

Deposition of aligned ZnO nanorods on HFCVD grown graphene oxide thin film for dye sensitized solar cells Sadia Ameen, Minwu Song, Hyung-Kee Seo, M. Nazim, Hyung-Shik Shin*

Energy Materials and Surface Science Laboratory, Solar Energy Research Center, School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju-561756, Republic of Korea

*Email: hsshin@jbnu.ac.kr

ABSTRACT

Vertically aligned zinc oxide (ZnO) nanorods (NRs) were grown by the low-temperature hydrothermal method on graphene oxide (GO) coated FTO substrates, where GO was directly deposited on fluorine doped tin oxide (FTO) substrates using hydrogen (H_2 , 65 sccm) and methane (CH_4 , 50 sccm) through hot filament chemical vapor deposition (HFCVD) technique. The vertically aligned ZnO NRs were applied as effective photoanode for the fabrication of efficient dye sensitized solar cells (DSSCs). A solar-to-electricity conversion efficiency of ~2.5% was achieved by DSSC fabricated with ZnO NRs deposited on graphene oxide (GO-ZnO NRs) thin film photoanode.

INTRODUCTION

The Graphene as a 2D carbon-based material is applied enormously in electronic applications because of its good conductivity, superior chemical stability, large surface-to-volume ratio, and suitable pore size distribution [1]. Various semiconducting metal oxides like SnO_2 , In_2O_3 , Nb_2O_5 and ZnO [2, 3] have been widely used as promising thin film photoanode materials for DSSCs. ZnO has wide band gap (3.37 eV), high exciton binding energy (60 meV), high electronic mobility and thus, actively explored as an alternative anode material in DSSCs. Importantly, the nanostructures of ZnO could be easily tailored by using different methods. The aligned ZnO nanostructures, are being grown because of their good electrical conductivity and high surface-to-volume ratio for high absorption of dye molecules, improved light absorption, and application of p-n junctions and photovoltaic devices [4,5]. In this work, the vertically aligned ZnO NRs are grown by the low temperature hydrothermal method on GO coated FTO substrates and applied as photoanode for the application of DSSCs. The direct coating of GO on FTO substrate is carried out through HFCVD with the introduction of hydrogen (H_2 , 65 sccm) and methane (CH_4 , 50 sccm) in a chamber. The GO-ZnO NRs photoanode delivers the solar-to-electricity conversion efficiency of ~2.5% with enhanced J_{SC} , V_{OC} , and FF.

EXPERIMENTAL

The FTO (FTO glass, Hartford Glass Co., 8 Ω /sq, 80% transmittance in visible spectrum) substrate was introduced into the HFCVD chamber and annealed in the presence of H_2 (65 sccm) for 30 min. Further annealing was performed by continuing H_2 with same flow rate, at the filament temperature of 1200 °C for 5 min to remove the traces of organic materials and oxide layers from the substrate. Finally, the methane (CH_4 , 50 sccm) as a carbon precursor

was introduced into the reactor for 5 min to produce a thin layer of GO on FTO. The vertically aligned ZnO NRs were grown by the hydrothermal method using HFCVD deposited GO-FTO substrate. Typically, an aqueous equimolar (0.1 M) reaction mixture of $(Zn(NO_3)_2 \cdot 6H_2O)$, and $(CH_2)_6N_4$, HMTA, was prepared. The prepared GO-FTO substrates were placed upside down into the Teflon beaker and transferred to the stainless steel autoclaves and maintained at the temperature at 85 °C for 3 h. After completion of the reaction, the vertically aligned ZnO NRs grown on GO-FTO (GO-ZnO NRs) substrates were taken out and washed with deionized (DI) water and methanol. For the fabrication of DSSC, the grown GO-ZnO NRs substrates were immersed in the ethanolic solution of ruthenium (II) 535 bis-TBA (0.3 mM, N-719, Solaronix) dye for 12 h at the room temperature under dark conditions. The platinum (Pt)-coated FTO substrate as counter electrode was placed over the dye-adsorbed GO-ZnO NRs thin film electrode and the edges of the cell were sealed with 60 μ m thick Surlyn sheet (SX 1170-60, Solaronix) by hot-pressing the two electrodes at 80°C. An electrolyte of the specified composition (0.5 M LiI, 0.05 mM I_2 , and 0.2 M tertbutyl pyridine in acetonitrile) was introduced through holes in the counter electrode using a syringe on the dye-immobilized thin film photoanode, and holes were sealed with small microscopic glass and Surlyn sheet.

