Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 1459−1463
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Photoluminescence of polyethylene oxide−ZnO composite electrospun fibers

Xiaomeng Sui, Changlu Shao, Yichun Liu*

Centre for Advanced Optoelectronic Functional Material Research, Northeast Normal University, Changchun 130024, P.R. China

Received 27 August 2006; received in revised form 17 January 2007; accepted 22 January 2007
Available online 25 January 2007

Abstract

Polyethylene oxide−ZnO (PEO−ZnO) composite fibers were prepared by electrospinning technique. The structural and optical properties were investigated using scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, and photoluminescence (PL). Results indicated that PEO passivated the interface defects and quenched the visible emission of ZnO quantum dots by forming O−Zn bonds with ZnO nanoparticles. To investigate the influence of electrospinning voltage on the PL of the composite fibers, the electrospinning voltage was adjusted from 12 to 18 kV. It was shown that the passivation effect of PEO could be enhanced by increasing the electrospinning voltage, and the fibers prepared at higher voltage exhibited more intense ultraviolet emission.

Keywords: Polyethylene oxide−ZnO; Electrospinning; Photoluminescence

1. Introduction

Being an important semiconductive oxide with a direct wide band gap (3.37 eV) and a large exciton binding energy at room temperature (about 60 meV), ZnO has attracted much attention due to the strong commercial desire for blue and ultraviolet (UV) light emitters and detectors [1], transparent electrodes in solar cells [2], gas sensors [3], and piezoelectric transducers [4]. It is well known that semiconductors with low dimensional size may have superior optical properties to bulk crystals owing to quantum confinement effects. These properties and potential applications have stimulated preparing and researching of well-controlled ZnO nanostructures. As a result, low dimensional ZnO, such as nanorods [5,6], nanowires [7], nanobelts [8], and nanorings [9], have been reported comprehensively.

Comparing to bulk ZnO, nanostructural ZnO exhibits stronger visible luminescence related to surface defects [10]. In the latter, the volume of a thin surface layer hosting the surface states increased relative to the weight of bulk-related volume, thereby increasing the deep-level emission at the expense of the band-edge emission [11]. To realize the application of nanosized ZnO in UV emitters, recently, inorganic materials and polymers such as polyvinyl alcohol, polymethyl methacrylate and polyvinyl pyrrolidone were employed to passivate ZnO nanoparticles [12,13] and suppress the deep-level emission [14], but the resulted materials were confined in zero dimensional structures. The investigation of photoluminescence properties of ZnO containing composites with one dimensional (1D) structure seems to be a great challenge.

Herein, 1D polyethylene oxide−ZnO (PEO−ZnO) fibers with intense UV emission were prepared by electrospinning method, which provides an alternative way to prepare fibers with solid or hollow interiors that are long in length, uniform in diameter, and diversified in composition [15,16]. The as-spun nonwoven mats were formed by the fibers of PEO−ZnO with diameters from 900 to 500 nm, which were controlled by adjusting the electrospinning voltages. Investigation showed the existence of strong interaction between PEO and ZnO, which passivates the visible emission of the latter. An

---

* Corresponding author. Tel.: +86 431 85098803; fax: +86 431 85684009.
E-mail address: ycliu@nenu.edu.cn (Y. Liu).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.01.039

interesting phenomenon was observed in the photoluminescence (PL) spectra of the samples, that is, with increasing the electrospinning voltages, the fibers get thinner, and the PEO–ZnO fibers show more intensive band-edge emission, which is not similar to traditional low dimensional ZnO structures.

2. Experimental details

The preparing process consisted of two steps: (1) preparing a solution of PEO containing ZnO quantum dots, and achieving the right rheology for electrospinning; (2) electrospinning the solution to obtain fibers of PEO–ZnO composite. Firstly, zinc acetate was dissolved in *N*,*N*-dimethylformamide (DMF, 0.5 M). Then tetramethylammonium hydroxide was added droplet to hydrolyze the precursor with a molar ratio of zinc acetate to tetramethylammonium hydroxide 1:1.4, followed by stirring in ice water bath for 1 h. UV–vis absorbance spectra showed that the average radius of the colloids was about 4 nm, according to the relationship between band gap and particle size obtained using the effective mass model for spherical particles with a Coulomb interaction term [17]. ZnO colloids were added to PEO in DMF solution ($M_{\mathrm{n\ PEO}} = 500{,}000$, about 8 wt.%) with a volume ratio of 1:2.5, and a viscous solution of PEO–ZnO composite was obtained. The electrospinning process was similar to our previous work [18,19]. The nonwoven mats composed of PEO–ZnO fibers with diameters ranging from 900 to 500 nm were collected on the grounded plate.

