

Synthesis and Electrical Properties of TiO₂ Nanoparticles Embedded in Polyamide-6 Nanofibers Via Electrospinning

R. Nirmala¹, Jin Won Jeong^{2,3}, R. Navamathavan⁴, Hak Yong Kim^{2,3,*}

(Received 17 March 2011; accepted 3 May 2011; published online 13 May 2011.)

Abstract: We report on the synthesis and characterizations of TiO₂ nanoparticles embedded in polyamide-6 composite nanofibers by using electrospinning technique. The influence of substrate on the electrical characteristics of polyamide-6/TiO₂ composite nanofibers was investigated. The resultant nanofibers exhibit good incorporation of TiO₂ nanoparticles. The doping of TiO₂ nanoparticles into the polyamide-6 nanofibers were confirmed by high resolution transmission electron microscopy and energy dispersive X-ray spectroscopy. Photoluminescence (PL) and cathodoluminescence (CL) spectroscopy were also used to characterize the samples. The PL and CL spectra reveal that the as-spun polyamide-6/TiO₂ composite nanofibers consisted of overlapping of two broad emission bands due to the contribution of polyamide-6 (centered at about 475 nm), which might originate from organic functional groups of polyamide-6 and TiO₂ nanoparticles (centered around 550 nm). The electrical conductivity of the polyamide-6/TiO₂ composite nanofibers on different substrates was carried out. It was found that the electrical conductivity of the polyamide-6/TiO₂ composite nanofibers on silicon substrate was in the range of 1~3 μ A, and about 1 to 20 pA for the paper and glass substrates.

Keywords: Electrospinning; Polyamide-6; Nanoparticles; Nanofibers; Electrical studies

Citation: R. Nirmala, Jin Won Jeong, R. Navamathavan and Hak Yong Kim, "Synthesis and Electrical Properties of TiO₂ Nanoparticles Embedded in Polyamide-6 Nanofibers Via Electrospinning", Nano-Micro Lett. 3 (1), 56-61 (2011). <http://dx.doi.org/10.3786/nml.v3i1.p56-61>

In recent years, much attention has been paid to the preparation of one-dimensional (1D) nanomaterials, such as nanofibers, nanowires, nanorods, nanotubes, and nanobelts, which exhibit novel physical and chemical properties due to their unique characteristics for huge ratio of diameter to length, superior mechanical toughness, and so on [1-6]. Polymer based devices have attracted considerable attention in the fields of flexible functional and large-area electronics. Recently, many methods have been utilized to prepare 1D nanomaterials which includes chemical or physical vapor deposition, arc discharge, laser ablation, vapor-

phase transport process, and a template-based method [7-12]. Among the various methods, electrospinning is simple, effective, and cost-effective approach for generating long fibers with diameters ranging from tens of nanometers up to micrometers. In the fabrication of polymer electronics, recent research has intensively focused on the electrospinning method as a unique way of synthesizing polymer nanofibers [13,14].

Nanofiber structures are investigated for their electrical properties and device characterizations. The electrical conductance is a fundamental property encountered in every study of electrical transport phenom-

¹Bio-nano System Engineering, Chonbuk National University, Jeonju, 561-756, South Korea

²Department of Organic Materials and Fiber Engineering, Chonbuk National University, Jeonju, 561-756, South Korea

³Center for Healthcare Technology & Development, Chonbuk National University, Jeonju, 561-756, South Korea

⁴School of Advanced Materials Engineering, Chonbuk National University, Jeonju 561-756, South Korea

*Corresponding author. Tel.: +82-63-270-2351; fax: +82-63-270-4249. E-mail: khy@jbnu.ac.kr (HakYong Kim).

ena in nanostructured materials. Polymer nanofibers can be more readily applicable if their electrical conductivities were enhanced. A semiconducting polymer, such as polyamide-6, decorated with metallic conducting nanoparticles furnishes an interesting system with the prospect of designing device functionality directly into the material. The electrical conductivities of polyamide-6 nanofibers can be significantly improved by adding metal nanoparticles with high conductivities. The electrical property is known to influence the characteristics of the device and its stability under an electric field. Therefore, research activities have thus been intensified on tailoring the electrical property of non-conducting polymer composites by adding with electrically active materials. In our previous report, we have investigated the electrical properties of polyamide-6/chitosan blended nanofibers [15]. Polymers and their composites have been used as sensing materials to detect targeted gases based on various sensing techniques [16,17]. However, the electrical properties of these polyamide-6/TiO₂ composite nanofibers have not been reported so far. Therefore, we have carried out the detailed electrical characterization of these composite polyamide-6 nanofibers.

