Quasi-Solid State Dye-Sensitized Solar Cells Based on the Cross-Linked Poly(ethylene glycol) Electrolyte with Tetraethoxysilane

Pinjiang Li,[1,2] Jihuai Wu,[1] Sancun Hao,[1] Zhang Lan,[1] Qinghua Li,[1] Yunfang Huang[1]

[1]Institute of Surface Micro and Nano Materials, Xuchang University, Xuchang, 461000, China
[2]Institute of Materials Physical Chemistry, Huaqiao University, Quanzhou, 362021, China

ABSTRACT: The cross-linked poly(ethylene glycol) (PEG-1000) was prepared by condensation reaction with tetraethoxysilane (TEOS). Using the cross-linked PEG-1000 as polymer host, 0.60 M KI and 0.06 M I_2 as ionic conductors, an ionic conductivity of the polymer electrolyte was achieved 3.12 mS cm^{-1}. Based on the optimized cross-linked PEG electrolyte, the best result of the quasi-solid state dye-sensitized solar cell (QS-DSSC) was the short-circuit photocurrent of 11.87 mA cm^{-2}, the open-circuit photovoltage of 706 mV, the fill factor of 0.593 and the light-to-electricity conversion efficiency of 4.97% at 100 mW cm^{-2} (AM 1.5). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1752–1757, 2011

Key words: dye-sensitized solar cells; electrolyte; quasi-solid state; poly(ethylene glycol); tetraethoxysilane

INTRODUCTION

Owing to low production cost and high efficiency for the conversion of solar energy to electric power, dye-sensitized nanocrystalline solar cells (DSSCs) have been attracting widespread scientific and technological interest and have evolved as potential alternatives to traditional photovoltaic devices in the past decade.[1] The function of such devices is based on the injection of an electron from a photoexcited state of the sensitizer dye into a conduction band of the nanocrystalline semiconductor. The solar cells are composed with a photoelectrode with a thin nanoporous film of TiO_2 particles adsorbed by ruthenium metal–organic dyes, an electrolyte dissolving redox couples (I^-/I_3^-), and platinum (Pt)-layered counter electrode.[2] The redox couple in the electrolyte is of crucial importance for stable operation of a dye-sensitized solar cell, because it must carry the charge between the photoelectrode and the counter electrode for regeneration of the dye. The most-used charge mediator is iodine/iodide redox couple in liquid solvent. However, there are some problems such as leakage of the electrolytes, evaporation of the organic liquid solvent, and high temperature instability, which cause difficulties in sealing and performance degradation of DSSCs.[3] Thus, the commercial exploitation of these devices needs the replacement of the liquid electrolyte by a solid or quasi solid-state charge-transport medium,[4–7] which not only offers hermetic sealing and stability, but also reduces design restrictions and endows the DSSCs with shape choice and flexibility.[8]

An alternative solution is to use iodine/iodide redox couple dissolved in polymer electrolyte,[9–11] which has the advantages of relatively high ionic conductivity and easy solidification.[12] With this approach in mind, we have made an attempt for employing a novel polymer electrolyte of cross-linked poly(ethylene glycol) (PEG) by tetraethoxysilane (TEOS) for DSSCs. PEG is a polyether polyol, which has relatively high ionic conductivity when complexed with alkali-metal salts and is an excellent base material of the electrolyte for application in many fields.[13–16] However, a major problem associated with PEG was the presence of crystalline structure and the PEG-salt system has poor mechanical stability and adhesiveness. In this research, the crystallinity of PEG was reduced significantly and its mechanical stability was improved by cross-linking reaction with TEOS. Besides, it has been reported that the silica network forms a "solid-like" matrix wrapped around by the polymer phase, which can be considered as a "solid solvent" in which various entities such as molecules, macromolecules or salts can be easily dissolved.[17–19]

In this article, the cross-linked PEG was prepared by condensation reaction with TEOS and used as a polymer matrix to dissolve potassium iodide (KI) and iodine to form a polymer electrolyte for quasi-solid state dye-sensitized solar cell (QS-DSSCs). The electrolyte composition was optimized and the photovoltaic performance of this system was also evaluated.

