XPS Study of Graphene-Based ZnO Hybrid Structures

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Introduction

we report the synthesis of high quality reduced graphene oxide – zinc oxide (rGO–ZnO) hybrid nanostructures. These hybrid nanostructures were produced directly on 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.

Experimental Details

The rGO was prepared by the modified Hummers' method. Pristine ZnO and rGO–ZnO hybrid nanostructures were synthesized on nickel foam substrates. Pure ZnO nanorods were grown on the substrates by hydrothermal method using zinc acetate dehydrate (Zn (O2CCH3) $_2$(H2O) $_2$) and liquid ammonia (NH_3) in aqueous solution.

Following way was adopted for the simultaneous growth of rGO–ZnO nanostructures directly on nickel foam substrate. In a separate beaker, as prepared 20 mg of reduced graphene powder was dispersed in 20 mL distilled water and sonicated for 7 h to obtain a uniform suspension. In another beaker, took the 50 mL of already prepared solution of Zinc acetate used for pure ZnO NWs. Both solutions were mixed together and magnetically stirred for 10 minutes. A schematic description for the synthesis of rGO-ZnO hybrid nanostructures.

Four samples of rGO–ZnO were synthesized by varying the 25-wt%, 20-wt%, 15-wt% and 10-wt% of rGO-dispersed solution while keeping constant molarity of zinc acetate solution. The novel methodology also ensures good control over reproducibility in fabricating the desired rGO–ZnO nanostructures. However, the optimized results depicting well defined rGO–ZnO NWs perpendicular to the substrate were obtained by using the 10-wt% of rGO with Zinc acetate solution which were checked by SEM.

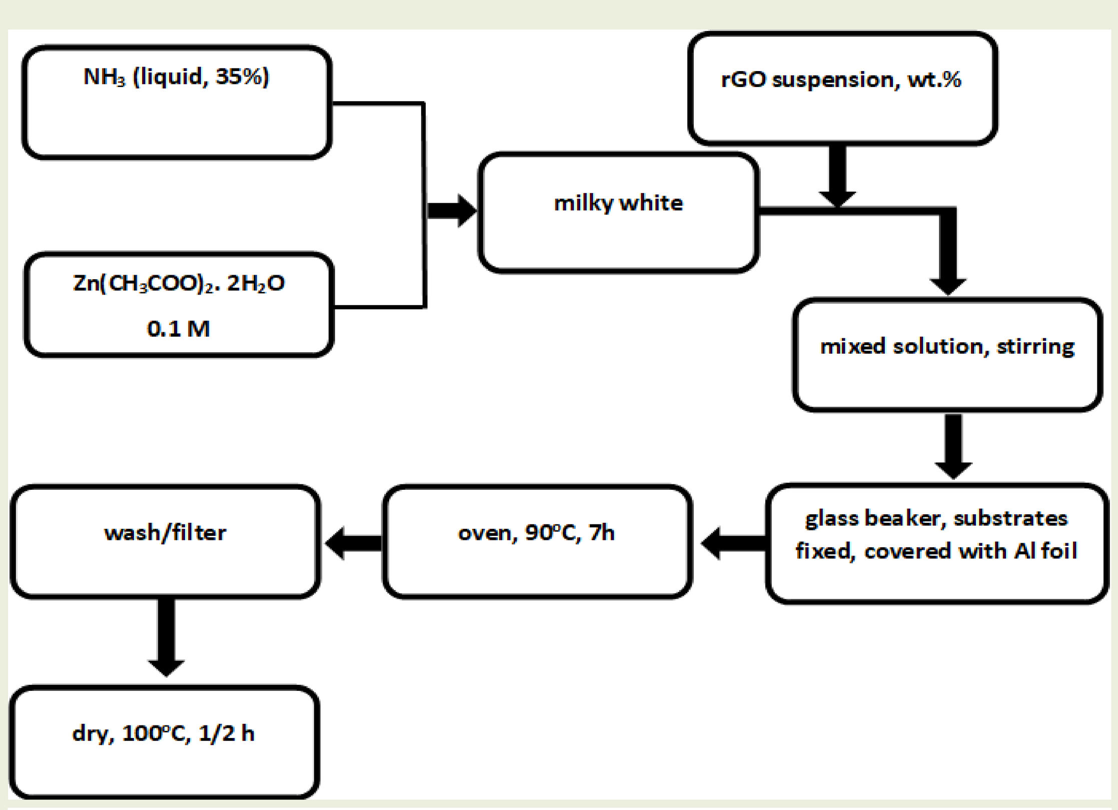
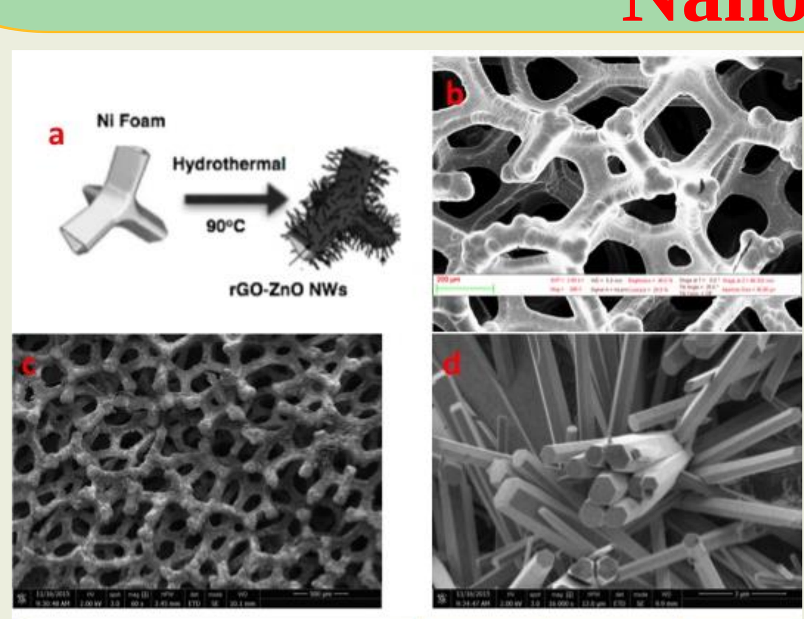