In this study, the effect of substrate type on the electrical properties of embedding of TiO₂ nanoparticles in polyamide-6 nanofibers has been investigated. We analyzed detailed electrical characteristics of these composite nanofibers as-spun on various substrates such as Si, paper and glass. The morphological, luminescence and electrical characteristics of the as-spun polyamide-6 composite nanofibers were investigated.

Polyamide-6 (KN120 grade, Kolon Industries, South Korea) and TiO₂ nanoparticles (Aeroxide P25, 80% anatase 20% rutile, average particle size of 21 nm and specific surface area of 50±15 m²g⁻¹, Sigma-Aldrich Inc.) were used in making the polymer solution. The nanofibers were produced by dissolving polyamide-6 pellets in 85% formic acid (analytical grade, Showa, Japan). After that the polymer solution was loaded into a 5 ml plastic syringe equipped with a polystyrene micro-tip (0.3 mm inner diameter and 10 mm length), which was connected with a high-voltage power supply (CPS-60 K02V1, Chungpa EMT, South Korea). Electrospinning was performed at a voltage of about 22 kV. A grounded iron drum was rotated at a constant speed by a DC motor to collect the developing nanofibers on the silicon, paper and glass substrates, which were kept at a distance of 15 cm from the micro-tip. All experiments were conducted at room temperature.

The phase and crystallinity of TiO₂ nanoparticles were characterized using a Rigaku X-ray diffractometer (XRD, Rigaku Co., Japan) with Cu K α ($\lambda=1.54056$ Å) radiation over a range of 2θ angles from 20° to 80°. The morphology of the as-spun polyamide-6 nanofibers was observed by using scanning electron microscopy

(SEM, Hitachi S-7400, Hitachi, Japan) and high resolution transmission electron microscopy (HR-TEM, JEM-2010, JEOL, Japan). To confirm the embedding of nanoparticles, the chemical composition of the as-spun nanofiber mats were analyzed by energy dispersive X-ray (EDX) spectrometer attached with HR-TEM. The optical property of polyamide-6/TiO₂ composite nanofibers was characterized by photoluminescence (PL) analysis using a 325 nm He-Cd laser and a cathodoluminescence (CL) attached to the field emission scanning electron microscopy (FE-SEM) system. Then the current-voltage (I-V) characteristic was measured for the ultrafine polyamide-6 nanofibers by using a semiconductor parameter analyzer (4200-SCS, Keithley). I-V characteristic measurement was performed: a bundle of nanofibers (with thickness of approximately few mm and a length of few μ m) composed of polyamide-6/TiO₂ was glued to metal contacts. The electrode was made by using silver paste glue which ensured a perfect electrical contact between the metal and the fibers. In the experiments an increasing DC voltage was applied from -20 to 20 V to the metal contacts. The current flowing through the bundle was measured as a function of the applied voltage.

Figure 1 shows XRD pattern of the TiO₂ nanoparticles. The anatase reflections are dominating in the reflection patterns and rutile is also present. As shown in the XRD data, the results affirm formation of the anatase, the existence of strong diffraction peaks at 2θ values of 25.25°, 37.80°, 38.50°, 48.05°, 53.9°, 55.05°, 62.65°, 68.85°, 70.30°, 75.05° and 76.10° corresponding to the crystal planes (101), (004), (112), (200), (105), (211), (204), (116), (220), (215) and (301), respectively, indicating the formation of the anatase (JCPDS card no 21-1272). And diffraction peaks at 2θ values of 36.00° can be well indexed to (101) reflection of rutile phase (JCPDS card no 21-1276). The average crystal size is estimated by the Scherrer's formula [18]. The average crystal sizes are calculated to be of 20 nm.