Scanning electron microscopic (SEM) measurement was performed on XL30 ESEM FEG scanning electron microscope of FEI Company with an accelerating voltage of 25 kV. Fourier transform infrared (FT-IR) spectra were obtained on Magna 560 FT-IR spectrometer with a resolution of 1 $\mathrm{cm^{-1}}$. PL was performed on HR-800 LabRam confocal Raman microscope made by JY Company in France, excited by a wavelength of 325 nm line of a continuous He–Cd laser at room temperature.

3. Results and discussion

Fig. 1 shows the SEM micrographs of the PEO–ZnO fibers. The length of each fiber can even reach decimeter grade, and the average diameters are about 900, 800, 650 and 500 nm at voltages of 12, 14, 16 and 18 kV, respectively. When a high voltage is applied, the pendent drop of the PEO–ZnO composite solution at the nozzle of the spinneret will be affected by two competitive forces: the electrostatic force and the surface tension. When the voltage is increased to the threshold value, a droplet of hybrid solution at the tip is deformed into a conical shape known as Taylor cone. In this case, charge or dipole orientation will be formed at the interface between air and the droplet. When the applied electric voltage overcomes the surface tension of the hybrid solution, one or several jets of the solution are ejected from the tip of the Taylor cone and fly towards the grounded plate. This electrified jet then undergoes a stretching and whipping process, leading to the formation of a long and thin thread. With increasing the voltages applied to the solution in a certain range, the electrostatic force (i.e. the extraction force) is larger than the surface tension, and the fibers become thinner when the other parameters remain unchanged.

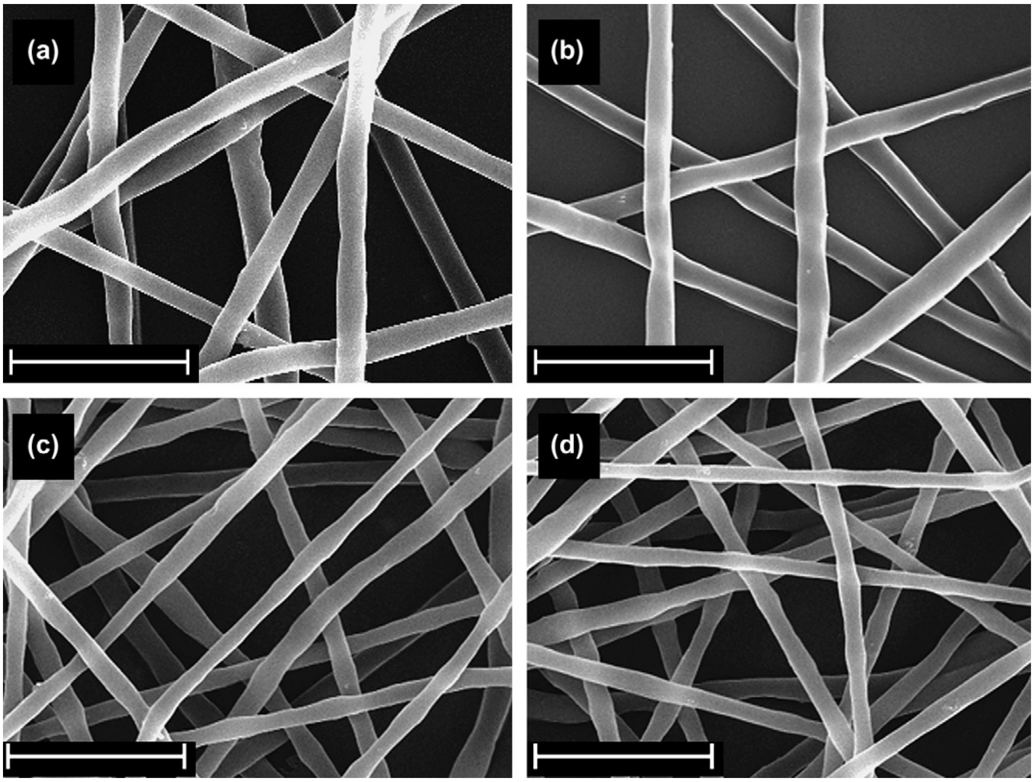
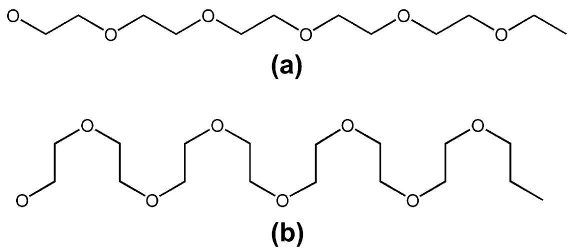


