

Templated Electrochemical Synthesis of Polyaniline/ZnO Coaxial Nanowires with Enhanced Photoluminescence

Neelam Saurakhiya,[†] Satinder K. Sharma,^{*,‡} Rudra Kumar, and Ashutosh Sharma*

Department of Chemical Engineering, Indian Institute of Technology Kanpur (IITK), Kanpur, Uttar Pradesh, India 208016

ABSTRACT: We demonstrate a simple and cost-effective synthesis of an organic (polyaniline, PANI)/inorganic (zinc oxide, ZnO) one-dimensional coaxial nanowire (1D-CNW) array directly on a conducting substrate by (1) electrochemical deposition of aniline and its polymerization to PANI on the pore walls of a track-etched polycarbonate membrane and (2) subsequent electrodeposition of ZnO in the core of hollow PANI nanowires (NWs). The surface morphology and heterojunction formation in 1D-CNWs at the interface of PANI (shell)/ZnO (core) are analyzed by field-emission scanning electron microscopy and transmission electron microscopy (TEM). The diameter and length of 1D-CNWs are in the ranges of 50–200 nm and 3–5 μ m, respectively. In addition, the single-crystalline nature of ZnO (inorganic core)/polycrystalline PANI (organic shell) and atomic composition of the inorganic/organic heterojunction are determined by selected-area electron diffraction and TEM-energydispersive X-ray spectroscopy, respectively. Amperometric analysis is used to explain the growth mechanism for formation of the core and shell in 1D-CNWs. Photoluminescence (PL) is found to be significantly larger by a factor \sim 3 in the case of PANI/ZnO 1D-CNWs compared to that of ZnO NWs. A model for PANI (shell)/ZnO (core) coaxial 1D-CNWs is also proposed based on heterojunction arrangement to explain the PL enhancement by generation of hole and electron pairs together with minimization of recombination losses upon UV illumination. Subsequently, it also explains the progression of conduction of a free electron all the way through to the polymeric sequence of PANI to get an amplified photocurrent to engender PL enhancement in the visible region.

1. INTRODUCTION

Devices based on nanosized hybrid materials have been extensively investigated as an alternative to most viable preference of thick silicon (Si) for applications in optoelectronics and photovoltaics (PVs) with the aim of exploring and improving the device performance.¹⁻³ Additionally, onedimensional (1D) nanostructure geometry is most attractive because of the tunable large surface-to-volume ratio including significantly affected charge-transport carriers compared to very thick Si layer used for conventional PV devices,⁴⁻⁶ and so it is advantageous to use the core/shell heterojunctions that utilize the quantum-mechanical nature of the electron transport through the radial structures.^{7,8} The other alternatives have been demonstrated by the coupling of inorganic and organic materials to form the heterojunctions composed of p-type donor polymers and n-type acceptor inorganic materials including semiconductors, metals, oxides, and polymers.9-14 Polyaniline (PANI) is generally considered to be one of the most promising p-type organic conducting polymers (CPs) owing to its tunable high conductivity, good processability, and environmental stability useful for the development of PV devices.^{15,16} The synthesis of 1D nanostructures of the CPs in the pores of a template has been the focus of some recent studies^{17,18} Zinc oxide (ZnO) is one of the most suitable photoluminscent inorganic material among the available metal oxides having characteristics of n-type semiconductors¹⁹ with a wide band gap $E_g \sim 3.37$ eV at 300 K. This is also an alternative material to integrating and replacing conventional Si-based PV devices.²⁰ Sharma et al.^{21,22} demonstrated the preparation of 1D nanostructures of ZnO in the form of nanowires (NWs) by using a track-etched membrane of polycarbonate as a template.

During the past few years, the template-assisted growth of ZnO nanostructures has been extensively investigated.^{23,24}

Wang et al.²⁵ have reported the interfacial effect of a PANI/c-Si heterojunction, which depends greatly on the conductivity of the PANI and therefore affects the photoemission capability. Xi et al.²⁶ synthesized the PANI/CdS coaxial nanocables and investigated the charge-transfer mechanism of the nanocables, where the enhanced photoluminescence (PL) property was observed by using PANI as a shell. Similarly, the monolayer of PANI was successfully used by Zhang and co-workers²⁷ for enhancement of the photoactivity for a ZnO catalyst by suppressing the photocorrosion effect of PV devices.

Zheng et al.²⁸ synthesized the ZnO/PANI coaxial nanowires (CNWs) through the dipping of an anodic aluminum oxide (AAO) membrane in a ZnO colloidal solution, which already holds the PANI nanotubules as the template, and reported a very significantly enhanced PL of CNWs without removal of the sacrificial AAO membrane. Thus, this enhancement is more likely due to retention of the AAO membrane rather than the coaxial nature of the NWs. This correlates with an observation of Li et al.,²⁹ who reported PL analysis of AAO membranes with different pore sizes from 7 to 60 nm, which showed blue shifts of visible emission and enhancement of PL with decreasing membrane pore size. A similar trend of the blue

Special Issue: Ganapati D. Yadav Festschrift

Received:	March 7, 2014
Revised:	May 12, 2014
Accepted:	May 13, 2014
Published:	May 27, 2014



Figure 1. Schematic illustration for the synthesis of PANI/ZnO 1D-CNWs via an electrochemical deposition method.

shift of visible emission is also stated by Zheng et al.²⁸ from ZnO/PANI CNWs embedded in AAO membrane nanopores.