RESULTS SUMMARY

Fig. 1 shows the cross section and surface FESEM images of HFCVD grown GO-FTO and ZnO-GO thin film substrates. The GO sheets are deposited and uniformly arranged on the FTO substrate with the GO thickness of ~600 nm, as shown in Fig. 1a. Fig. 1(b) demonstrates that the ZnO NRs are vertically aligned on the GO-FTO thin film. ZnO NRs exhibits the average length of ~2-4 μ m and obtains the average thickness of ~5 μ m including the GO thin layer. The surface images clearly show that ZnO NRs are highly dense and grown vertically on GO-FTO substrates, as shown in Fig.1(c, d). The high resolution image (Fig. 1(d)) reveals that the obtained ZnO NRs possess hexagonal morphology with average diameter of ~200-300 nm.

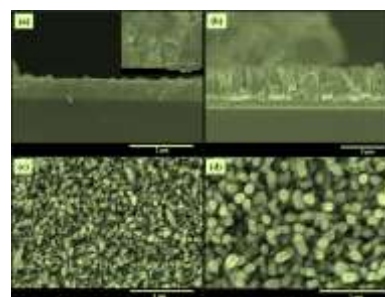


Fig. 1. Cross-sectional FESEM images of (a) GO-FTO and (b)

GO-ZnO NRs thin film. Surface FESEM images of GO-ZnO NRs thin film at (c) low magnification and (d) high magnification. Inset shows the surface view of GO-FTO thin film.

Fig. 2 shows the transmission electron microscopy (TEM), high-resolution (HR) TEM, fast Fourier transform (FFT) of HRTEM and a selected area electron pattern (SAED) of GO-ZnO NRs. Similar to FESEM images, Fig. 2(a) deduces the morphology of ZnO NRs with the diameter and length of ~200–300 nm and ~2–4 μm , respectively. It is noticed that the sheets morphology are seen at the end of ZnO NRs which suggests the presence of GO layer in GO-ZnO NRs substrates. The grown GO-ZnO NRs show the typical pattern of a wurtzite single-crystal ZnO with preferentially grown in (0001) direction, as observed in SAED patterns (Fig. 2 (b)). Furthermore, the HRTEM image (Fig. 2 (c)) of ZnO NRs present well-resolved lattice fringes of crystalline ZnO NRs with the interplanar spacing of ~0.52 nm which is well indexed with the lattice constant in the reference (JCPDS No. 36–1451). The FFT of HRTEM (Fig. 2(d)) again confirms the interplanar spacing of two adjacent fringes of ZnO NRs.

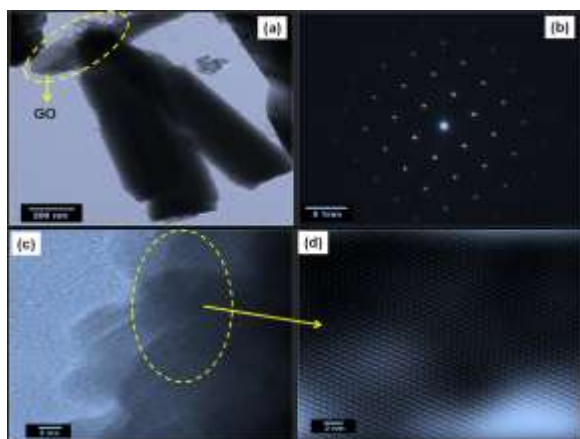


Fig. 2. (a) TEM image, (b) SAED pattern, (c) HR-TEM, and (d) corresponding FFT of GO-ZnO NRs thin film.