Fig. 1. SEM images of fibers of ZnO–PEO synthesized at voltages of 12 kV (a), 14 kV (b), 16 kV (c) and 18 kV (d). Scale bars are 5 μm.

From the SEM micrographs of all samples we can also observe that the fibers align in random orientation. Electrostatic force associated with Coulomb interactions at different sections of the jet makes it unstable when subjected to bending perturbations [20,21]. This bending instability rearranges the jet into a sequence of connected loops. As the solvent evaporates, the whole group of solidifying loops is pulled towards the grounded plate, where it is deposited and ultimately discharges to form nonwoven mat.

FT-IR measurements on pure PEO powder and electrospun fibers of PEO–ZnO (the electrospinning voltage of 12 kV) were performed, as shown in Fig. 2. For pure PEO (I), the bands at about 1456 and 1350 cm^{-1} are attributed to the vibrations of $-CH_2-$ group, and the bands at about 1100 and 962 cm^{-1} are signed as solid circles for the vibrations of C–O group. In the FT-IR spectrum of PEO–ZnO fibers (II), besides the characteristic vibration bands of PEO, the intense broad band in the vicinity of 460–500 cm^{-1} is assigned to the Zn–O vibration [22]. As known, PEO is one of such polymers with hydrophilic oxygen atom and hydrophobic ethylene group aligned alternatively. PEO exhibits two configurations at different conditions: in nonpolar environment, most of the polar oxygen atoms embedded in the PEO chain, and the PEO molecule shows zigzag configuration (Scheme 1a); while in polar environment such as in DMF, the oxygen atoms extend outside of the PEO molecular chain under strong interactions (e.g. chemical bonds) with other species (including the solvent molecules and other polar molecules) in the solution (Scheme 1b). In the FT-IR spectrum of pure PEO, the intensity of the vibration bands of $-CH_2-$ group is close to that of C–O group, which indicates that the weight of extended oxygen atom is small and the PEO molecule keeps the zigzag configuration. However, for the fibers of PEO–ZnO, the vibration bands of C–O group become sharp and intense, and the intensity of C–O group vibration band gets even stronger than that of $-CH_2-$ group. Notably, red shift of the band located at 1456 cm^{-1} implies the weakening of the C–H bond of $-CH_2-$ group after the introduction of ZnO. These mean that the chemical interactions between ZnO nanoparticles and PEO molecules can affect the chemical environment of PEO. At the same time, ZnO nanoparticles provide polar environment to make the oxygen atoms of the backbone of PEO molecules to stretch out. And the stretching out O atoms can form Zn–O band with surplus Zn atoms and thus modify the surface of ZnO.



Scheme 1. Configurations of PEO molecule in nonpolar (a) and polar conditions (b).