Mridha and Basak³⁰ also demonstrated the photodiode characteristics of a heterojunnction of PANI/ZnO and concluded that the resulting hybrid material exhibited a better performance for harvesting light. More recently, Xia et al.³¹ demonstrated a better performance from $Co_3O_4/PANI$ and $TiO_2/PANI$ core/shell nanostructures for electrochromic and electrochemical energy storage applications.

All of these examples emphasize interest in forming the heterojunctions composed of organic and inorganic 1D nanostructures with the improved efficiency for future PV and optoelectronic devices. In this context, one of the major challenges in PV device fabrication using 1D nanostructures of inorganic/organic hybrid materials is to innovate the synthesis and fabrication methods that are adaptable to material choice and offer control over structural and dimensional flexibility.^{32–34} Thus, the growth of a 1D heterojunction directly from a substrate ensures intimate adhesion and better current conduction. It is still a challenge to fabricate 1D organic/inorganic heterojunctions directly from a substrate with control of the morphology, function diversity, and small diffusion lengths, allowing fast electric/optical transport kinetics and fast switching speeds in nanodevices.

We demonstrate a simple and cost-effective technique to fabricate one-dimensional CNWs (1D-CNWs) of PANI/ZnO via electrodeposition and electropolymerization of aniline into PANI and subsequent electrodeposition of ZnO, both within the pores of a polycarbonate track-etched membrane, one face of which is made conductive by deposition of a metal. One of the advantages of this technique is the growth of the heterostructure directly from the electrode, thus ensuring good adhesion, minimal contact resistance, and elimination of the need for transfer of the arrays to an electrode after synthesis. Characterization by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) coupled with electron diffraction (EDX) confirmed heterojunction formation as well as its compositions. These organic/inorganic, PANI (shell)/ZnO (core), 1D-CNW heterojunctions exhibit greatly enhanced PL in ultraviolet and visible illumination compared to the pure ZnO NWs.

Moreover, the fabrication technique allows tuning of the size and composition of the core/shell (ZnO/PANI) 1D-CNWs, which indicates potential applications in the nanoenabled PVs requiring enhanced efficiencies for a broad solar-light spectrum.

2. MATERIALS AND METHODS

2.1. Synthesis of a CP Shell. The synthetic procedure is schematically illustrated in Figure 1. As the first step, one side of the polycarbonate membrane template (Watman) was subjected to gold (Au) sputtering for a Au layer thickness of about 60 nm. The Au-coated side serves as an electrode, which was then placed onto a commercially available copper (Cu) substrate, which acts as a working electrode in a three-electrode electrochemical cell. The working electrode assembly was then placed inside the electrochemical cell. The electrolyte solution of aniline monomer (>99.5% from Fluka) was prepared by dissolving it in deionized water (Milli-Q ~18 MQ·cm) and shaking vigorously for around 3 min with the help of a magnetic stirrer to produce a homogeneous 0.3 M aniline solution. H_2SO_4 (3 M; Fisher Scientific) was then added to this solution in order to obtain the actual electrolyte solution with pH < 1. The resulting solution was then left for around 4–6 h at room temperature to achieve a stabilized pH.

To begin with the electrochemical polymerization of aniline, the electrolyte solution of 0.3 M aniline monomer (pH < 1) was then poured into an electrochemical cell containing the working electrode assembly along with two other reference (Ag/AgCl in a saturated KCl salt bridge) and counter (platinum) electrodes. Polymerization was carried out by a potentiostat/galvanostat (Auto Lab PGSTAT model 302) at a fixed applied oxidation potential of ~0.9 V at temperatures of 35-40 °C for 1-2 h.

2.2. Synthesis of a ZnO Core. After completion of the aniline deposition and PANI polymerization process on the pore walls, the polycarbonate membrane was immediately lifted and placed on another Cu substrate, which is used again as a working electrode for subsequent deposition of the ZnO core within the synthesized PANI shells (tubes), as shown in Figure 1. After drying for 24 h under normal environmental conditions, the new working electrode was again placed inside the electrochemical cell. This time, the aqueous solution of

 $Zn(NO_3)_2$ · GH_2O was used for electrodeposition of the ZnO core at a fixed applied potential of -1.2 V for a longer period of time than that of the shell (PANI). The detailed experimental procedure for deposition of the ZnO core is given in the previous work from our group.²¹ The ZnO core deposition time varied from 1 to 3 h in order to achieve vertical dimensions (lengths) similar to those of the PANI shell to slightly extend the ZnO core. Finally, an optional removal of the polycarbonate membrane could be carried out by using a chloroform solution after completion of the deposition process.

2.3. Characterization. To characterize the samples, we employed field-emission scanning electron microscopy (FESEM; Ziess supra-40), TEM (TECNAI T20 UTWIN, 200 kV), and energy-dispersive X-ray spectroscopy (EDAX). The room temperature PL data were also collected by using a xenon lamp with an excitation wavelength of 330 nm.

