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Structure of Graphene Oxide – Tin Oxide Hybrid Nanomaterials for Gas Sensors

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Hybrid materials composed of carbon nanostructures decorated with transition metal oxide nanocrystals have shown tremendous potential for gas sensing applications due to their ability to detect various gases at room temperature with high sensitivity. The atomic structure, size, distribution, and morphology of the components ultimately determine the performance of these sensors. We have used transmission electron microscopy (TEM) and Selected Area Diffraction (SAD) to study the structural characteristics of materials consisting of tin oxide nanocrystals deposited on Graphene Oxide (GO).

GO layers were fabricated via Flow Directed Assembly (FDA) [1]. SnO_2 nanocrystals were synthesized with a mini-arc source using a tin precursor, and subsequently deposited by Electrostatic Force Directed Assembly (ESFDA) [2] onto the GO layers supported on a TEM grid with lacy carbon. SAD studies, performed with 300keV electrons in a Hitachi H9000 NAR microscope, were used to establish the crystallinity and distribution of the GO sheets.

Figure 1 shows SAD patterns from three GO regions, confirming that the FDA GO preparation preserves the honeycomb structure of pure graphene. The experimental 0.142 nm spacing matches the C-C spacing of graphene and graphite. Regions indicative of a few ordered GO layers (Fig. 1a) as well as single and multiple disordered GO layers (Fig.1b and c) were observed. The intensity ratio of $[1\bar{1}00]$ to $[1\bar{1}20]$-type reflections is smaller for a hexagonal lattice with AB-type stacking compared to that of a monolayer and/or disordered stacking of monolayers [3]. The experimental intensity profiles in Fig. 1 display both types of behavior, with dominant presence of individual monolayers (1b) and monolayers with disordered layering (1c), with thickness of up to 25 GO monolayers, and minority of ordered monolayers (1a). The lack of reflections other than those corresponding to GO or graphite indicates that there is no in-plane superlattice ordering from oxygen functional groups. Figure 2 shows Bright-field (BF) and Dark-field (DF) TEM images of the GO sheet that produced the SAD pattern of figure 1(b). The images show extended regions with nearly constant electron transparency with dimensions of the order of 500 nm. The contract is composed of patches indicative of regions with different number of GO layers, in agreement with the SAD data. Electron irradiation experiments found that the stacks of GO layers can transform to amorphous carbon upon receiving high electron doses (Fig. 3). Figure 4 shows a BF-TEM image of 6 tin oxide nanocrystals with the corresponding SAD pattern. Most of the nanocrystals observed ranged in size between 6-30 nm. The SAD pattern shows the expected rings of the supporting GO nanosheets as well as sparse rings due to reflections from the nanocrystals. The most intense ring corresponds to a lattice spacing of .2364 nm, similar to the spacing of [200]-type planes of bulk rutile SnO_2. Prior HRTEM studies have also found rutile SnO_2 nanocrystals on amorphous carbon and on carbon

nanotubes [2], with minority tetragonal SnO nanocrystals. Studies are underway to determine the phase purity of the nanocrystals in the present system.

References:

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[2] Lu, G.H. et al., *J. of Nanomater.* (2006) 60828

[3] Wison, N et al., *ACS Nano.,* 3 (2009) 9

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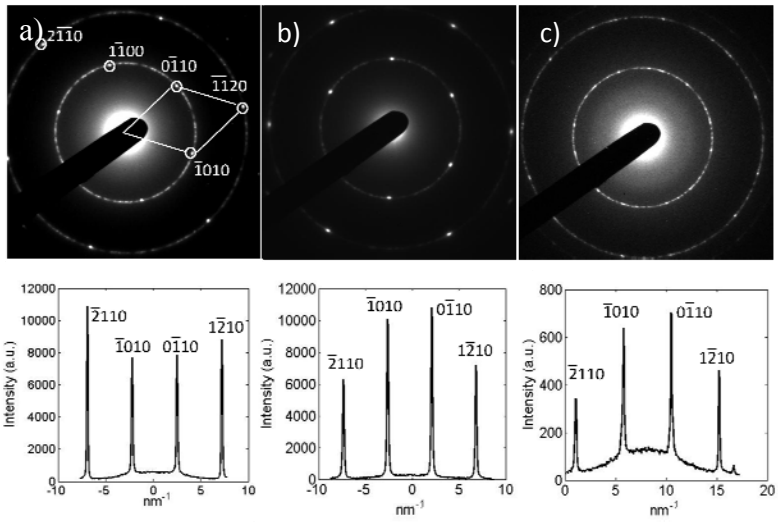

Figure 1: SAD patterns (top) and intensity profiles (bottom) from several areas of the GO support. The intensity ratio is indicative of graphite-like stacking in area (a), and of random graphene monolayer stacking in areas (b) and (c). The presence of oxygen and hydrogen does not give additional Bragg reflections, indicative of random ordering.

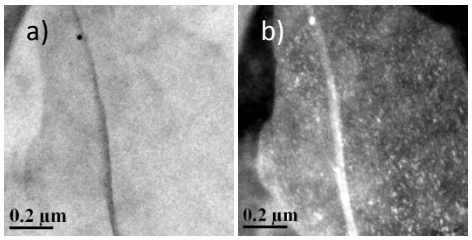

Figure 2: BFTEM (a) and DFTEM (b) images of the GO sheet generating the SAD pattern in figure 1(a). The DF image is generated from a $[2\bar{1}\bar{1}0]$-type reflection.

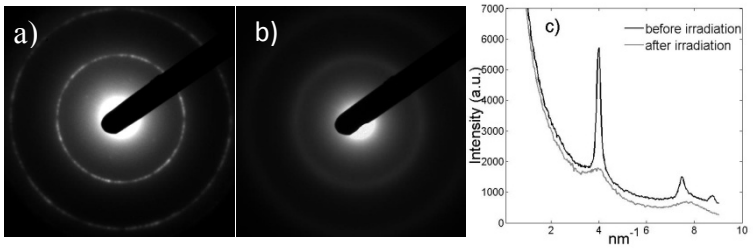

Figure 3: SAD patterns of a GO sheet before (a) and after (b) an electron dose of ~ 6.3×10^6 electrons /nm^2. Line profiles of the two ring patterns are shown in figure 3(c), demonstrating the broadening of the rings associated with amorphousness.

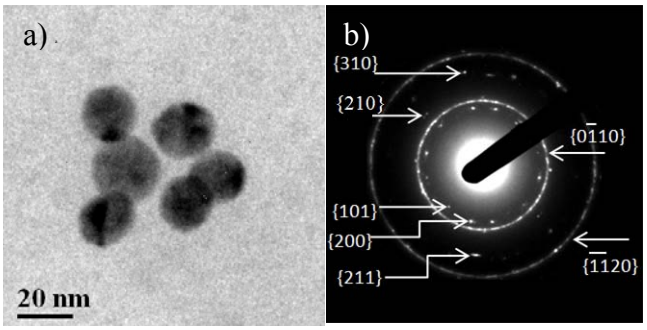

Figure 4: BFTEM image of an aggregate of six SnO_2 nanoparticles (a) and the corresponding SAD pattern (b). The nearly continuous GO rings are indexed in hexagonal notation and the sparse rings due to SnO_2 fit the rutile structure as indexed.

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