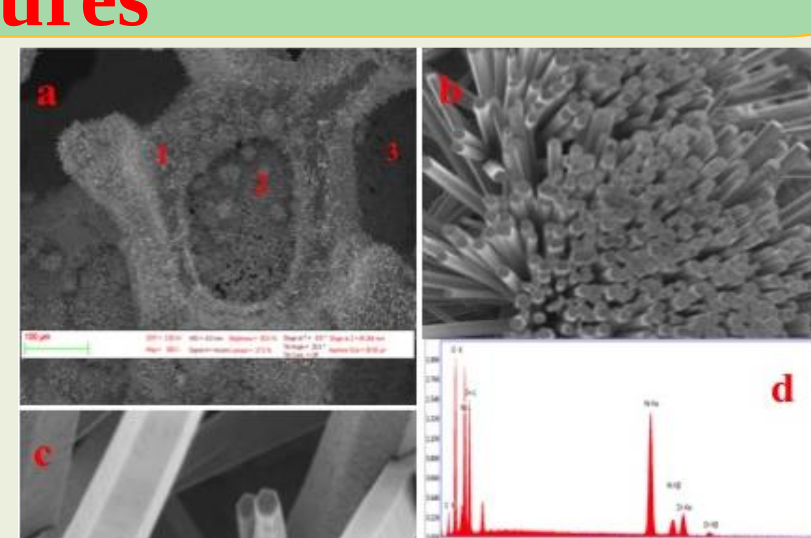
Figure 1 A schematic description for the synthesis of rGO-ZnO hybrid nanostructures.