3. RESULTS AND DISCUSSION

3.1. Amperometric Analysis for the Growth Mechanism. Core/shell hybrid nanostructures of ZnO/PANI were synthesized by an electrochemical deposition technique using chronoamperometry (deposition at a constant potential). Figure 2 describes the typical amperometric (current vs time)



Figure 2. Amperometric (I-t) analysis for synthesis of PANI shells within a Au-coated polycarbonate membrane and deposition of ZnO cores within PANI shells.

curve obtained during PANI shell formation within the pores of the Au-coated polycarbonate membrane and the amperometric (current vs time) curve for the later deposition of the ZnO core within the conducting PANI shell. It is clear that the already deposited PANI shell (p-type) acts as a template for growth of the ZnO core (n-type), which leads to the creation of heterojunctions. The other experimental parameters were carefully controlled and kept constant, except the deposition time in both cases. In order to understand the deposition mechanism, the current was recorded as a function of time. Typically, we can delineate the deposition process into three different zones. Figure 2 shows the current-time (I-t)characteristics recorded during the entire process at a fixed applied potential of 0.9 V for growth of the PANI shells. In the beginning of the polymerization process of the PANI shell, no external voltage is applied for 15 s until the open-circuit voltage between the cathode and anode is stabilized. The optimized potential is then applied, and the current exhibits a sharp increase in region I that is ascribed to fast charge-transport kinetics in the electrical double layer. Following this, the

reduction of aniline ions located immediately at the cathode surface occurs, which creates a concentration gradient that causes a flux of polymerized aniline ions toward the cathode. After this stage, a decrease in the current indicates the formation of a diffusion layer onto the surface of Au-coated pores of the membrane followed by growth of the PANI shells along the walls of the pores. Next, the sudden drop in the current from 1200 to 1300 s could be associated with growth of the open-ended conical-shaped shells around the inner surfaces of the pores. This variation might be due to the concentration gradient of the deposited Au thin film onto the pore walls, which decreases from the bottom to the top, as seen from the schematic representation in Figure 2. After this region, the current remains nearly constant in region II from 1300 to 1600 s, which is associated with the smooth growth of the PANI shells. After this region, PANI shell formation and elongation is initiated toward the other end opening of the pore, which could result in increased current from transition region II to III owing to the broadening of the shell diameter because of the larger available surface area for growth within the pore. Similarly, the growth of core ZnO NWs within the PANI shells at a fixed reduction potential of -1.2 V is followed by a chronoamperometry technique, as shown in Figure 2. The slight enhancement in the current in region I at the beginning of the ZnO core deposition process indicates the filling up of the PANI shells with a higher rate. The steady variation in the current between 75 and 230 s reveals that the PANI shells do not have a uniform surface area, but rather the area varies from the bottom to the top. When all of the PANI shells are completely filled with ZnO core, the extended part of the ZnO core starts to deposit by crystallization of ZnO over the top surface of the ZnO core in the PANI/ZnO 1D-CNWs with a gradual increase in the current. Therefore, in this particular process, the rate of filling the pores is found to be saturated from transition region II to III. This is also attributed to the number of reducible Zn²⁺ ions present in the zinc nitrate electrolyte, ³⁵ which are sufficient for the fast kinetics of filling within the PANI shells, thus providing control over the aspect ratio of core/shell (ZnO/ PANI) 1D NWs. In this context, Izaki and Omi presented an analogous reduction in the deposition rate of the ZnO film with the reduction potential.³⁶ The current is saturated after 1600 and 450 s, at applied potentials of +0.9 and -1.2 V for PANI (shell) and ZnO (core), respectively, as shown in Figure 2. This saturated current behavior reflects the uniform subsequent growth of PANI shells and the ZnO core during synthesis of a 1D-CNW array. However, in addition to this, there is a combined effect of the deposition potential, diffusion of reacting species, and pore-filling rate that could also affect the dimensions and morphology of grown PANI/ZnO heterojunctions.

3.2. Morphological and Structural Properties of PANI/ ZnO 1D-CNWs. Parts a–i of Figure 3 illustrate the SEM images of the bare polycarbonate membranes of pore sizes 15 and 100 nm as well as PANI/ZnO 1D-CNWs grown through the pores. More specifically, the clear difference of the pore size and distribution of two kinds of polycarbonate membranes was observed through the SEM images in Figure 3a,d.

The vertically aligned 1D-CNWs were grown within the cylindrical pores of the membrane; they collapsed after removal of the polycarbonate membrane template. Although the membrane was carefully removed by using a chloroform solution, randomly oriented 1D-CNWs were obtained on the substrate, as observed in Figure 3b,e. Therefore, the height of



Figure 3. SEM images (a and d) of a polycarbonate membrane with pore sizes 15 and 100 nm, respectively, (b and e) of synthesized PANI/ZnO 1D-CNWs within the pores of the membranes after membrane removal, (c) at high magnification of CNWs within 15 nm pores, and (f and g) of an isolated CNW and its magnified image, and (h and i) clear images of the heterojunction formation between PANI/ZnO.

the PANI shell and ZnO core can be tailored with control over the electrodeposition time. The heterojunction formation of p-PANI and n-ZnO is clearly visible by careful inspection of the SEM images, as illustrated in Figure 3f–i. The PANI shell and an extended ZnO core provide a contrast for comparison. The observed height of these coaxial 1D nanostructures was ~3–5 μ m, whereas the diameter was in the range of 50–200 nm, allowing easy collapse after membrane removal. It was also understandable that the presence of H₂SO₄ in an electrolyte solution for the electropolymerization process of the PANI shell broadens the membrane pores, which is reflected in the slightly larger diameter of 1D-CNWs than that of the template pores.