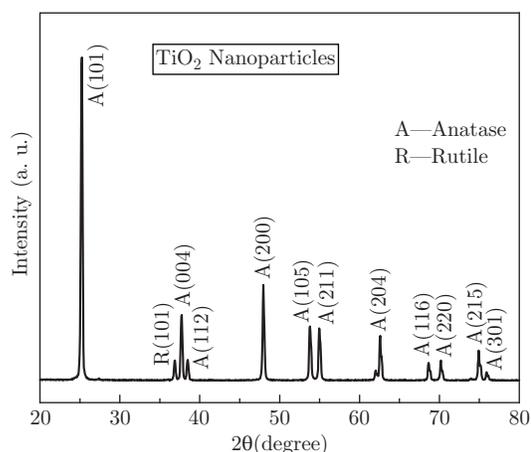


Fig. 1 XRD pattern of the TiO₂ nanoparticles.

Figure 2 shows the typical SEM image of polyamide-6/TiO₂ composite nanofibers. This image shows the composite nanofibers exhibited smooth surface and bead-free uniform diameters along their lengths. On the other hand, the incorporation of TiO₂ nanoparticles can be seen in the SEM images as shown in Fig. 2. The resultant composite nanofibers diameters were observed to be in the range of 100 to 150 nm.

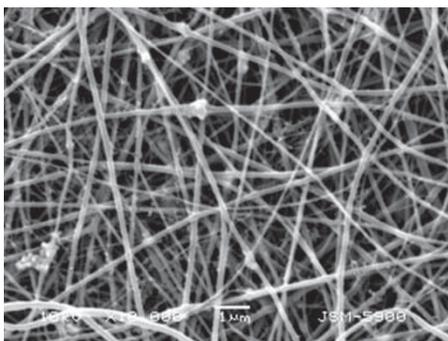


Fig. 2 SEM image of electrospun polyamide-6/TiO₂ composite nanofibers.

In order to confirm the embedding of the nanoparticles into the nanofibers, we further performed HR-TEM analysis. Figure 3 shows the HR-TEM images of electrospun polyamide-6 composite nanofibers. The HR-TEM samples were obtained by placing the TEM grid very closely to the syringe micro-tip end for very short time during electrospinning. The as-spun polyamide-6 nanofibers with the incorporation of TiO₂ nanoparticles in polyamide-6 nanofibers are clearly visible, as shown in Fig. 3(a). The crystal orientation in polyamide-6 nanofibers was further investigated by using selected area electron diffraction (SAED) pattern. Figure 3(b) presents a typical SAED pattern for a polymorphous phase, which shows that the TiO₂ nanoparticles blended in polyamide-6 nanofibers are of polymorphous nature. This consists of a series of fairly dotted concentric rings, which indicates that polyamide-6/TiO₂ composite nanofibers contained a polycrystalline phase. From this result, it can be concluded that the polyamide-6/TiO₂ composite nanofibers contains both amorphous and polycrystalline phases.

The chemical composition of the as-spun nanofiber mats were analyzed by EDX spectrometer attached with TEM. Figure 4(a) and 4(b) shows the EDX spectrum of the polyamide-6/TiO₂ composite nanofibers. As shown in Fig. 4(b), the signals of oxygen and Ti were clearly observed for the composite nanofibers. The successful embedding of nanoparticles into polyamide-6 nanofibers was confirmed by the EDX spectrum.

