5 | 3.7  | 2.7   |
| ‘10% ZnO’    | 77.0 | 12.2 | 10.7  |
| ‘10% mixture’| 81.2 | 10.9 | 8.0   |
| ‘100% ZnO’   | 6.5  | 41.5 | 52.0  |
closer inspection, the full width half max (FWHM) in the ‘10% ZnO’ spectrum of each of the four ZnO peaks between 30° and 50° is wider than in either the ‘10% mixture’ or ‘100% ZnO’ spectra.

The FWHM of a peak in powder XRD is inversely proportional to the crystallite size, and the Scherrer equation can be used to approximate the mean size of each ZnO crystalline domain as a function of the wavelength of the instrument (0.154 nm in this case) [42]. The Scherrer equation is shown below in equation (4), where \( L \) is the average linear dimension of a crystallite in a given direction, \( K \) is a dimensionless ‘shape factor’ which is typically close to unity, \( \lambda \) is the wavelength of the incident x-rays, \( \beta \) is the FWHM of the peak in radians, and \( \theta \) is the Bragg angle in radians.

\[
L = \frac{K \lambda}{\beta \cos \theta}
\]  

Assuming that \( K \) is unity, the ZnO crystallite sizes of the ‘10% ZnO’ sample, and ‘10% mixture’ and ‘100% ZnO’ controls are shown numerically in table 2, and graphically in figure 3. In all likelihood, \( K \) is a value closer to 0.9 or even smaller, but this would only serve to linearly decrease all calculated values and not affect the comparison [42].

It makes sense that the FWHM for the ‘10% mixture’ and ‘100% ZnO’ spectra are nearly identical, as the mixture contains ZnO from the ‘100% ZnO’ sample. On average, the ZnO crystallite size is nearly two-fold smaller in all directions in the ‘10% ZnO’ sample than it is in either of the controls. Additionally, the ZnO crystal growth seems to favor the (100) and (002) directions in the controls, while growth is much more uniform in all directions in the ‘10% ZnO’ sample. This indicates that the ZnO particles in the synthesized sample are fundamentally different from those in the homogeneous mixture. It is likely that the high-carbon environment during the decomposition and annealing phase of the synthesis affects ZnO crystal growth. It is even possible that the \( \text{ZnC}_2\text{O}_4 \) decomposition pathway is altered by the solid-state solution, thus discouraging crystallization of ZnO. Regardless, it is clear that synthesis of the hybrid material by this method has encouraged interaction between the ZnO and graphitic domains that are otherwise not present due to the proximity of simply mixing ZnO and graphene into a solid-state solution.

To probe the chemical bonds of the hybrid material, ATR-IR was utilized. Infrared spectroscopy is an established methodology for characterizing the bonds of terminal oxygen defect atoms common in reduced graphene oxide [43, 44]. Since graphene absorbs so strongly in essentially all regions of the electromagnetic spectrum, including the IR, each sample was diluted by a factor of 100 using potassium bromide (KBr, Kodak, technical grade), as KBr has no significant absorption features in the region of interest [45]. The full spectrum is shown for each of the samples in Supplementary Information, but an excerpt of the region of interest can be seen.

![Representative SEM image of the ‘10% ZnO’ sample (a), and spatially mapped signals for carbon (b), zinc (c), and oxygen atoms (d) in the region.]

Figure 1.
in figure 4. Absorption bands in this region are typically associated with carbon-oxygen bonds, such as the inevitable terminal oxygen impurities in the graphitic phase, or possibly oxygen atoms bridging carbon atoms and zinc atoms between the two hybrid phases [4, 10, 31, 43, 46–48]. Ignoring vertical offsets, the ‘10% mixture’
sample in (b) is essentially identical to the ‘0% ZnO’ sample shown in (a). However, the ‘10% ZnO’ sample in (d) has distinct extra features at between 1200 and 1100 cm$^{-1}$.

All of the spectra in figure 4 were fit using Gaussian curves, the results of which are shown in table 3 for direct comparison. With the exception of the peak at 1212 cm$^{-1}$, all of the peaks in the ‘10% mixture’ spectrum are redshifted by about 5 cm$^{-1}$, allowing the peaks to be reasonably assigned to related, if not identical vibrational

Figure 3. Graphical representation of data from table 2 for visual comparison.

Figure 4. ATR-IR spectra of the ‘0% ZnO’ control (a), the ‘10% mixture’ control (b), the ‘100% ZnO’ control (c), and the ‘10% ZnO’ hybrid product (d). Raw absorbance data is shown in black, with the fit in dashed red, from the Gaussian curves shown.
phenomena. Interestingly the ‘10% ZnO’ spectrum contains features that are simply not present in the ‘0% ZnO’ or ‘10% mixture’ spectra. It was impossible to achieve a good fit to this region of the IR spectrum with any fewer than six Gaussian curves, unlike the other two spectra. A comparison of the fits of the four spectra indicates that the ‘10% ZnO’ sample shows vibrational modes that are not clearly related to either the pure graphitic phase, or the pure ZnO phase, or the appropriate mixture of the two. The best explanation is that these are new vibrational modes related to chemical bond formation between the ZnO and graphitic phases of the hybrid material; likely through a Zn–O–C bridging oxygen mode.