Further, transmission electron microscopy (TEM) studies were performed to investigate the 1D-CNWs of PANI/ZnO in greater detail, and the results are shown in Figure 4a-f. The figure exhibits the clearly detectable inorganic, ZnO core (with darker contrast), and organic, PANI shell (with lighter contrast), in TEM images and eventually verifies growth of the core/shell and heterojunction formations, as seen previously in SEM analysis. Parts a and b of Figure 4 are also in agreement with the growth mechanism explained in section 3.1 for the open-ended conical-shaped shells and the thickness variation from the bottom to the top (the schematic representation in Figure 2). From these images, the thickness variation of the PANI shell is approximately in the range of 5-25 nm (Figure 4c,f). The diameter of the ZnO core also varied along the length in conjunction with the thickness of the PANI shell, which is clear from Figure 4c,e,f. A high-magnification TEM image of 1D-CNWs is shown in Figure 5a. The selectedarea electron diffraction (SAED) pattern taken from the top portion of 1D-CNWs, as shown in Figure 5b, revealed the polycrystalline nature of PANI/ZnO (organic/inorganic) hybrid CNWs. Similarly, the SAED pattern (Figure 5f) of an area where the PANI layer was almost absent (Figure 5e) showed more single-crystalline nature of the ZnO core



Figure 4. TEM analysis of synthesized CNWs through the pores (size $\sim 100 \text{ nm}$) of the template: (a) image showing the upper portion of a CNW with the thickness variation of the PANI shell onto the ZnO core; (b) image of the lower portion of the same coaxial NW; (c) HRTEM image of the same; (d) image of a bunch of CNWs; (e) magnified image of another CNW; (f) magnified image of one more CNW clearly showing the thickness variation as well as a very thin shell of PANI along the length.



Figure 5. (a) Magnified images and SAED patterns of CNWs with a clearly visible thin layer of PANI. (b) Diffraction pattern of the same showing the polycrystalline nature of the wires. (c and d) Magnified images of the same. (e) Another CNW with an almost extremely thin invisible layer of PANI. (f) Diffraction pattern showing a shift toward single-crystalline nature because of the higher percentage of the ZnO core exposed as a result of the extremely thin layer of PANI. (g) TEM–EDAX of a CNW synthesized through the pores of the template (pore size ~15 nm) at point P, where only the ZnO core appeared as a dominant part. (h) EDX for the area A, where both the PANI shell and ZnO core are exposed to the TEM beam.

Article

Industrial & Engineering Chemistry Research

surrounded by PANI, which makes the resulting 1D-CNWs polycrystalline. Likewise, the existence of core/shell materials and their proportion were also detected by TEM–EDAX investigation, as shown in Figure 5g,h. Figure 5g shows a higher percentage of zinc when the measurement was done at point P, whereas the detected percentage was significantly lower when the area A was examined by the TEM beam, as shown in Figure 5h. The different percentages of elemental composition are also in excellent agreement toward the presence of the PANI shell onto the ZnO core.

3.3. PL Spectral Response. Figure 6 shows the room temperature PL spectra at an excitation wavelength of 330 nm



Figure 6. (a and b) Room temperature PL spectra collected with a xenon lamp under an excitation wavelength of 330 nm of the cluster of ZnO NWs of smaller diameter onto the Cu substrate and PANI/ZnO 1D-CNWs grown onto the Cu substrate after removal of the polycarbonate template. (c and d) SEM images of the respective samples. (e) Spectra of the ZnO core. (f) Spectra of the randomly mixed ZnO core with PANI. (g) Spectra of PANI.

along with the SEM images of the smaller-diameter ZnO NW pristine cluster²¹ and PANI/ZnO organic/inorganic heterojunction 1D-CNWs grown on a Cu substrate. The strong dominant UV emission is evident, whereas a weak green emission band is also observed for all cases including the ZnO NW cluster as well as PANI/ZnO 1D-CNWs. The signature of the peaks in the visible range starting from 400 nm and at \sim 468 and 513 nm shows the significant response. It is probably due to the defect state luminescence.37 The PL spectra of PANI/ ZnO 1D-CNWs exhibit enhancement in the overall intensity in conjunction with the green band intensity related to the adsorbed oxygen at the defect sites. ZnO has numerous merits, but a fundamental hindrance in its utilization for solar cell applications is the fast recombination of charge carriers, which offers very poor response to visible light.^{38,39} On the other hand, the CP PANI has unique properties such as it can be excited by UV as well as visible light. It has also been observed that the presence of conjugated π -bonding coordination in PANI facilitates the transportation of photogenerated electrons and holes. Thus, the assorted hybrid forms of ZnO and PANI nanostructures must have excellent illumination in the UV and visible regions.^{27,40,41} Additionally, the PL properties of electrochemically deposited ZnO nanostructures are also dependent on its diameter.⁴² Therefore, the PL results indicate that the overall PL intensity of the ZnO/PANI core/shell CNW hybrid system is enhanced by a factor of ~3 compared to the pristine cluster of ZnO NWs, as depicted in the visible