The Raman spectra of GO thin film and GO-ZnO NRs thin film are shown in Fig. 3. HFCVD grown GO thin film shows two Raman shifts at ~1348 cm^{-1} and ~1592 cm^{-1} , correspond to D and G bands respectively, as shown in Fig. 3 (b). In general, the G band and D band represent the breathing mode of κ -point phonons of A_{1g} symmetry and the E_{2g} phonon of $C\text{ sp}^2$ atoms, respectively. The lower D Raman band originates from the structural defects due to the presence of the hydroxyl and epoxide groups on the carbon basal plane. However, GO Figure ZnO NRs thin film (Fig. 3 (a)) possesses similar nature of D and G along with three Raman shifts at ~331.4, ~437, and ~587 cm^{-1} . The strong Raman shift at ~437 cm^{-1} is assigned to E_2 mode of ZnO E_2 mode of ZnO crystal, which is consistent with Raman peak of bulk ZnO crystals. The two small peaks at ~331 cm^{-1} and ~587

cm^{-1} are designated to the second order Raman spectrum arising from zone-boundary phonons $3E_{2H}-E_{2L}$ for wurtzite hexagonal ZnO single crystals and E_1 (LO) mode of ZnO associated with oxygen deficiency in ZnO nanomaterials respectively. It is estimated that the I_D/I_G of GO thin film is 0.848 which significantly decreases to 0.601 for GO-ZnO NRs thin film. It suggests that most of the oxygenated groups on the carbon basal plane in GO thin film might interact with surface hydroxyl groups of ZnO NRs.

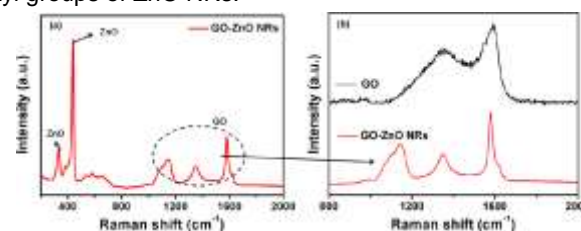


Fig. 3. Raman spectra of (a) GO-ZnO NRs thin film and (b) a part of Raman spectra of GO-ZnO NRs and GO-FTO thin film in the range of 1000–2000 cm^{-1} .

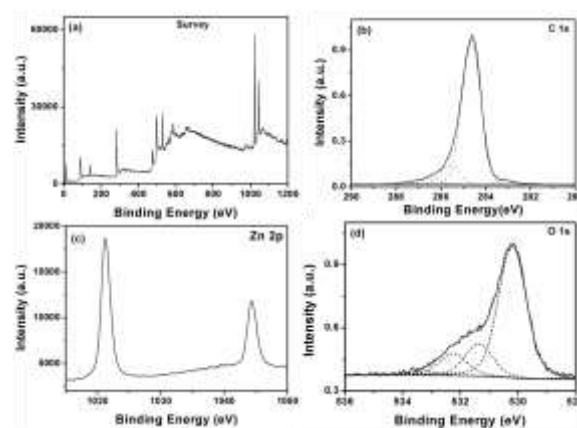


Fig. 4. XPS spectra of (a) survey, (b) C 1s, (c) Zn 2p and (d) O 1s of GO-ZnO NRs thin film.