Investigation of Graphene-Based ZnO Hybrid Nanostructures



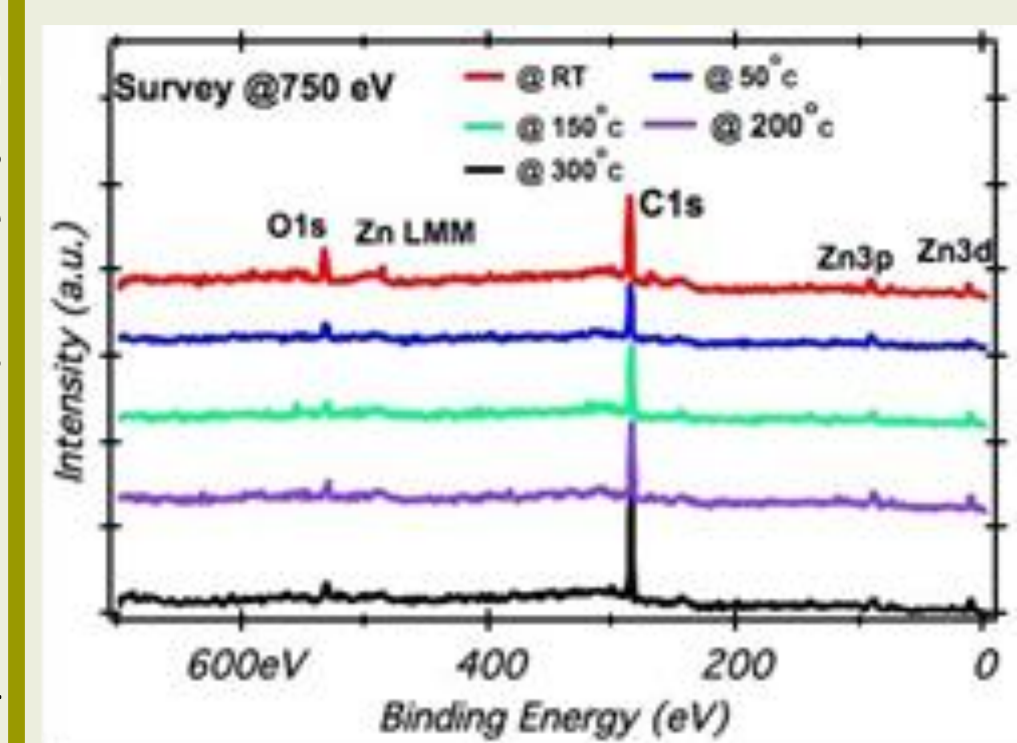
Element	Weight %	Atomic %
OK	9.68	29.59
NiK	33.75	28.1
ZnK	56.56	42.3

Figure 1 (a) Schematic illustration of growth of ZnO nanostructures and rGO–ZnO hybrid nanostructures by hydrothermal process in a single step process. SEM images, (b) collected from bare nickel foam substrate, c) micrograph of Ni foam after growth of ZnO NWs nanostructures, (d) High-resolution image of as grown Pure ZnO nanostructures on Nickel foam. (e) EDS spectra received from as grown pure ZnO nanostructures.



Element	Weight %	Atomic %
C K	10.99	10.99
O K	23.31	23.31
NiK	46.26	46.26
ZnK	19.44	19.44

Figure 2, SEM images, (a) Low magnification micrograph of as grown rGO–ZnO hybrid nanostructures on the nickel foam substrate. 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