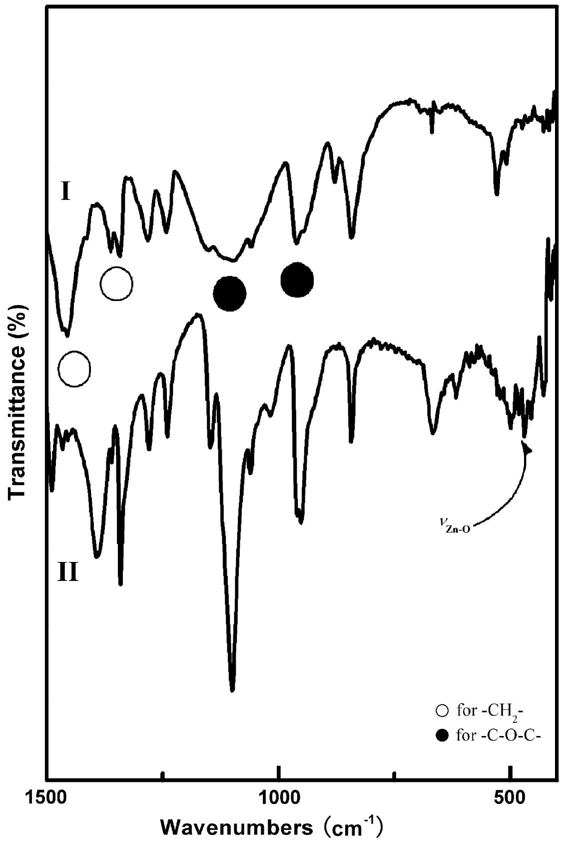


Fig. 2. FT-IR spectra of pure PEO powder (I) and electrospun fibers of ZnO–PEO under voltage of 12 kV (II). The arrow indicated the vibration band of Zn–O.

With the interactions between ZnO and PEO, the existence of PEO may make up for the oxygen vacancy and passivate the surface defects of ZnO nanoparticles, thereafter enhance the UV photoluminescence of ZnO. Fig. 3a shows the PL spectra of PEO–ZnO fibers with electrospinning voltage from 12 to 18 kV. Inset is the PL spectrum of ZnO quantum dots. The UV emission at 3.40 eV which is consisted with the band-edge emission typically originated from the exciton combination of ZnO [23]. The weak and broad green emission at about 2.25 eV is related to the transition between the electron close to the conduction band and the hole at vacancy associated with the surface defects [24,25]. All fiber samples exhibit the characteristic PL spectra of ZnO. These results show that the green PL is associated with the oxygen vacancy on the surface of ZnO nanoparticles. In the PL spectra of all fibers, the UV emission band is significantly enhanced compared to that of ZnO nanoparticles, which demonstrates that PEO has effectively passivated the defects on the surface of ZnO. Besides, the position of the UV emission band does not shift, indicating that size dispersion of the ZnO nanoparticles remains unchanged during the electrospinning process. In PEO molecules, there are oxygen atoms on the backbone, as shown in Scheme 1, which can form Zn–O bonds and fill the oxygen vacancy on the surface of ZnO. These observations suggest that PEO has the effect of removing the shallow surface traps

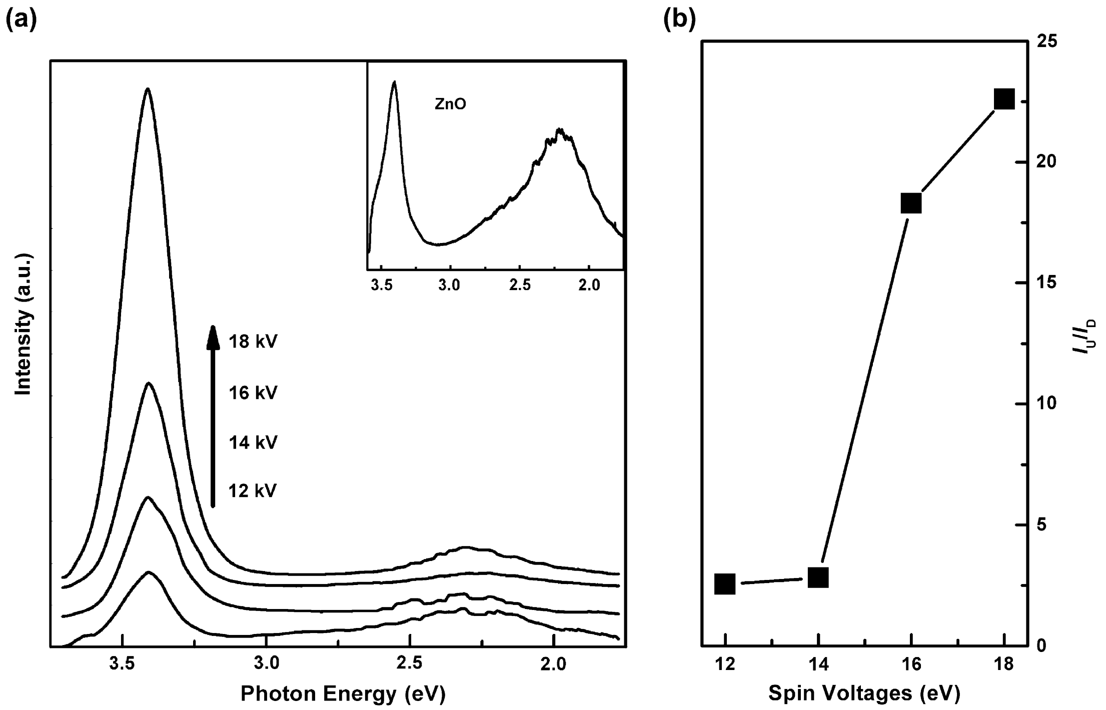
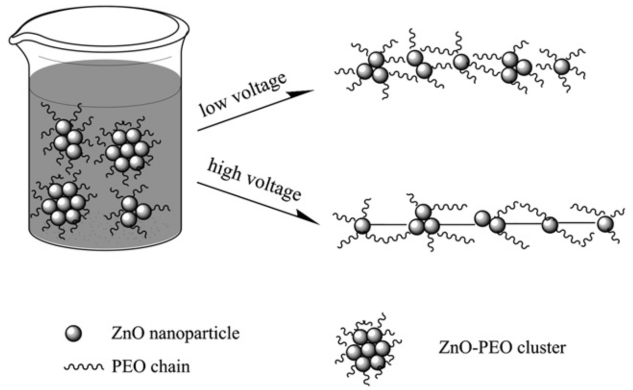