The luminescence properties of polyamide-6/TiO₂ are useful in understanding the physics of nanostructures and their potential applications in various fields. PL and CL spectra can also be used in order to study

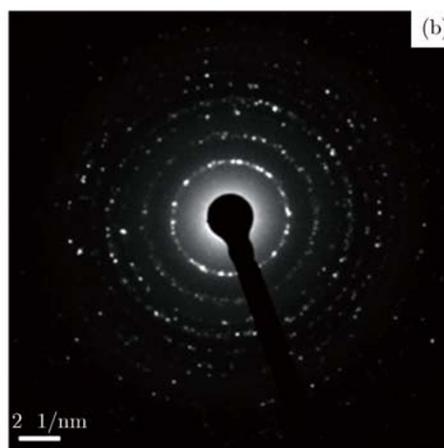
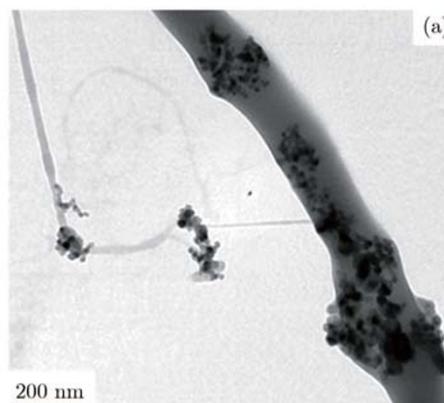


Fig. 3 HR-TEM image of electrospun polyamide-6/TiO₂ composite nanofibers and (b) its SAED pattern.

the polyamide-6/TiO₂ composite nanofibers energy levels and to provide information about the surface oxygen vacancies and defects based on the electronic structure and optical characteristics. Figure 5(a) shows the room-temperature PL spectrum of the electrospun polyamide-6/TiO₂ composite nanofibers. The PL spectrum of polyamide-6/TiO₂ is dominated by the broad band emission in the range of 350~600 nm with a maximum of about 475 nm. A broad green photoluminescence peak in the visible range centered at about 550 nm was only detected in polyamide-6/TiO₂ composite nanofibers and could be attributed to the radiative recombination of self-trapped excitons localized within the surface defects of polyamide-6/TiO₂ composite nanofibers [19,20]. The broad band emission from the PL spectrum at room temperature indicates that the polyamide-6/TiO₂ nanofibers have good luminescence quality. The CL spectrum of electrospun polyamide-6/TiO₂ composite nanofibers was further investigated. The representative CL spectrum of electrospun polyamide-6/TiO₂ composite nanofibers is shown in Fig. 5(b), which has identical shape as the PL emission spectrum. The CL spectrum of the as spun polyamide-6/TiO₂ composite nanofibers shows an overlapping of two broad emission bands due to the con-

tribution of polyamide-6 (centered at about 475 nm), which might originate from organic functional groups of polyamide-6 and TiO₂ nanoparticles (centered around 550 nm).

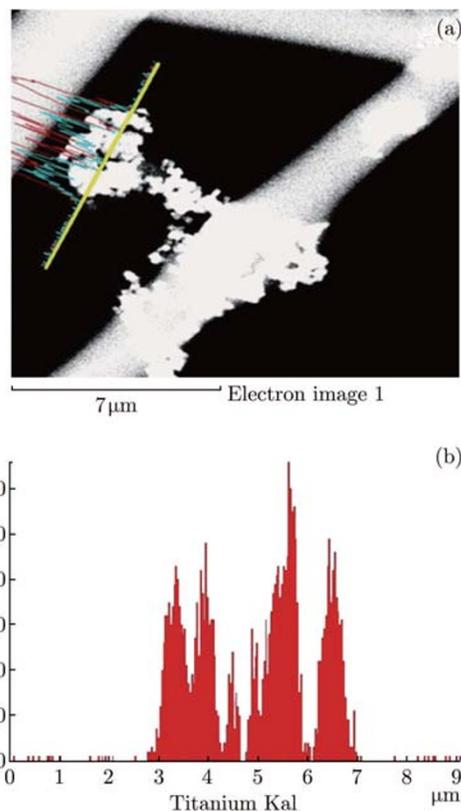


Fig. 4 (a) TEM-EDX spectrum of polyamide-6/TiO₂ composite nanofibers, showing the presence of Ti in the composite nanofibers (b).