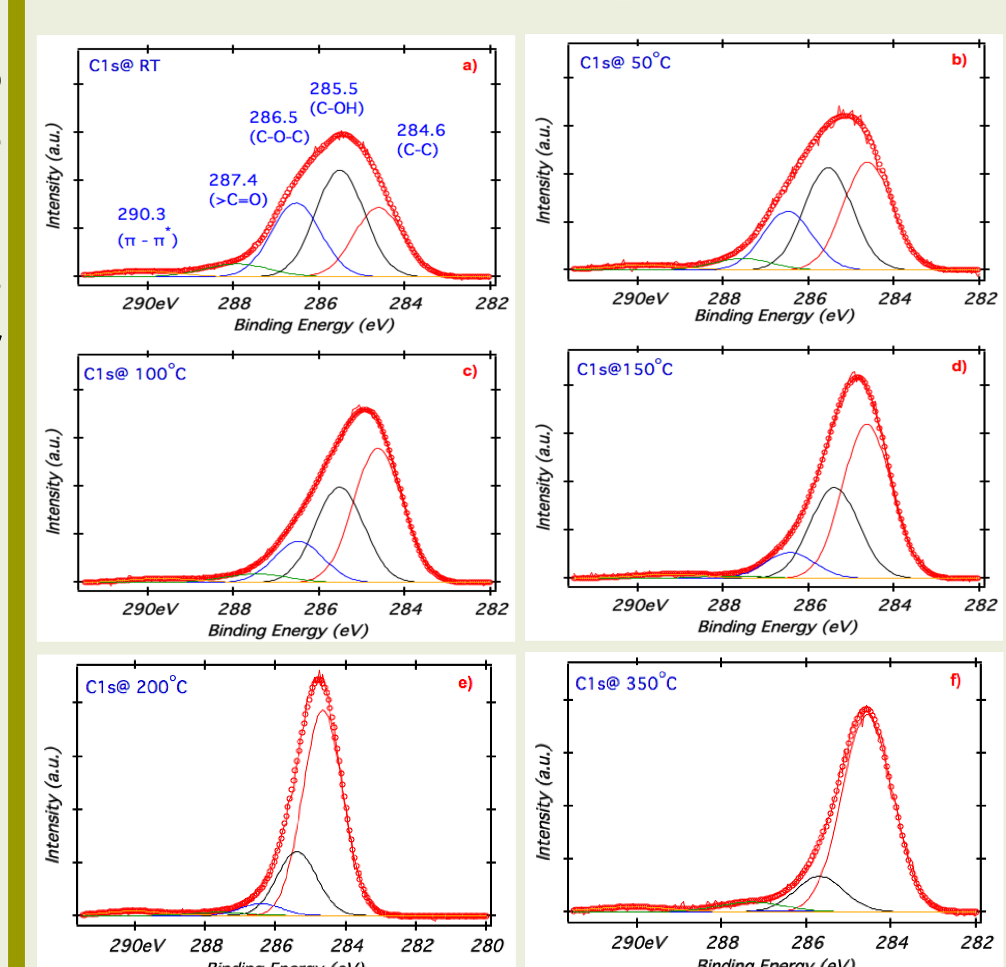


Figure 3 C1s core level spectra collected from as grown rGO–ZnO core shell hybrid nanostructures at RT (25 °C), and during annealing at 50°C, 100 °C, 150 °C, 200 °C, and at 350 °C.