The survey spectrum (Fig. 4(a)) shows the peaks of C 1s, Zn 2p, and O 1s for the GO-ZnO NRs. The deconvoluted C1s XPS spectra of the GO-ZnO NRs are comprised of five peaks, as depicted in Fig. 4(b). The binding energies at ~285.3 eV is assigned to C-C and C=C/C-H bonds. Other binding energies at ~286.3 eV, ~287.2 eV and ~288.2 eV represent the C-OH, C=O and -O-C=O bonds respectively [6]. The appearance of binding energy at ~283.7 eV might arise from the C-O-M bond [7], suggesting the formation of bond between C and Zn in the GO-ZnO. In Fig. 4(c), two binding energies peaks at ~1021 eV and ~1044 eV are observed in the Zn 2p XPS spectra, corresponding to the Zn 2p_{3/2} and Zn 2p_{1/2} respectively. The binding energies are slightly lower than the binding energies of the Zn 2p core level of bulk ZnO (~1022 eV and ~1046 eV) [8], which reveals the interaction between GO and ZnO NRs. Fig. 4(d) displays the four deconvoluted peaks at ~530.2 eV, ~531.4 eV, ~532.2 eV and weak peak at ~533.4 eV. The main binding energy peak at ~530.2 eV is attributed to the O ion of ZnO lattice, however other two peaks at ~531.4 eV and ~532.2 eV are associated to the surface oxygenated species such as C-O or O-H and the adsorbed H₂O respectively. The appearance of C-O bond again confirms the

interaction between GO and ZnO NRs. Thus, the grown ZnO NRs are significantly attached on the GO layer via the bonding between GO and ZnO.

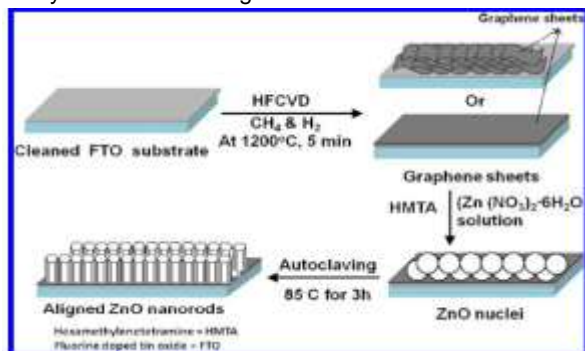


Fig. 5. Possible growth mechanism of GO-ZnO NRs thin film.

The schematic illustration defines the growth of vertically aligned ZnO NRs on the GO-FTO substrate. The adsorbed Zn^{2+} ions provide the spherical ZnO nuclei with the reaction of OH⁻ ions. Zn atoms of ZnO nuclei might create the bonding between O atoms of the functional groups on GO layer via a covalent coordination bond, which might act as the nucleation center for the growth of ZnO crystals. At the elevated temperature with prolonged time, the ZnO nuclei become larger along the planes and the edges to originate the hexagonal structure on the GO-FTO substrate. Moreover, likewise the seeded FTO substrates, the GO layer might decrease the surface energy between ZnO nuclei and FTO substrate, which simplifies the growth pathway for the upstanding or upwards structures. Thus, the highly dense vertically aligned ZnO NRs are formed on the surface of the GO-FTO substrates.

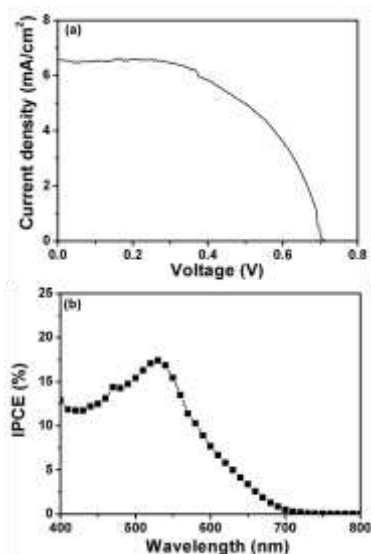


Fig.6. (a) J-V curve and (b) IPCE curve of the DSSCs fabricated with GO-ZnO NRs thin film photoanode