spectral region 400–600 nm. This significant increase in the intensity could be primarily attributed to two occurrences: (1) the charge-transfer mechanism of very thin conducting shells of PANI onto the surfaces of ZnO; (2) defect state luminescence correlated with the oxygen vacancies at the interface of 1D-CNWs. However, it is reported that PANI does not show strong emission in the visible spectral region.²⁶ Hence, the PL spectra of the hybrid 1D-CNW system shown here might be due to the interaction between the NH group of PANI (organic) and Zn²⁺ of ZnO (inorganic) heterojunction and the presence of interfacial defects. These defects can act as adsorption sites for the physisorption of oxygen molecules. As shown in Figure 6, the peaks around 468 and 513 nm could be due to defect state luminescence and correlated with the oxygen vacancies at the interface of 1D-CNWs.^{43,29}

Parts e–g of Figure 6 show the PL spectra of the ZnO core, its random mixture with PANI, and PANI nanostructures, respectively. The emission intensity of the ZnO core is higher than that of the randomly mixed PANI and ZnO core. The resultant spectra show a dominant UV peak at \sim 373 nm associated with exciton emission, whereas the broad visible emission starting from 400 nm originates from the electron– hole recombination, which is most likely attributed to the oxygen vacancies or zinc interstitial defects.

Our observations of the 1D-CNW morphology indicate the presence of excess defects and increased adsorption sites for oxygen molecules on the interface of 1D-CNWs. The increased emission intensity for 1D-CNWs in the visible region starting from 400 nm has intense peaks in the visible region attributed to excess defects at the interface in 1D-CNWs.

TEM analysis in Figure 5d,c revealed the existence of a large number of variety of defect sites at the surface of ZnO and the interface of 1D-CNW heterojunctions as well. The defects can act as adsorption sites to physically adsorb oxygen molecules that undergo reduction. The reduction of oxygen molecules $[O_2(m)]$ converts them into oxygen ions $[O_2^-(ion)]$ by accepting the free electrons (e⁻) available in the conduction band (CB) of the ZnO core.^{44,45} The reactions are i and ii:

$$O_2(m) + e^- = O_2^-(ion)$$
 (i)

$$O_2^{-}(ion) + h^+ = O_2(m)$$
 (ii)

Afterward, these generated O_2^- are recombined with the holes (h^+) generated via illumination. The photogenerated holes (h^+) at the junction drift to the surface of the ZnO core and interact with the negatively charged surfaces, as indicated in eq ii.

This results in enhanced conductivity because of variation in the number density of excited unpaired electrons. The conducting shell of PANI also promotes a high rate of diffusion and collection of e^-h^+ pairs through the NH groups of the polymeric chain. Therefore, the enhanced PL intensity is likely to originate from the efficient bond formation between the imine group of PANI and the hydroxyl group of ZnO. Similarly, the demonstrated enhancement of photoactivity could also be a consequence of absorbed photons (h⁺) and emitted photogenerated electrons (e⁻) in the 1D-CNW system. In fact, these photogenerated electrons (e⁻) of ZnO do not have to travel a long distance and transferred to the nano interfacial layer of PANI. In other words, this greatly enhances the efficiency caused by the nanoscale diffusion paths and extremely large carrier collection due to the low-dimensional structures (Figure 7a).



Figure 7. (a) Mechanism of additional negative charge in 1D-CNWs. (b) Energy band diagrams for the proposed model of the 1D-CNW heterojunction system at thermal equilibrium. Direction of transfer of charge carriers (c) upon visible illumination and (d) upon UV illumination.

In addition to the above mechanisms, we discuss another model⁴⁶⁻⁴⁸ to describe the improved photoconductivity in 1D-CNWs, as shown in Figure 7. Figure 7b represents the energy band diagram for the proposed model of the ZnO/PANI heterojunction system at thermal equilibrium and in the dark without photoexcitation. Amplification in the case of the ultraviolet (UV)-light illumination photogeneration activity is primarily due to the high efficiency of charge separation in ZnO/PANI heterojunction diode arrangement and smaller band gap.49 Parts c and d of Figure 7 represent the band diagram in the visible and UV regions, respectively. In the UV region, as shown in Figure 7d, the valence band position of ZnO is lower than the highest occupied molecular orbital of PANI, so the latter could serve as an acceptor for the photogenerated h⁺, and therefore the recombination of e⁻ and h^+ is greatly suppressed, leading to a higher photocurrent activity of 1D-CNWs.^{49,50} Similarly, in the visible region, the position of the CB in ZnO is lower than the lowest unoccupied molecular orbital of PANI,^{49,51} implying that the PANI layer absorbs visible light to stimulate electrons to the excited state, and therefore the photoexcited electrons freely transfer to the CB of ZnO. This could influence the photogenerated current, as indicated in Figure 7c, and subsequently will enhance photogeneration even in the visible region.

Hence, the resulting ZnO/PANI coaxial heterojunction could be an alternative nanoscale architecture for its use in future solar cell applications with higher photocurrent due to reduction in the number density of photogenerated electron– hole pair recombination. It is anticipated that these ZnO/PANI coaxial heterojunctions will enable us to design highly efficient, stable, and UV-to-visible-light-driven solar energy harvesting devices.

