Carbon-based hybrid materials: growth, characterization and investigation of properties

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2018

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Download date: 30-01-2020
Chapter 6

Reduced graphene oxide-zinc oxide hybrid nanostructures*

In this chapter we report the synthesis of high quality reduced graphene oxide-zinc oxide (rGO–ZnO) hybrid nanostructures. These hybrid nanostructures were produced directly on 3D nickel foam substrates through a hydrothermal approach at low temperature. Scanning and transmission electron microscopy and energy dispersive X-ray spectroscopy results confirmed the formation of ZnO rods wrapped with rGO forming core-shell nanostructures. The interface study of rGO–ZnO nanostructures, by employing the in-situ ambient pressure core level photoemission spectroscopy, revealed that thermal annealing (25 °C - 350 °C) led to the detachment of oxides/epoxides from the surface, and a more robust rGO–ZnO interface. Our study provides a basis for rational design of hybrid materials with application specific interfaces to enhance the device performance.

*The results presented in this chapter are in preparation for publication as: M. Arshad*, P. Rodolf, A. Khan, S. K. Husnain, Saqlain A.Shah, C. Cepek “Interface Study of Reduced Graphene Oxide-Zinc Oxide Core Shell Nanostructures”.
6.1 Introduction

In materials science the development of hybrid structures has seen a remarkable and rapid development during the past decade because such structures can be tailored to obtain new device concepts with controlled physical properties. The optimized application specific design of materials has been achieved by tuning the reactivity, properties and morphology of the material at the interface. It is acknowledged that a control of the nature and abundance of functionalities at the surface and interface of hybrids is highly desirable. For instance, Zinc oxide (ZnO) with a band gap of 3.37 eV at room temperature, is a well-known semiconductor and a widely reported material for photovoltaic cells\textsuperscript{[1,2]}, gas sensors\textsuperscript{[3]}, transparent conductors\textsuperscript{[4]} and photo-catalytic hydrogen evolution applications. However, upon light irradiation, in pristine ZnO photogenerated charge carriers display a high recombination rate and poor charge transfer behaviour.\textsuperscript{[5,6]} To address this problem, hybrids of graphene (owing to its extraordinary optical, mechanical and electrical properties) and ZnO have been extensively employed.\textsuperscript{[7-11]}

In particular, for photovoltaic applications, Sahoo \textit{et al.}\textsuperscript{[12]} have synthesized composite structures of reduced graphene oxide (rGO) and ZnO which exhibited an improved response in dye-sensitized solar cells. In a similar study Song and Wang\textsuperscript{[13]} showed the effects of rGO incorporation on ZnO based dye sensitized solar cells with enhanced device performance. In another work, Park \textit{et al.}\textsuperscript{[14]} have described a graphene-based cathode, where ZnO hybrids were grown hydrothermally on graphene. Liu \textit{et al.}\textsuperscript{[15]} have prepared carbon-doped ZnO/reduced graphene oxide (rGO) hybrid nanocomposites by ultrasonic mixing of rGO and carbon-doped ZnO nanowires in isopropanol and shown improved photocatalytic activity. Furthermore, rGO–ZnO based composite structures have been successfully employed for photocatalytic hydrogen evolution\textsuperscript{[16]} and in supercapacitors.\textsuperscript{[17-19]} The formation of a well-matched (\textit{e.g.} showing weak binding between the two surfaces) and stable interface can be achieved by reducing the number of OH functional groups at the surface of\textsuperscript{[20]} rGO-ZnO hybrids and confers superior capacitive properties. The photoconductivity of self-
assembled rGO–ZnO structures can be enhanced instead by a controlled increase of the intrinsic defect states at the interface. Recently, it has been reported that perovskite materials exhibit excellent stability on top of rGO/ZnO layer after annealing at 100 °C due to the reduced amount of functional groups at the interface of rGO and ZnO structures.[21] Similarly, Galstyan et al. have demonstrated that rGO–ZnO nanocomposites show improved chemical gas sensors properties due to the surface/interface changes.[22] While some attempts have been made to probe the nature of rGO–ZnO functional surface by XPS at room temperature[5 15 17 23-25], a detailed study of the surface/interface behaviour, an essential element for the device performance, is still missing.