Fig. 6(a) shows the current density–voltage (J–V) characteristics of DSSCs fabricated with GO-ZnO NRs photoanode under 100 mW cm^{-2} light intensity (1.5AM). DSSC fabricated with GO-ZnO NRs thin film photoanode the conversion efficiency have significantly improved than the other reported DSSCs, fabricated with aligned ZnO NRs photoanodes grown by the solution methods. The better photovoltaic properties might associate with the highly dense uniform aligned nanorods, existence of GO layer and the increased optical properties, which collectively results to the high absorption of dye and light harvesting efficiency. Additionally, the contact area between GO layer and ZnO NRs might provide larger surface area of $29.4 \text{ m}^2 \text{ g}^{-1}$ for absorbing dye molecules and make a better pathway for the fast electron transfer. Thus, the improved photovoltaic properties of DSSC with GO-ZnO NRs photoanode is attributed to sufficiently high surface area, dye absorption and light harvesting efficiency. It is studied that ZnO photoanodes with aligned morphology like NRs, NTs arrays increases the charge collection and transfer properties. DSSC fabricated with GO-ZnO NRs photoanode shows a maximum IPCE value of $\sim 17.8\%$ at the absorption wavelength of $\sim 530 \text{ nm}$, shown in Fig. 6(b). As discussed above, the presence of GO layer has significantly enhanced the surface area of GO-ZnO NRs photoanode and dye absorption through the good interfacial contact between GO-ZnO layer and FTO layer, resulting in the reasonably high IPCE. Thus, the enhanced IPCE of GO-ZnO NRs photoanode based DSSC are resulted from the high J_{sc} , V_{oc} , and the improved photovoltaic performances.

CONCLUSION

The vertically aligned ZnO NRs are grown on HFCVD deposited GO-FTO substrates by the low temperature hydrothermal method and applied as photoanode for the fabrication of efficient DSSCs. The uniform vertically aligned ZnO NRs on GO-FTO substrates are highly crystalline with typical wurtzite hexagonal crystal structure. By the structural, surface and optical studies, a partial hydrogen bonding between surface functional groups of GO and ZnO NRs confirms the role of GO layer in the formation of aligned ZnO NRs. A solar-to-electricity conversion efficiency of $\sim 2.5\%$ with J_{sc} of $\sim 6.56 \text{ mAcm}^{-2}$, V_{oc} of $\sim 0.71 \text{ V}$ and FF of ~ 0.54 are achieved by DSSC fabricated with GO-ZnO NRs thin film photoanode. The presence of GO on FTO substrate substantially increases the surface area of GO-ZnO photoanode, which tends to high dye loading as well as high light harvesting efficiency and thus, results to the increased photocurrent density and the performance of DSSCs.

References

- (1) Lu, T.; Zhang, Y.; Li, H.; Pan, L.; Li, Y.; Sun, Z. *Electrochim. Acta* 2010, 55, 4170–4173.
- (2) (8) Zhang, Q. F.; Chou, T. P.; Russo, B.; Jenekhe, S. A.; Cao, G. Z. *Angew. Chem., Int. Ed.* 2008, 47, 2402–2406.

- (3) Hsu, Y. F.; Xi, Y. Y.; Yip, C. T.; Djurisi, A. B.; Chan, W. K. J. Appl.Phys. 2008, 10, 083114–083117.
- (4) Galoppini, E.; Rochford, J.; Chen, H.; Lu, G. Y.; Hagfeldt, A.; Boschloo, G. J. Phys. Chem. B 2006, 110, 16159–16161.
- (5) Y. F.; Gao, M.; Nagai, T. C.; Chang, J. J Shyue,. Cryst. Growth.Des. 2007, 7, 2467–2471.
- (6) S. Yumitori, J. Mater. Sci. 2000, 35(1), 139-146.
- (7) D.; Fu, G.; Han, Y.; Chang, J. Dong, Mater. Chem.Phys. 2012,132, 673-681.
- (8) S.; Ameen, M. S.; Akhtar, Y.S.; Kim, O. B.; Yang, H. S. Shin, Microchim. Acta 2011, 172, 471-478.