4. CONCLUSIONS

We describe a new method of synthesis of PANI/ZnO 1D-CNWs by an electrodeposition approach within the pores of a track-etched polycarbonate membrane as the template, one side of which is made conductive by metal deposition. Aniline deposition and polymerization to PANI on the pore walls are followed by ZnO deposition in the core. An advantage of the method is the formation of NW arrays directly on the electrode, thus promoting good adhesion and contact. This approach is simple and cost-effective in producing radial heterojunctions at nanoscale with enhanced PL properties. The coating of UVand visible-light-responsive PANI exhibited a huge increase of in the photocurrent. The core/shell architecture with radial heterojunction geometry should thus find applications in PV and optoelectronic structures.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: satinder@iitmandi.ac.in.

*E-mail: ashutos@iitk.ac.in.

Present Addresses

[†]N.S.: Rajiv Gandhi Institute of Petroleum Technology, Raebareli, India 229316.

*S.K.S.: School of Computing and Electrical Engineering, Indian Institute of Technology Mandi, Himanchal Pradesh, India 175001.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for support from the Department of Science and Technology, New Delhi, India, to the Center of Nanosciences at IITK. We thank Sri Sivakumar (IITK) for help with the PL measurements reported. We are very happy to be a part of the Ganapati D. Yadav Festschrift honoring his multifaceted contributions.

REFERENCES

(1) Bourdo, S. E.; Saini, V.; Piron, J.; Al-Brahim, I.; Boyer, C.; Rioux, J.; Bairi, V.; Biris, A. S.; Viswanathan, T. Photovoltaic Device Performance of Single-Walled Carbon Nanotube and Polyaniline Films on n-Si: Device Structure Analysis. *ACS Appl. Mater. Interfaces* **2012**, *4*, 363–368.

(2) Guo, Y.; Zhang, Y.; Liu, H.; Lai, S.-W.; Li, Y.; Li, Y.; Hu, W.; Wang, S.; Che, C.-M.; Zhu, D. Assembled Organic/Inorganic p-n Junction Interface and Photovoltaic Cell on a Single Nanowire. *J. Phys. Chem. Lett.* **2010**, *1*, 327–330.

(3) Acharya, K. P.; Hewa-Kasakarage, N. N.; Alabi, T. R.; Nemitz, I.; Khon, E.; Ullrich, B.; Anzenbacher, P.; Zamkov, M. Synthesis of PbS/ TiO₂ Colloidal Heterostructures for Photovoltaic Applications. *J. Phys. Chem. C* **2009**, *114*, 12496–12504.

(4) Garnett, E. C.; Yang, P. Silicon Nanowire Radial p-n Junction Solar Cells. J. Am. Chem. Soc. 2008, 130, 9224–9225.

(5) Tian, B.; Zheng, X.; Kempa, T. J.; Fang, Y.; Yu, N.; Yu, G.; Huang, J.; Lieber, C. M. Coaxial silicon nanowires as solar cells and nanoelectronic power sources. *Nature* **2007**, *449*, 885–890.

(6) Kelzenberg, M. D.; Turner-Evans, D. B.; Kayes, B. M.; Filler, M. A.; Putnam, M. C.; Lewis, N. S.; Atwater, H. A. Photovoltaic Measurements in Single-Nanowire Silicon Solar Cells. *Nano Lett.* **2008**, *8*, 710–714.

(7) Kayes, B. M.; Atwater, H. A. Comparison of the device physics principles of planar and radial p-n junction nanorod solar cells. *J. Appl. Phys.* **2005**, *97*, 114302.

(8) Chuang, C.-H.; Doane, T. L.; Lo, S. S.; Scholes, G. D.; Burda, C. Measuring Electron and Hole Transfer in Core/Shell Nanoheteros-tructures. *ACS Nano* **2011**, *5*, 6016–6024.

(9) Zhang, F.; Liu, D.; Zhang, Y.; Wei, H.; Song, T.; Sun, B. Methyl/ Allyl Monolayer on Silicon: Efficient Surface Passivation for Silicon-Conjugated Polymer Hybrid Solar Cell. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4678–4684.

(10) Peng, K.-Q.; Wang, X.; Li, L.; Wu, X.-L.; Lee, S.-T. High-Performance Silicon Nanohole Solar Cells. J. Am. Chem. Soc. 2010, 132, 6872–6873.

(11) Wang, G.; Chu, S.; Zhan, N.; Lin, Y.; Chernyak, L.; Liu, J. ZnO homojunction photodiodes based on Sb-doped p-type nanowire array

and n-type film for ultraviolet detection. Appl. Phys. Lett. 2011, 98, 041107.

(12) Tang, Y. B.; Chen, Z. H.; Song, H. S.; Lee, C. S.; Cong, H. T.; Cheng, H. M.; Zhang, W. J.; Bello, I.; Lee, S. T. Vertically Aligned p-Type Single-Crystalline GaN Nanorod Arrays on n-Type Si for Heterojunction Photovoltaic Cells. *Nano Lett.* **2008**, *8*, 4191–4195.