In order to produce robust rGO–ZnO hybrid structures several synthesis schemes have been developed, namely co-precipitation in aqueous media[12], photocatalytic reduction of GO on fabricated ZnO,[25 26], microwave assisted methods[27], thermal dissociation of precursors[28 29], ultrasonic mixing[15], and growth of ZnO nanowires on graphene sheets by CVD.[30] Samera et al.[31] have developed a single step process for synthesis of randomly oriented ZnO (core)/graphite (shell) nanowires, but these core shell nanostructures are produced at a very high temperature (1300 °C), which is very expensive and not suitable for the direct synthesis on substrates stable only at lower temperature. Further, although the aforementioned techniques have been extensively used, they usually demand harsh experimental conditions and a multistep synthesis to generate the desired material. To be able to explore the interface properties and their dependence on the interface defects, a precise control over size, surface morphology and interface of rGO–ZnO nanostructures is required, which is a challenging task. To address the various scientific and technological needs, a facile and inexpensive low temperature process for the synthesis of rGO–ZnO hybrid structures has to be developed. To address these issues, we conceived and realized a single step hydrothermal process for the production of high quality and stable rGO–ZnO hybrid nanostructures. We systematically studied the role of reduction temperature in controlling the interface structure by probing the change in surface functionalities through ambient pressure in situ X-ray photoelectron
spectroscopy (AP-XPS). Our results clearly indicate the dissociation of functional groups and the formation of rGO–ZnO nanostructures with fewer defects, suggesting that annealing of these hybrid nanostructures may be a practical way to design application specific interfaces.

6.2 Experimental details

The rGO was prepared by the modified Hummers’ method\textsuperscript{32,33} starting from graphite powder (Sigma Aldrich, 97\%). The graphite powder was first treated with hydrofluoric acid to remove the intercalated impurities. In a typical reaction, 2 g of purified and dried graphite powder was mixed with 1 g of NaNO\textsubscript{3} (Sigma Aldrich, 99 \%) and mixed with 100 ml of concentrated H\textsubscript{2}SO\textsubscript{4} while cooling with an ice bath. 6 g of KMnO\textsubscript{4} (Sigma Aldrich, 97 \%) was added gradually under stirring, keeping the temperature below 20 °C. The stirring was then continued for another 18 h while maintaining the temperature at 35 °C. After 18 h, the mixture turned into a thick brown paste. About 390 ml of H\textsubscript{2}O was then added followed by an addition of 5 ml of H\textsubscript{2}O\textsubscript{2}, which turned the solution bright yellow and generated bubbling. After stirring for another 2 h, the mixture was washed in 250 ml of 10 \% HCl aqueous solution, de-ionized water and ethanol, then filtered and subsequently dried at 80 °C to yield black graphene oxide sheets. 2 g of the as-prepared graphene oxide was mixed with 500 ml distilled water and sonicated for 2 h. The solution was poured into soxhlet apparatus mantle and 10 ml of hydrazine hydrate was added. The temperature was raised to 100 °C, and set in water-cooled condenser for 24 h; the reduced graphene oxide (rGO) precipitated in the form of a black solid.

Pure 3D ZnO and rGO–ZnO hybrid nanostructures were synthesized on nickel foam substrates (Goodfellow, 99.5\%). Before the growth the nickel foam substrates were ultrasonicated for 20 min in ethanol solution, then washed with distilled water and subsequently dried in air. Pure 3D ZnO nanowires (NWs) were grown on the substrates by a hydrothermal method using zinc acetate dihydrate Zn(CH\textsubscript{3}COO)\textsubscript{2} \cdot 2H\textsubscript{2}O and liquid ammonia (NH\textsubscript{3}) in aqueous solution. The 0.1 M aqueous solution of zinc acetate was prepared in a 150 ml glass beaker. Then 5 ml of ammonium hydroxide
solution (35%, Sigma Aldrich) was slowly added to the aqueous solution of zinc acetate. This initially turned the solution cloudy white in colour but upon further addition of ammonia, the solution became more transparent. The already dried nickel foam substrates were fixed in Teflon sample holding rods and placed in the solution (just dipping from the top), which was placed for 7 h in an oven (Lab-Tech, LDO-030 E) at 90 °C. The ramp rate of oven was set to 10 °C/min. After 7 h the oven was left to cool down to room temperature, after which the substrates were retrieved and washed with distilled water to remove all the solid residual particles. The washed substrates were subsequently dried at 100 °C for 30 min.