Figures 6~8 show the electrical properties of the electrospun polyamide-6/TiO₂ composite nanofibers on silicon, paper and glass substrates, respectively. I-V dependence is typical for a metal-polymer-metal configuration, i.e., it is formed by the characteristics of two point-to-point contacts. The first evidence is the ohmic behavior of the composite nanofibers was due to the I-V curves being linear. Figure 6 shows the I-V characteristics of electrospun polyamide-6/TiO₂ composite nanofibers on silicon substrate for the applied bias voltage in the range between -20 and 20 V. The surface potential of the embedded nanoparticles were directly attributed to the enhanced electrical conduction in which field induced polarization was occurred due to applied bias voltage. The electrical conductivity of the polyamide-6/TiO₂ composite nanofibers on silicon substrate was of the order of 1~3 μA. However, this phenomenon may be attributed to the related contacts

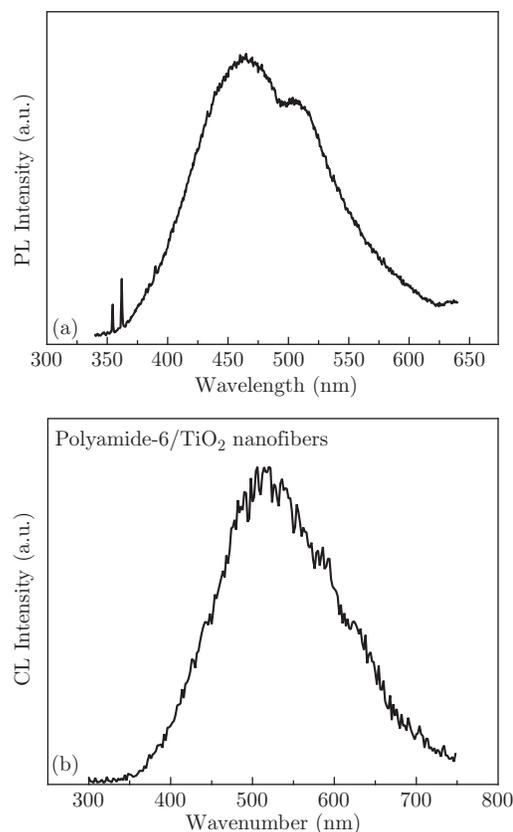


Fig. 5 (a) PL and (b) CL spectrum of electrospun polyamide-6/TiO₂ composite nanofibers.

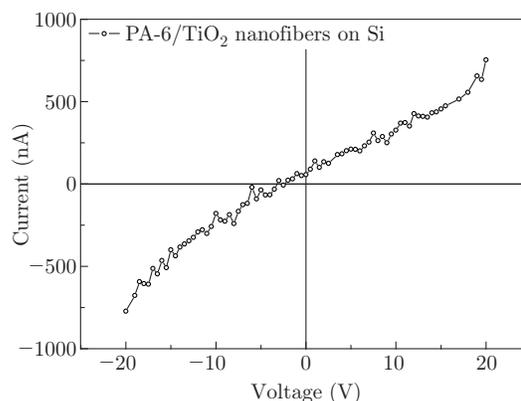


Fig. 6 I-V characteristics of electrospun polyamide-6/TiO₂ composite nanofibers on silicon substrate.

between the composite nanofibers, Ag electrodes, and Si substrate. Actually, we believe that the use of Si substrate when measuring the I-V properties of semiconductor nanostructures or polymers, the current may be leaking into the substrate. In order to understand the electrical transport of polyamide-6/TiO₂ composite nanofibers in a better way, we performed I-V characteristics on paper and glass substrates. The conductivity of the composite nanofibers on the paper and glass substrates were determined to be in the range of 1 to 20 pA as shown in Figs. 7 and 8. The conductivity of the

composite nanofibers was increased by about 6 orders of magnitude when compared to that of the paper and glass substrates. These observations indicate that the electrical conductivity of the polyamide-6/TiO₂ composite nanofibers can be significantly enhanced with the use of silicon substrates. The conductance measured on polyamide-6/TiO₂ composite nanofibers over different substrates was significantly affected. At the same time, we should also consider the electrical leakage occurred through the substrate when Si substrates were utilized [21,22]. In addition, in order to obtain good electrical characteristics with high stability, we should be further improved the interface and electrode contacts, which would extend the possibilities of high quality performance as per the device applications are concerned. In addition, we plan to optimize the experimental parameters so as to improve the electrical characteristics for device fabrication.