(13) Czaban, J. A.; Thompson, D. A.; LaPierre, R. R. GaAs Core-Shell Nanowires for Photovoltaic Applications. *Nano Lett.* 2009, 9, 148–154.

(14) Wang, W.; Schiff, E. A. Polyaniline on crystalline silicon heterojunction solar cells. *Appl. Phys. Lett.* **2007**, *91*, 133504.

(15) Wang, W.; Schiff, E.; Wang, Q. Amorphous silicon/polyaniline heterojunction solar cells: Fermi levels and open-circuit voltages. *J. Non-Cryst. Solids* **2008**, 354, 2862–2865.

(16) Tan, S.; Zhai, J.; Xue, B.; Wan, M.; Meng, Q.; Li, Y.; Jiang, L.; Zhu, D. Property Influence of Polyanilines on Photovoltaic Behaviors of Dye-Sensitized Solar Cells. *Langmuir* **2004**, *20*, 2934–2937.

(17) Tran, B. H. D.; Li, D.; Kaner, R. B. One-Dimensional Conducting Polymer Nanostructures: Bulk Synthesis and Applications. *Adv. Mater.* **2009**, *21*, 1487–1499.

(18) Park, D. H.; Kim, B. H.; Jang, M. G.; Bae, K. Y.; Joo, J. Characteristics and photoluminescence of nanotubes and nanowires of poly.3-methylthiophene. *Appl. Phys. Lett.* **2005**, *86*, 113116.

(19) Mridha, S.; Basak, D. Ultraviolet and visible photoresponse properties of *n*-ZnO/*p*-Si Heterojunction. *J. Appl. Phys.* **2007**, *101*, 083102.

(20) Takanezawa, K.; Hirota, K.; Wei, Q.-S.; Tajima, K.; Hashimoto, K. Efficient Charge Collection with ZnO Nanorod Array in Hybrid Photovoltaic Devices. J. Phys. Chem. C 2007, 111, 7218–7223.

(21) Sharma, S. K.; Rammohan, A.; Sharma, A. Templated one step electrodeposition of high aspect ratio n-type ZnO nanowire arrays. *J. Colloid Interface Sci.* **2010**, *344*, 1–9.

(22) Sharma, S. K.; Saurakhiya, N.; Barthwal, S.; Kumar, R.; Sharma, A. Tuning of structural, optical, and magnetic properties of ultrathin and thin ZnO nanowire arrays for nano device applications. *Nanoscale Res. Lett.* **2014**, *9*, 122.

(23) Kumar, N.; Srivastava, A. K.; Nath, R.; Gupta, B. K.; Varma, G. D. Probing the highly efficient room temperature ammonia gas sensing properties of a luminescent ZnO nanowire array prepared *via* an AAO-assisted template route. *Dalton Trans.* **2014**, *43*, 5713–5720.

(24) Ottone, C.; Bejtka, K.; Chiodoni, A.; Farías, V.; Roppolo, I.; Canavese, G.; Stassi, S.; Cauda, V. Comprehensive study of the templating effect on the ZnO nanostructure formation within porous hard membranes. *New J. Chem.* **2014**, *38*, 2058–2065.

(25) Wang, W.; Schiff, E.; Wang, Q. Amorphous silicon/polyaniline heterojunction solar cells: Fermi levels and open-circuit voltages. *J. Non-Cryst. Solids* **2008**, 354, 2862–2865.

(26) Xi, Y.; Zhou, J.; Guo, H.; Cai, C.; Lin, Z. Enhanced photoluminescence in core-sheath CdS-PANI coaxial nanocables: A charge transfer mechanism. *Chem. Phys. Lett.* **2005**, *412*, 60–64.

(27) Zhang, H.; Zong, R.; Zhu, Y. Photocorrosion Inhibition and Photoactivity Enhancement for Zinc Oxide via Hybridization with Monolayer Polyaniline. J. Phys. Chem. C 2009, 113, 4605–4611.

(28) Zheng, Z. X.; Xi, Y. Y.; Dong, P.; Huang, H. G.; Zhou, J. Z.; Wu, L. L.; Lin, Z. H. The enhanced photoluminescence of zinc oxide and polyaniline coaxial nanowire arrays in anodic oxide aluminium membranes. *Phys. Chem. Commun.* **2002**, *5*, 63–65.

(29) Li, G. H.; Zhang, Y.; Wu, Y. C.; Zhang, L. D. Photoluminescence of anodic alumina membranes: pore size dependence. *Appl. Phys. A: Mater. Sci. Process.* **2005**, *81*, 627–629.

(30) Mridha, S.; Basak, D. ZnO/polyaniline based inorganic/organic hybrid structure: Electrical and photoconductivity properties. *Appl. Phys. Lett.* **2008**, *92*, 142111.

(31) Xia, X.; Chao, D.; Qi, X.; Xiong, Q.; Zhang, Y.; Tu, J.; Zhang, H.; Fan, H. J. Controllable Growth of Conducting Polymers Shell for Constructing High-Quality Organic/Inorganic Core/Shell Nanostructures and Their Optical–Electrochemical Properties. *Nano Lett.* **2013**, 13, 4562–4568.

(32) Wu, S.; Tai, Q.; Yan, F. Hybrid Photovoltaic Devices Based on Poly(3-hexylthiophene) and Ordered Electrospun ZnO Nanofibers. *J. Phys. Chem. C* 2010, *114*, 6197–6200.