To simultaneously grow rGO–ZnO nanostructures directly on nickel foam substrate, in a separate beaker, 20 mg of as prepared reduced graphene powder was dispersed in 20 ml distilled water and sonicated for 7 h to obtain a uniform suspension; in another beaker, 50 ml of the solution of zinc acetate dihydrate $\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}$ as used for pure ZnO NWs was prepared. Both solutions were mixed and magnetically stirred for 10 min. Then the synthesis was continued in a similar fashion as adopted for pure ZnO NWs (steps discussed above).

Four samples of rGO–ZnO were synthesized with varying amounts of the rGO dispersion, namely 25 wt%, 20 wt%, 15 wt% and 10 wt%, while keeping a constant molarity of the zinc acetate dihydrate $\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}$ solution. The novel methodology also ensures a good control over reproducibility in fabricating the desired rGO–ZnO nanostructures. However, the best results with well-defined rGO-ZnO NWs perpendicular to the substrate were obtained by using the 10 wt% of rGO with the zinc acetate dihydrate $\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}$ as discussed below.

6.3 Results and discussion

6.3.1 Scanning and transmission electron microscopy analysis

The first proof of the successful synthesis of pure ZnO and rGO–ZnO core shell nanowires comes from the scanning electron microscopy. Figure 6.1 (a) presents the schematic illustration of ZnO and rGO–ZnO nanostructures...
grown on the Ni foam substrate through the one-step hydrothermal process. The figure 6.1 (b) and (c) illustrate the morphology of the Ni foam substrate before and after the growth of ZnO, respectively. A high-resolution SEM image (figure 6.1 (d) shows that pure ZnO grows in hexagonal rod-like structures. Furthermore, elemental analysis of as synthesised sample confirms the presence of Zn, O, and Ni only.

Figure 6.1: Schematic illustration of growth of ZnO nanostructures and rGO–ZnO hybrid nanostructures by hydrothermal process in a single step process (a). SEM images, (b) collected from bare 3D nickel foam substrate, (c) micrograph of Ni foam after growth of pure
ZnO nanostructures, (d) High-resolution image of as-grown pure ZnO nanostructures on 3D Ni foam. (e) EDS spectra collected from as grown pure ZnO nanostructures.

Figures 6.2 and 6.3 display the SEM images collected from rGO–ZnO hybrid nanostructures synthesized with different wt% of the rGO dispersion in the

Figure 6.2 SEM Images of as synthesized rGO–ZnO nanostructures on 3D Ni foam obtained with 25 wt% (a), 20 wt% (b), and 15 wt% (c, d) of dispersed rGO solution (details see text). (d) SEM micrograph obtained from sample(c) at higher magnification.
Figure 6.3 SEM images of the sample obtained with 10wt% rGO dispersion, (a) Low magnification micrograph of as grown rGO–ZnO hybrid nanostructures on 3D nickel foam. The numbers 1, 2, 3 in the image refer to branches of the nickel foam at three different depths. (b, c) SEM images of same sample at lower and higher magnifications. (d) EDS spectra collected from as grown rGO–ZnO hybrid nanostructures.

dihydrated zinc acetate solution (constant molarity). The SEM analysis revealed that there is a very low growth of rod/wire-like hybrid structures when 25 wt% dispersed rGO solution was used (figure 6.2 a). With 20 wt% and 15 wt% of dispersed rGO solution, the growth of rod-like structures was found to have increased significantly, however the density of these structures was not too high. At 10 wt%, it is evident from figures 6.3 (b) and (c) that rod-like structures have uniformly grown perpendicularly to the Ni foam surface and that individual rods are well separated. The analysis of randomly selected rGO–ZnO nanostructures (figure 6.3 (b) and (c)) shows diameters of ca. 100 nm and lengths of ca. 1 μm.