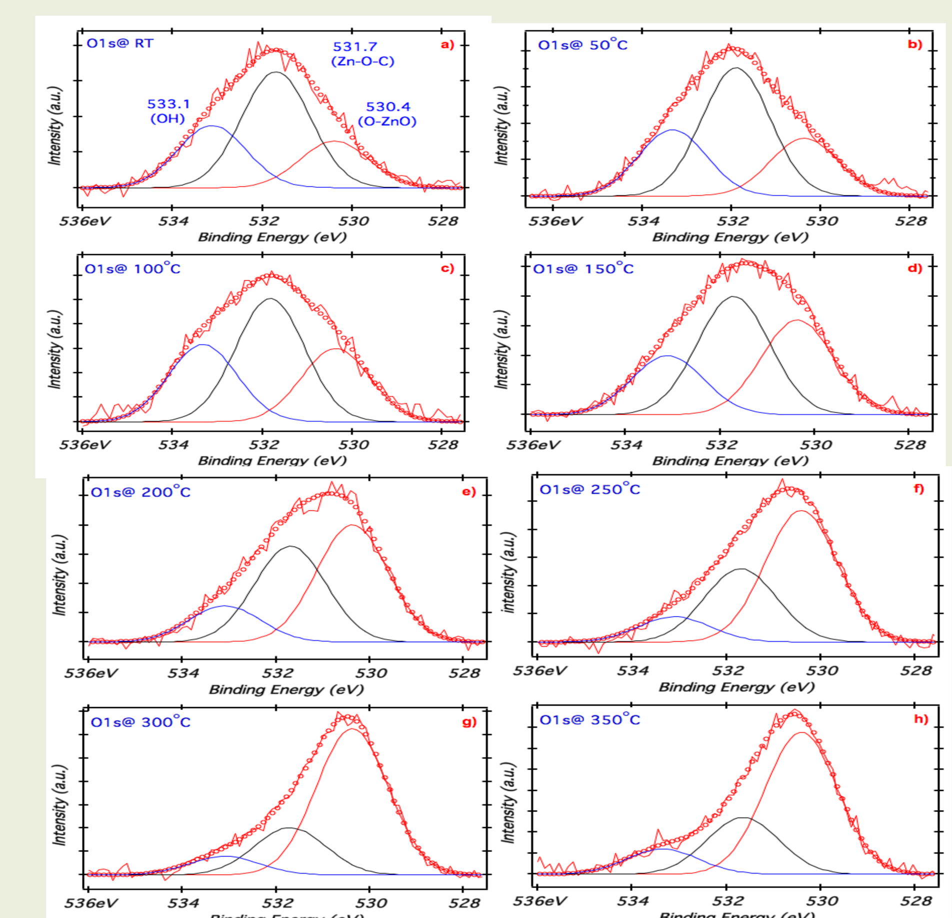


Figure 4 O1s core level photoemission spectra received from as-grown rGO–ZnO core shell hybrid nanostructures at room temperature (RT), and during annealing at 50°C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C and at 350 °C

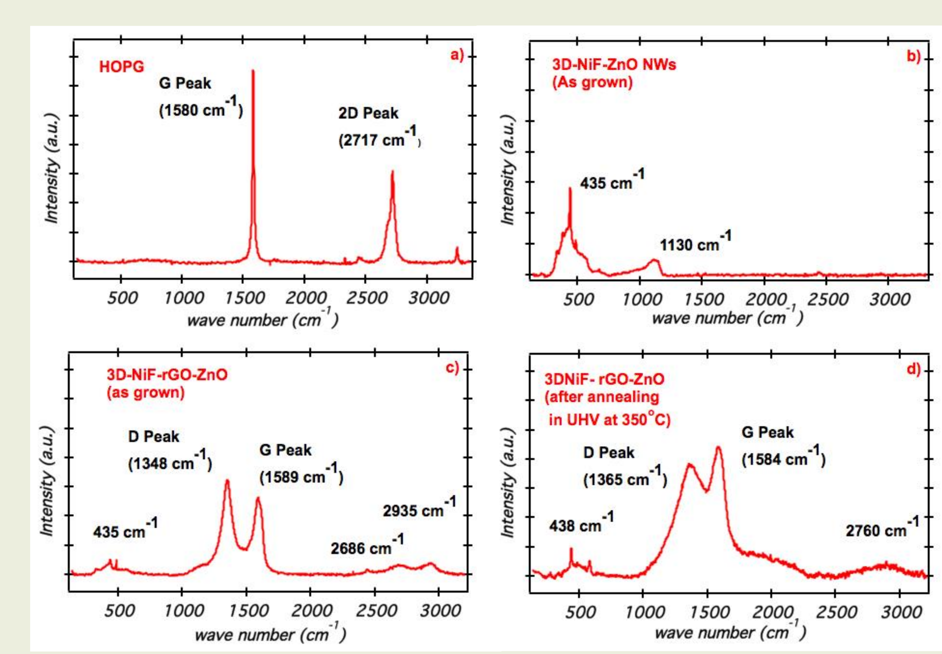


Figure 5, Raman spectra obtained from HOPG (a), as grown pure ZnO NWs on nickel foam substrate (b), as grown rGO – ZnO core shell nanowire hybrid structures on 3D nickel foam substrate(c), and after annealing rGO – ZnO core shell nanowire hybrid structures at 350°C (After performing XPS studies)