(33) Briseno, A. L.; Holcombe, T. W.; Boukai, A. I.; Garnett, E. C.; Shelton, S. W.; Frechet, J. J. M.; Yang, P. Oligo- and Polythiophene/ ZnO Hybrid Nanowire Solar Cells. *Nano Lett.* **2010**, *10*, 334–340.

(34) Liu, J.; Wang, S.; Bian, Z.; Shan, M.; Huang, C. Organic/ inorganic hybrid solar cells with vertically oriented ZnO nanowires. *Appl. Phys. Lett.* **2009**, *94*, 173107.

(35) Elias, J.; Zaera-Tena, R.; Lévy-Clément, C. Electrochemical deposition of ZnO nanowire arrays with tailored dimensions. *J. Electroanal. Chem.* **2008**, *621*, 171–77.

(36) Izaki, M.; Omi, T. Transparent zinc oxide films prepared by electrochemical reaction. *Appl. Phys. Lett.* **1996**, *68*, 2439.

(37) Jiang, P.; Zhou, J.-J.; Fang, H.-F.; Wang, C.-Y.; Wang, Z. L.; Xie, S.-S. Hierarchical Shelled ZnO Structures Made of Bunched Nanowire Arrays. *Adv. Funct. Mater.* **2007**, *17*, 1303–1310.

(38) Fox, M. A.; Dulay, M. T. Heterogeneous Photocatalysis. *Chem. Rev.* **1993**, *93*, 341–357.

(39) Jongh, D. P. E.; Meulenkamp, E. A.; Vanmaekelbergh, D.; Kelly, J. J. Charge Carrier Dynamics in Illuminated, Particulate ZnO Electrodes. J. Phys. Chem. B 2000, 104, 7686–7693.

(40) Gospodinova, N.; Terlemezyan, L. Conducting Polymers Prepared by Oxidative Polymerization: Polyaniline. *Prog. Polym. Sci.* **1998**, 23, 1443–1484.

(41) Kang, E. T.; Neoha, K. G.; Tanh, K. L. Polyaniline: A polymer with many interesting intrinsic redox states. *Prog. Polym. Sci.* **1998**, *23*, 211–324.

(42) Yang, P.; Yan, H.; Mao, S.; Russo, R.; Johnson, J.; Saykally, R.; Morris, N.; Pham, J.; He, R.; Choi, H. J. Controlled Growth of ZnO Nanowires and Their Optical Properties. *Adv. Funct. Mater.* **2002**, *12* (5), 323–331.

(43) Wu, X. L. Photoluminescence and cathodoluminescence studies of stoichiometric and oxygen-deficient ZnO films. *Appl. Phys. Lett.* **2001**, 78 (16), 2285–2287.

(44) Lao, C. S.; Park, M. C.; Kuang, Q.; Deng, Y. L.; Sood, A. K.; Polla, D. L.; Wang, Z. L. Giant Enhancement in UV Response of ZnO Nanobelts by Polymer Surface Functionalization. *J. Am. Chem. Soc.* **2007**, *129*, 12096–12097.

(45) Li, Y.; Valle, F. D.; Simonnet, M.; Yamada, I.; Delaunay, J.-J. Competitive surface effects of oxygen and water on UV photoresponse of ZnO nanowires. *Appl. Phys. Lett.* **2009**, *94*, 023110.

(46) Liao, Z. M.; Hou, C.; Zhou, Y. B.; Xu, J.; Zhang, J. M.; Yu, D. P. Influence of temperature and illumination on surface barrier of individual ZnO nanowires. *J. Chem. Phys.* **2009**, *130*, 084708.

(47) Park, W.; Jo, G.; Hong, W.-K.; Yoon, J.; Choe, M.; Lee, S.; Ji, Y.; Kim, G.; Kahng, Y. H.; Lee, K.; Wang, D.; Lee, T. Enhancement in the photodetection of ZnO nanowires by introducing surface-roughnessinduced traps. *Nanotechnology* **2011**, *22*, 205204.

(48) He, Y.; Wang, J. A.; Zhang, W.; Song, J.; Pei, C.; Chen, X. ZnOnanowires/PANI inorganic/organic heterostructure light-emitting diode. *J. Nanosci. Nanotechnol.* **2010**, *10* (11), 7254–7.

(49) Li, Y.; Gong, J.; McCune, M.; Hea, G.; Deng, Y. I-V characteristics of the p-n junction between vertically aligned ZnO nanorods and polyaniline thin film. *Synth. Met.* **2010**, *160*, 499–503.

(50) Soci, C.; Zhang, A.; Xiang, B.; Dayeh, S. A.; Aplin, D. P. R.; Park, J.; Bao, X. Y.; Lo, Y. H.; Wang, D. ZnO Nanowire UV Photodetectors with High Internal Gain. *Nano Lett.* **2007**, *7*, 1003– 1009.

(51) An, W.; Wu, X.; Zeng, X. C. Adsorption of O_2 , H_2 , CO, NH₃, and NO₂ on ZnO Nanotube: A Density Functional Theory Study. *J. Phys. Chem. C* **2008**, *112*, 5747–5755.