XPS allows for probing of different environments of C and O atoms within the materials by effectively measuring their 1s orbital energies. XPS survey scans for the four materials studied are shown in Supplementary Information, but high resolution scans of the carbon 1s and oxygen 1s regions are shown in figures 5 and 6 respectively. The peak parameters of the de-convoluted spectra are shown in table S1 is available online at stacks.iop.org/MRX/7/065005/mmedia of the Supplementary Information as well. The C 1s region scans are a close reflection of the ATR-IR data in figure 4: the ‘0% ZnO’ and ‘10% mixture’ spectra are essentially identical to each other, while there is a subtle difference present in the ‘10% ZnO’ spectrum. The ‘100% ZnO’ spectrum, as

| Sample            | 0% ZnO Peak Positions/cm⁻¹ | 10% Mixture | 100% ZnO |
|-------------------|-----------------------------|-------------|----------|
| 0% ZnO            | 1003                        | 994         | 1010     | 1009     |
|                   | 1061                        | 1057        | 1070     | —        |
|                   | 1102                        | 1096        | —        | 1084     |
|                   | 1158                        | 1155        | 1163     | —        |
|                   | 1210                        | 1212        | —        | 1221     |

Figure 5. High-resolution XPS scans of the C 1s regions of the ‘0% ZnO’ (a), ‘10% mixture’ (b), ‘100% ZnO’ (c), and ‘10% ZnO’ (d) samples. Raw data is shown in solid black, with the baseline and fit shown in dashed black and light-blue respectively. De-convoluted peaks used to produce each fit are illustrated inside each curve.
established by EDS in table 1, has a much lower carbon content than the other samples, and this is reflected by the nearly ten-fold lower signal in figure 5(c). This signal is likely due to residual ZnC2O4, or some other carbon-containing impurity, as well as any adventitious carbon signal typical to XPS spectra. Since both of those sources involve sp² C=O carbon sites, their signals are convoluted into one peak at 286.4 eV. In the spectra of the remaining three samples, the red peak at about 284.8 eV is attributed to graphitic sp² carbon [19, 20, 47, 49]. The peaks around 285.4 and 287.1 eV are attributed to C–O and C=O respectively, and the very broad peak around 290 eV is the result of the sp² carbon π→π* 'shake-up' satellite [50].

The O 1s region scan of '0% ZnO', figure 6(a), reflects a fairly typical surface-oxidized graphene spectrum [51]. In the other samples, the peaks shown in red all are centered at about 531.5 eV with a FWHM of about 1.6, and the peaks shown in orange are centered at about 533 eV with a FWHM of about 2.6. These similarities in width and binding energy suggest that all three samples contain oxygen atoms primarily in two common environments. The peaks near 531.5 eV are attributed to O atoms within the ZnO lattice [19, 52]. The other peaks near 533 eV are attributed to terminal O atoms. The broad range of possible terminal O atom environments contributes to the much broader FWHM of the peaks near 533 eV.

Figure 6(d) indicates that the ratio of terminal O atoms to ZnO lattice atoms is much larger in '10% ZnO' than it is in '10% mixture'. This is due in part to the smaller ZnO crystallite size in '10% ZnO' as indicated by XRD in figure 3. As nanoparticles decrease in size, the number of internal atoms decreases much more quickly than the number of surface atoms, thus increasing the terminal to lattice O ratio. However, it is evident from figure 5(d) that the number of C–O single bonds is significantly larger in '10% ZnO' compared to '10% mixture', as the peak at 285.4 eV is approximately 1.3-fold larger in area. This fact, combined with the appearance of completely new C–O vibrational modes in figure 4(d), suggests the existence of bridging O atoms (C–O–Zn) in '10% ZnO' that are not present in '10% mixture'. While these bridging atoms are not strictly 'terminal', as they are between the graphitic and ZnO phases, one would still expect their 1s electrons to have similar binding energy—it is still an sp³ hybridized O bonded to atoms significantly more electropositive than itself, (C, H, and/or Zn).
Conclusions

The thermal decomposition of ZnC$_2$O$_4$ in a homogeneous solid-state solution with graphene is an inexpensive, safe, and industrially viable method for synthesizing a ZnO/graphene hybrid material. This method allows for tuning the band structure of the resulting material by varying the stoichiometry of the two precursors. During the decomposition reaction, the graphic environment inhibits the normal ZnO nanocrystal growth pattern, resulting in smaller ZnO crystallite sizes, as well as bridging oxygen atoms which serve to hold the two phases of the hybrid together via chemical bonds. This endows the resulting hybrid material chemical properties that are different from those observed from a solid-state mixture of graphene platelets and ZnO nanoparticles of the same stoichiometry.

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