The TEM images collected from rGO–ZnO nanostructures (figure 6.4 (b) and (c)) confirm that indeed hybrid structures have formed: Graphene oxide layers are wrapped around the ZnO rods surface as sketched in figure 6.4 (a) and hair-like rGO can also be seen pointing out from the surface. The EDS spectra obtained from the rGO–ZnO hybrid nanostructures showed the
6.3.2 Raman spectroscopy

In order to establish the presence of a wrapped reduced graphene oxide layer on ZnO and gain information on the quality of the rGO, Raman spectroscopy was employed. The main feature in the Raman spectra of carbon structures is the appearance of the G and D bands at around 1560 cm$^{-1}$ and 1360 cm$^{-1}$, respectively. The G band is associated with the bond stretching of sp$^2$ bonded carbon structures. In graphitic material it corresponds to a degeneracy of the in-plane transversal and longitudinal optical phonons around the centre of the Brillouin zone. The D band corresponds to the breathing modes of sp$^2$ atoms in rings of poly-aromatic hydrocarbons, and in graphene it stems from a second-order scattering process, that involves defects and edges; hence its intensity is commonly taken as a fingerprint of the amount of defects.\[34\]
Figure 6.5 shows the Raman spectra of (a) highly oriented pyrolytic graphite (HOPG), (b) bare ZnO NWs and (c) rGO–ZnO hybrid nanostructures on the 3D nickel foam and (d) the same rGO–ZnO nanostructures after annealing in UHV at 350 °C. The Raman spectrum of HOPG was collected for comparison. Figure 6.5 (a) shows the typical D, G bands and 2D features at 1360 cm$^{-1}$, 1582 cm$^{-1}$ and 2720 cm$^{-1}$ respectively. The relative high intensity of the D band infers the presence of defects in the lattice structure of graphite, while G and 2D peaks are indicative of pure sp$^2$ bonded carbon. Moreover, the lower the intensity ratio of I_D/I_G, the better is the quality of the graphitic structures. In the Raman spectrum of the ZnO nanorods (figure 6.5 (b)), the peak at 330 cm$^{-1}$ originates from the second order scattering from zone boundary phonons of the hexagonal ZnO structure. Moreover, the intense sharp peak at 440 cm$^{-1}$ is assigned to the $E_2$ (high energy) mode of the hexagonal wurtzite ZnO phase, whereas the peak at 582 cm$^{-1}$ is associated with the $E_2$ (low energy) mode attributed to oxygen deficiency.
or defects in ZnO.\textsuperscript{[37]} It is well established that in wurtzite ZnO the non-polar phonon modes with symmetry $E_2$ have two frequencies, $E_2$ (high) associated with oxygen atoms and $E_2$ (low) associated with the Zn sub-lattice.\textsuperscript{[38 39]} Furthermore, the peak at $\sim 1130$ cm$^{-1}$ is due to the multiple phonon scattering.\textsuperscript{[40]}

In the case of rGO–ZnO (figure 6.5 (c)) the Raman spectrum shows the D, G, 2D$^1$ and 2D$^2$ bands at 1348 cm$^{-1}$, 1589 cm$^{-1}$, 2686 cm$^{-1}$ and 2935 cm$^{-1}$, which confirms the formation of integrated rGO–ZnO nanostructure. The peak intensity of $E_2$ (high energy) mode of ZnO (figure 6.5 b) is reduced in rGO–ZnO nanostructures (figure 6.5 c, & d), as expected if rGO \textsuperscript{[41]} wraps around the ZnO NWs. We interpret the fact that the 2D$^2$ peak is at higher wavenumbers than the usual 2D$^1$ peak as a sign of the presence of structural defects due to C–H sp$^3$ carbon as well as of the interruption in translational symmetry of the sp$^2$-bonded carbon at the interface of the rGO–ZnO nanostructures. For the thermally annealed rGO–ZnO sample all the D, G, 2D$^1$ and 2D$^2$ features are preserved. Interestingly, the relative intensity of G band to D band is increased and the $I_D/I_G$ intensity ratio, which was 1.2 for the as-synthesized rGO–ZnO nanostructures, has decreased to 0.8 for the thermally annealed rGO–ZnO sample. In fact, to quantify the improvement after annealing we used the approach developed by Lucchese \textit{et al.}\textsuperscript{[42]}, to determine the average distance between two point defects ($L_D$) in the reduced graphene oxide layers, based on the ratio of intensities of the G and D peaks. According to this model for the as-synthesized rGO–ZnO $L_D \approx 9$ nm, but increases to $\approx 11$ nm after annealing. In other words the amount of structural defects has significantly decreased, in good agreement with previously reported results for annealed rGO.\textsuperscript{[43 44]} This improvement agrees with the fact that the 2D$^1$ and 2D$^2$ bands have merged together forming a single 2D band appearing at $\sim 2760$ cm$^{-1}$, which implies partial restoration of the graphene lattice by thermal annealing in UHV, as seen previously.\textsuperscript{[45 46]} In the case of ZnO, the intensity of the peak appearing at 438 cm$^{-1}$ has increased in comparison to the peak intensity of as synthesised rGO–ZnO nanostructures. This points to a thinning of rGO on ZnO after thermal annealing.
6.3.3 X-ray photoelectron spectroscopy results