Fig. 3. PL spectra of ZnO–PEO electrospun fibers under voltages of 12, 14, 16 and 18 kV at room temperature (a). Inset is the PL spectrum of ZnO composite fibers. The UV emission peak I_U/I_D of ZnO–PEO electrospun fibers as a function of the electrospinning voltages (b).

on the surface of ZnO nanoparticles and enhancing the UV emission efficiency.

Fig. 3b shows the change of I_U/I_D as a function of electrospinning voltages. In the existence of PEO, the PL intensity ratio of the UV band-edge emission to the deep-level green emissions (I_U/I_D) is drastically higher than that of ZnO quantum dots without PEO. Due to the decrease of the oxygen vacancy and quenching of the deep-level emission further, the increase of the voltage does not increase the deep-level emission, but result in the increase of I_U/I_D, which means that the passivation effect of PEO is strengthened by increasing electrospinning voltage.

Based on the above results, a potential mechanism is presented, as shown in Scheme 2. With the interaction of ZnO and PEO, the PEO molecules are assembled on the surface of ZnO, and ZnO nanoparticles are partly covered by PEO long chains. There also exists interaction between ZnO nanoparticles because of the high Gibbs' surface free energy of the small sized ZnO. The two competitive interactions induce larger PEO–ZnO cluster with different diameters in the solution of the composite of PEO–ZnO. And the surface defects are partly passivated by PEO. Being prepared before mixing with PEO and protected by PEO, ZnO nanoparticles do not grow in the sequent process, with the position of the UV emission band of all the samples remains unchanged in the PL spectra. By applying high voltages to the composite solution, the curved PEO chains spread and the PEO–ZnO clusters are embedded in PEO with smaller size under the extraction of fibers. The high electrospinning voltage may induce the polarization and orientation of ZnO nanoparticles, and the ZnO nanoparticles are embedded in and aligned along the PEO matrix fibers. With the increase of the voltages, more ZnO nanoparticles with low aggregation were extracted. Then the dispersion of the PEO–ZnO clusters is narrower, and the passivation is more effective, resulting in larger I_U/I_D ratio of the as-spun fibers.



Scheme 2. Scheme of the translation from ZnO–PEO clusters to ZnO–PEO fibers at the extraction forces of electric field.

According to Shalish and co-workers' report, nanostructural ZnO exhibits stronger visible luminescence related to surface defects than the bulk counterparts, and the intensity of the visible luminescence tends to get stronger as the size of ZnO gets smaller [11]. While in this article, by combining the electrospinning technology and passivation effect of PEO, the ZnO containing 1D composites show strong ultraviolet photoluminescence with large I_U/I_D.