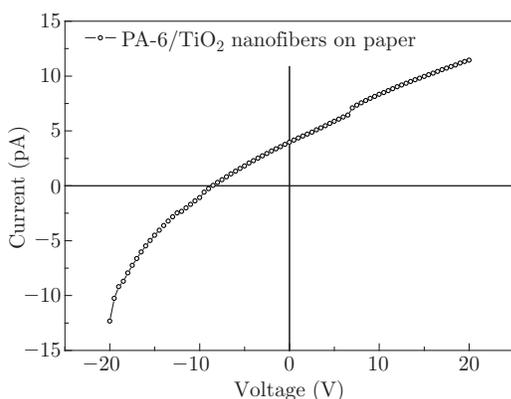


Fig. 7 I-V characteristics of electrospun polyamide-6/TiO₂ composite nanofibers on paper substrate.

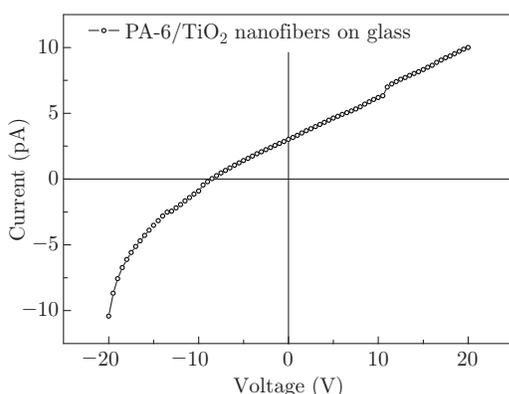


Fig. 8 I-V characteristics of electrospun polyamide-6/TiO₂ composite nanofibers on glass substrate.

On the basis of our experimental analysis, we conclude that the substrate play a significant role on the electrical properties of polyamide-6/TiO₂ composite nanofibers. It is worth noting that the improvement of electrical properties by addition of nanoparticles in

the polyamide-6 nanofibers is of key significance for the nano-device fabrication.

In summary, the electrical characteristics of polyamide-6 nanofibers embedded with TiO₂ nanoparticles via electrospinning process have been investigated. The as-spun nanofibers were observed to be of smooth with uniform diameters along their lengths. The resultant composite nanofibers diameters were in the range of 100 to 150 nm. The electrospinning process could be used to prepare polyamide-6/TiO₂ composite nanofibers with a well-defined morphology. The incorporation of TiO₂ nanoparticles into the polyamide-6 nanofibers were confirmed by HR-TEM and EDX analysis. The electrical characterization of the polyamide-6/TiO₂ composite nanofibers showed a pure resistive behavior of the conductive nanofibers and a good stability of the as-spun nanostructures. The significantly enhanced electrical properties of these polyamide-6 composite nanofibers can be utilized for promising nanotechnological applications. This observation will continue to drive researchers toward developing future organic based nano-devices.

Acknowledgements

This work was supported by a grant from the Korean Ministry of Education, Science and Technology (The Regional Core Research Program/Center for Healthcare Technology & Development, Chonbuk National University, Jeonju 561-756 Republic of Korea).

References

- [1] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo and P. D. Yang, *Science* 292, 1897 (2001). <http://dx.doi.org/10.1126/science.1060367>
- [2] W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science* 295, 2425 (2002). <http://dx.doi.org/10.1126/science.1069156>
- [3] R. Ramaseshan, S. Sundararajan and R. Jose, *J. Appl. Phys.* 102, 111101 (2007). <http://dx.doi.org/10.1063/1.2815499>
- [4] Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science* 291, 1947 (2001). <http://dx.doi.org/10.1126/science.1058120>
- [5] K. Tsukagoshi, B. W. Alphenaar and H. Ago, *Nature* 401, 572 (1999). <http://dx.doi.org/10.1038/44108>
- [6] D. F. Zhang, L. D. Sun, C. J. Jia, Z. G. Yan, L. P. You and C. H. Yan, *J. Am. Chem. Soc.* 127, 13492 (2005). <http://dx.doi.org/10.1021/ja054771k>
- [7] H. Zhang, H. W. Song and H. Q. Yu, *J. Phys. Chem. C* 111, 6524 (2007). <http://dx.doi.org/10.1021/jp0684123>