To probe the structural change at the surface/interface of rGO–ZnO nanostructures as a function of thermal annealing in UHV, \textit{in situ} core level photoemission spectroscopy was employed. The survey scans (figure 6.6)

![Survey scans collected from rGO–ZnO nanostructures](image)

\textit{Figure 6.6:} X-ray photoemission survey scans collected from rGO–ZnO nanostructures (10 wt% of rGO) at room temperatures (25 °C), 50 °C, 150 °C, 200 °C and 300 °C.
collected at various annealing temperatures shows the presence of carbon, oxygen and zinc only. For the surface/interface study of rGO–ZnO hybrid nanostructures, detailed C1s, O1s and Zn3p photoemission spectra were collected at 25 °C, 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C and at 350 °C.

As seen in figure 6.7, the C1s spectrum of rGO–ZnO nanostructures at room temperature (25 °C) comprises five contributions: the peak at a binding energy (BE) of 284.6 eV is assigned to C-C/C-H related species, whereas the peaks positioned at BE of 285.6 eV, 286.5 eV and 288.1 eV are ascribed to the hydroxyl group (C–OH), epoxy groups (C–O–C) and >C=O respectively,
and the peak at a higher binding energy (290.2eV) characterizes the shake-up satellite (π-π*) features of C–C aromatic rings.\cite{47-50} As the annealing temperature is increased, a progressive decrease in the peak intensity of O-C and >C=O functional groups are observed, while the peak intensity of C–C/C–H increases steadily.

Figure 6.8: O1s core level photoemission spectra received from as-grown rGO–ZnO core shell hybrid nanostructures at room temperature (RT), and during annealing at 50°C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C and at 350 °C.
In the corresponding O1s spectra, shown in figure 6.8, one can identify three contributions; the first at a BE of 530.4 eV is attributed to $O^{2-}$ ions in ZnO,[40] the second one at a BE of 531.7 eV corresponds to oxygen bonded with carbon and Zn at the surface forming a Zn–O–C bond[51,52] and the last contribution at 533.1 eV can be assigned to chemisorbed oxygen/hydroxyl species.[40,53]

![Figure 6.9: XPS analysis of deconvoluted peak intensities of C1s (a) and O1s (b) as a function of annealing temperature.](image)

In order to quantify the structural change, intensities of the various functional groups from surface/interface of rGO–ZnO nanostructures were also studied as a function of temperature and the result is summarized in figure 6.9. A decrease in relative intensity of the functional groups started to occur already for annealing at 50 °C and when temperature reached 200 °C and beyond the contributions from C–O–C and >C=O bonds (figure 6.9 (a)) became negligible. This dissociation of chemisorbed/surface oxide species at the surface/interface is mirrored by increase in peak intensity of O–ZnO in figure 6.9 (b). Moreover, a decrease in the intensity of the peak of Zn–O–C is evident. Analysis of C–OH groups related peak intensity (figure 6.9 (a) and (b)) shows that about 1/3 of the initial intensity, for both C1s and O1s component remains even after thermal annealing in UHV at 350 °C, suggesting that for complete deoxygenating and dehydrogenation a thermal treatment at higher temperature is required in UHV.[48]
6.4 Conclusions

We have demonstrated that the hydrothermal process is an effective method for the synthesis of high quality ZnO and rGO–ZnO hybrid nanostructures in a single step process at low temperature (90 °C). These hybrid nanostructures were synthesized by varying the wt% of rGO dispersion in the zinc acetate dehydrate solution. The optimized rGO–ZnO hybrid nanostructures were obtained with 10 wt% of rGO dispersion. The SEM and TEM analysis revealed an interface where rGO adhered to the ZnO nanowires in the hybrid nanostructures. The amount of functional groups at the interface between rGO and ZnO can be tuned with annealing temperature as confirmed by Raman and X-ray photoelectron spectroscopy. This provides a practical way to design application specific interfaces to enhance the performance of graphene-based hybrid materials.

References