4. Conclusion

In summary, fibers of PEO–ZnO with diameters from 900 to 500 nm were successfully prepared by electrospinning technology and the structural and optical properties were characterized. The results show that PEO effectively passivates the oxygen related defects on the surface of ZnO by forming chemical bonds with ZnO nanoparticles, which leads quenching of the green emission of ZnO. Moreover, the electrospinning voltage is found to play an important role on enhancing the passivation effect of PEO and strengthens the quantum confinement effect of ZnO nanoparticles, i.e. the fibers electrospun at higher voltage exhibit more intense UV emission with small FWHM and large I_U/I_D. In short, this method can control the PL of PEO–ZnO composite fibers, and might also be applied to other composite materials containing semiconductors such as CdS, CdSe, ZnS, TiO_2, etc. These kinds of 1D nanomaterials are wished to have potential applications in nano-optoelectronic devices.

Acknowledgements

This work was supported by National High Technology Research and Development Program of China (2006AA03Z311), the National Natural Science Foundation of China Grant No. 60576040, the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China No. 704017, and the Science Foundation for Young Teachers of Northeast Normal University (20050301).

References

[1] Morkoc H, Strite S, Gao GB, Lin ME, Sverdlov B. Journal of Applied Physics 1994;76(3):1363–98.
[2] Michelotti F, Belardini A, Larciprete MC, Bertolotti M, Rousseau A, Schoer A, et al. Applied Physics Letters 2003;83(22):4477–9.
[3] Muller J, Weissenrieder S. Fresenius Journal of Analytical Chemistry 1994;349(5):380–4.
[4] Karanth D, Fu HX. Physical Review B: Condensed Matter and Materials Physics 2005;72(6):064116.
[5] Liu B, Zeng HC. Journal of the American Chemical Society 2003; 125(15):4430–1.
[6] Tseng YK, Huang CJ, Cheng HM, Lin IN, Liu KS, Chen IC. Advanced Functional Materials 2003;13(10):811–4.
[7] Vayssieres L. Advanced Materials 2003;15(5):464–6.
[8] Pan ZW, Dai ZR, Wang ZL. Science 2001;291(5510):1947–9.
[9] Kong XY, Ding Y, Yang R, Wang ZL. Science 2004;303(5662):1348–51.
[10] Li D, Leung YH, Djurisic AB, Liu ZT, Xie MH, Shi SL, et al. Applied Physics Letters 2004;85(9):1601–3.
[11] Shalish I, Temkin H, Narayanamurti V. Physical Review B: Condensed Matter and Materials Physics 2004;69(24):245401.
[12] Kumar RV, Elgamiel R, Koltypin Y, Norwig J, Gedanken A. Journal of Crystal Growth 2003;250(3–4):409–17.
[13] Shim JW, Kim JW, Han SH, Chang IS, Kim HK, Kang HH, et al. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2002;207(1–3):105–11.
[14] Guo L, Yang S, Yang C, Yu P, Wang J, Ge W, et al. Applied Physics Letters 2000;76(20):2901–3.
[15] Li D, Xia YN. Advanced Materials 2004;16(14):1151–70.
[16] Ki CS, Baek DH, Gang KD, Lee KH, Um IC, Park YH. Polymer 2005; 46:5094–102.
[17] Brus LE. Journal of Chemical Physics 1984;80(9):4403–9.
[18] Sui XM, Shao CL, Liu YC. Applied Physics Letters 2005;87(11): 113115.
[19] Yang XH, Shao CL, Liu YC, Mu RX, Guan HY. Thin Solid Films 2005; 478(1–2):228–31.
[20] Reneker DH, Yarin AL, Fong H, Koombhongse S. Journal of Applied Physics 2000;87(9):4531–47.
[21] Yarin AL, Koombhongse S, Reneker DH. Journal of Applied Physics 2001;89(5):3018–26.
[22] Liufu SC, Xiao HN, Li YP. Polymer Degradation and Stability 2005; 87(1):103–10.
[23] Scott JF. Physical Review B: Condensed Matter and Materials Physics 1970;2(4):1209.
[24] Van Dijken A, Meulenkamp E, Vanmaekelbergh D, Meijerink A. Journal of Physical Chemistry B 2000;104(8):1715–23.
[25] Wood A, Giersig M, Hilgendorff M, Campos AV, Lizmarzan LM, Mulvaney P. Australian Journal of Chemistry 2003;56(10):1051–7.