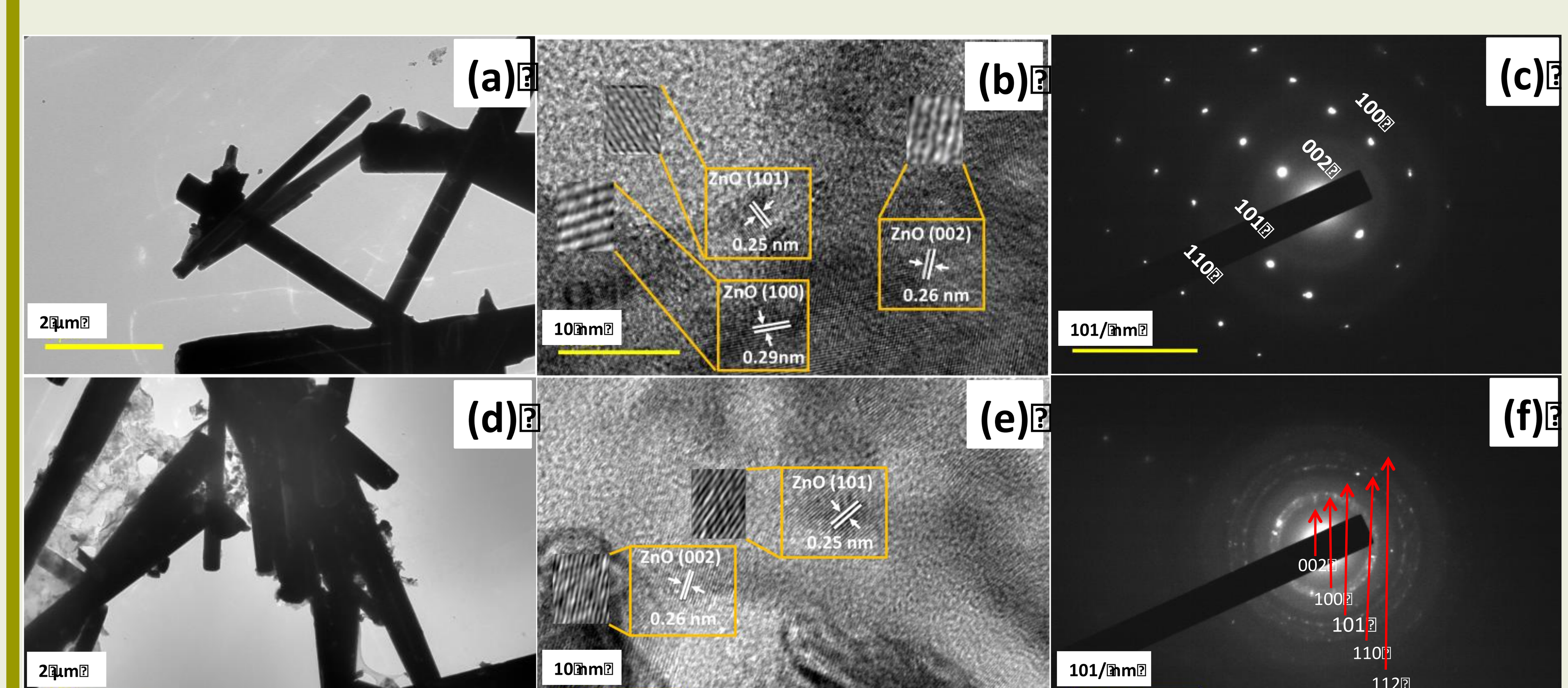


Figure 6 TEM results of as synthesized pristine ZnO nanostructures, (a) & (b) low & high resolution images, respectively and SAED pattern. TEM images of as grown rGO - ZnO (10 wt.%) hybrid nanostructures (d) & (e) low & high resolution images, respectively, and SAED pattern of ZnO-rGO hybrid nanostructures (c).

Conclusions

It is demonstrated that the hydrothermal process is an effective method to synthesise the high quality rGO–ZnO hybrid nanostructures in a single step process and at low temperature (90 °C). It is shown that surface/interface structure of hybrid rGO–ZnO was can be tuned with the change in annealing temperature. The ratios of I_D/I_G of rGO–ZnO nanostructures show that thermal annealing (50-350 °C) reduces the defects of surface/subsurface. The qualitative and quantitative analysis of XPS data confirmed the dissociation of functional groups from the surface/interface of rGO–ZnO nanostructures. This provides a practical way to design application specific interface to enhance the performance hybrid materials.