- [8] H. Zhang, H. W. Song and H. Q. Yu, *Appl. Phys. Lett.* 90, 103103 (2007). <http://dx.doi.org/10.1063/1.2711380>
- [9] Y. C. Choi, W. S. Kim, Y. S. Park, S. M. Lee, D. J. Bae, Y. H. Lee, G. S. Park, W. B. Choi and N. S. Lee, J. M. Kim, *Adv. Mater.* 12, 746 (2000). [http://dx.doi.org/10.1002/\(SICI\)1521-4095\(200005\)12:10\\$<\\$746::AID-ADMA746\\$>\\$3.0.CO;2-N](http://dx.doi.org/10.1002/(SICI)1521-4095(200005)12:10$<$746::AID-ADMA746$>$3.0.CO;2-N)
- [10] X. F. Duan and C. M. Lieber, *Adv. Mater.* 12, 298 (2000). [http://dx.doi.org/10.1002/\(SICI\)1521-4095\(200002\)12:4\\$<\\$298::AID-ADMA298\\$>\\$3.0.CO;2-Y](http://dx.doi.org/10.1002/(SICI)1521-4095(200002)12:4$<$298::AID-ADMA298$>$3.0.CO;2-Y)
- [11] Y. Wu and P. Yang, *Chem. Mater.* 12, 605 (2000). <http://dx.doi.org/10.1021/cm9907514>
- [12] Y. Li, G. W. Meng, L. D. Zhang and F. Phillip, *Appl. Phys. Lett.* 76, 2011 (2000). <http://dx.doi.org/10.1063/1.126238>
- [13] R. Kessick and G. Tepper, *Appl. Phys. Lett.* 83, 557 (2003). <http://dx.doi.org/10.1063/1.1594283>
- [14] J. Venugopal and S. Ramakrishna, *Appl. Biochem. Biotech.* 125, 147 (2005). <http://dx.doi.org/10.1385/ABAB:125:3:147>
- [15] R. Nirmala, R. Navamathavan, M. H. E. Newehy and H. Y. Kim, *Mater. Lett.* 65, 493 (2011). <http://dx.doi.org/10.1016/j.matlet.2010.10.066>
- [16] B. Ding, M. Wang, J. Yu and G. Sun, *Sensors* 9, 1609 (2003). <http://dx.doi.org/10.3390/s90301609>
- [17] Q. D. Ling, D. J. Liaw, C. Zhu, D. S. H. Chan, E. T. Kang and K. G. Neoh, *Prog. Polym. Sci.* 33, 917 (2008). <http://dx.doi.org/10.1016/j.progpolymsci.2008.08.001>
- [18] J. Ananpattarachai, P. Kajitvichyanukul and S. Seraphin, *J. Hazard. Mater.* 168, 253 (2009). <http://dx.doi.org/10.1016/j.jhazmat.2009.02.036>
- [19] W. F. Zhang, M. S. Zhang, Z. Yin and Q. Chen, *Appl. Phys. B: Lasers Opt.* 70, 261 (2000). <http://dx.doi.org/10.1007/s003400050043>
- [20] J. Liqiang, S. Xiaojun, C. Weimin, X. Zili, D. Yaoguo and F. Honggang, *J. Phys. Chem. Solid* 64, 615 (2003). [http://dx.doi.org/10.1016/S0022-3697\(02\)00362-1](http://dx.doi.org/10.1016/S0022-3697(02)00362-1)
- [21] S. M. Kim, J. W. Son, K. R. Lee, H. Kim, H. R. Kim, H. W. Lee and J. H. Lee, *J. Electroceram.* 24, 153 (2010). [http://dx.doi.org/10.1016/S0022-3697\(02\)00362-1](http://dx.doi.org/10.1016/S0022-3697(02)00362-1)
- [22] A. Cattaneo, L. Pirozzi, B. Morten and M. Prudenziati, *Electrocomponent Sci. Technol.* 6, 247 (1980).