EXPERIMENTAL

Materials

PEG with average molecular weight of 1000 (PEG-1000), TEOS, acetic acid, KI, iodine, and titanium iso-propoxide were all A.R. grade and all purchased from Sinopharm Chemical Reagent (Shanghai, China). PEG was used after drying at 60°C for 48 h in vacuum and then stored in a desiccator before use. Other reagents were used as received.

Conducting glass plates (FTO glass, Fluorine doped tin oxide over-layer, sheet resistance 8 Ω cm^{-2}, purchased from Hartford Glass, (Hartford, USA)) were used as a substrate for precipitating TiO$_2$ porous film and were cut into 2 × 1.5 cm^2 sheets. Sensitizing organometallic dye cis-bis(isothiocyanato)bis(2, 2'-bipyridyl-4, 4'-dicarboxylato) ruthenium (II) [RuL$_2$(NCS)$_2$] was purchased from SOLAR-ONIX, SA (Switzerland).

Preparation of cross-linked PEG electrolytes

Cross-linked PEG was prepared by a condensation reaction and catalyzing with acetic acid. PEG (0.025 mol), TEOS (0.025 mol), and acetic acid (1 mL) were mixed in a three-neck flask. Nitrogen gas was continuously purged to prevent oxidation. The reaction was conducted at 120°C for 3 h. Then, the products were transferred to a teflon autoclave and treated at 120°C for 6 h autoclaved for complete reaction.

The appropriate amounts of KI and I$_2$ (10 mol % of KI) were dissolved in the cross-linked PEG-1000, the resulting mixture was heated at 80°C under vigorous stirring until a homogeneous composite was obtained, followed by cooling down to room temperature and stored in a desiccator before use.

Preparation of TiO$_2$ colloid

A volume of 0.05 mol of acetic acid was added to 0.05 mol of titanium iso-propoxide under stirring at room temperature. The mixture was rapidly poured into 120 mL distilled water with vigorous stirring and a white precipitate was formed immediately. After a half an hour stirring, acetic acid (12 mL) and nitric acid solution (65 wt %, 1.2 mL) were added to

the mixture. Then the mixture was heated to 80°C and peptized for 12 h. The resultant mixture was autoclaved at 200°C for 12 h to form a white suspension with some precipitate. The resultant suspension was concentrated to 1/4 of its volume, PEG-20000 (10 wt % TiO$_2$) and a few drops of emulsification regent of Triton X-100 was added to the resultant colloidal solution with stirring. Then the colloidal solution was concentrated to form a TiO$_2$ paste of suitable concentration.
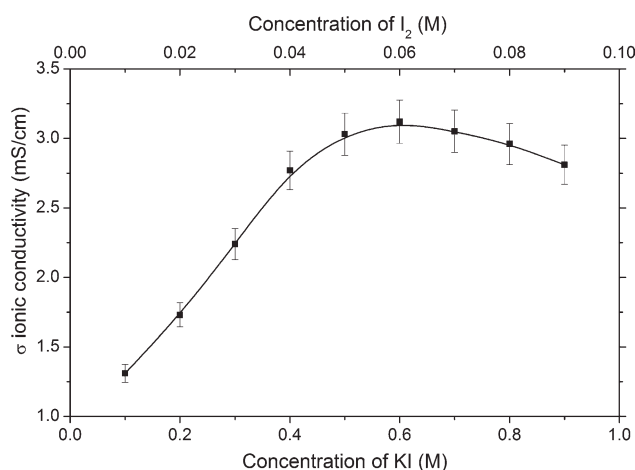
Fabrication of the QS-DSSCs

A QS-DSSC (active area of 0.25 cm^2) was assembled according to the following procedure. Conducting glass sheet (FTO) was washed with ethanol and immersed in 50 mM TiCl$_4$ aqueous solution for 12 h to make a good mechanical contact between the following printed TiO$_2$ layer and conducting glass substrate. The TiO$_2$ electrode (TiO$_2$ film thickness about 6 μm) was obtained by spreading the TiO$_2$ paste on the conducting glass substrate using a "doctor blade method" and then sintered at 450°C for 30 min in air. After cooling to 80°C, the TiO$_2$ electrode was dye-sensitized with 0.5 mM cis-[(dcbH$_2$)$_2$Ru(SCN)$_2$] solution in absolute ethanol for 24 h at room temperature. Afterwards, the dye-sensitized TiO$_2$ electrode was rinsed with absolute ethanol and dried in moisture-free air.

A quasi-solid-state dye-sensitized solar cell was fabricated by sandwiching a slice of polymer gel electrolyte between a dye-sensitized TiO$_2$ electrode and a platinum counter electrode (prepared by electrodeposition). The cell was heated at 60°C for 30 min for complete penetration of the polymer gel electrolyte through the void of nanopores and then cooled to room temperature. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant. Epoxy resin was used for further sealing the cell. From the above process, the polymer gel electrolyte had a good contact with the TiO$_2$ electrode.

Measurements

The ionic conductivity of gel polymer electrolytes was measured by using a Russell RL060C digitized conductivity meter (Thermo Electron Corporation). A FTIR spectrum sample in KBr was performed using a Nicolet Impact 410 spectrometer. FT-Raman spectra for polymer electrolytes were recorded at room temperature using a NEXUS 670 FT-Raman spectrometer (Nicolet, Thermo Fisher Nicolet, USA). The photovoltaic test of dye-sensitized TiO$_2$ nanocrystalline solar cells was carried out by measuring the J–V character curves under irradiation of white light from a 100 W xenon arc lamp (XQ-500 W,

Shanghai Photoelectricity Device Company, China) under ambient atmosphere. The incident light intensity and the active cell area was 100 mW cm^{-2} and 0.25 cm^2, respectively.

The photoelectronic performances were calculated by the following equations[20]:

$$FF = \frac{V_{max} \cdot J_{max}}{V_{oc} \cdot J_{sc}}$$

$$\eta(\%) = \frac{V_{max} \cdot J_{max}}{P_{in}} \times 100\% = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}} \times 100\%$$

where FF is fill factor, η is the light-to-electricity conversion efficiency, J_{sc} is the short-circuit current density (mA cm^{-2}), V_{oc} the open-circuit voltage (V), P_{in} is the incident light power, and J_{max} (mA cm^{-2}) and V_{max} (V) are the current density and voltage in the J–V curves, respectively, at the point of maximum power output.

RESULTS AND DISCUSSION

Characterization of the cross-linked PEG

The reaction mode of PEG and TEOS by the condensation reaction is schematically represented in Figure 1.[21] After the reaction, the polymer was turned into gel from liquid under the room temperature. Figure 2 shows the FTIR spectra of PEG-1000 (curve a), TEOS (curve b), and cross-linked PEG-1000 (curve c). The IR bands around the wave numbers of 3400 and 1100 cm^{-1} were attributed to the ─OH and Si─O groups, respectively. Compared with the curve a of PEG-1000, the decreased band intensity at about 3400 cm^{-1} and increased band intensity at about 1100 cm^{-1} after condensation reaction in the curve c implied that cross-links were formed after the reaction. And the disappearance of the band at about 1960 cm^{-1}, which is from the characteristic vibration of the PEG crystallization state,[22] indicates that the degree of the PEG crystallization state was decreased by the cross-linking reaction with TEOS. The amorphous state of the cross-linked PEG is favorably enhancing the ionic conductivity of the polymer electrolyte.

Figure 1 Schematic reaction mode of the cross-linked PEG with TEOS.

Figure 2 The infrared spectra of samples: (a) PEG-1000, (b) TEOS, and (c) cross-linked PEG-1000.

FT-Raman spectra of the cross-linked PEG electrolyte

The formation of I$_3^-$ plays an important role in the redox reactions between I$^-$ and I$_3^-$ contributed to the charge transfer process in DSSCs.[23,24] To investigate the formation of I$_3^-$ and the complete dissolution of iodine in polymer electrolytes, the FT-Raman spectroscopy was employed and the spectra of

Figure 3 FT-Raman spectra of the cross-linked PEG electrolytes with different molar ratios of KI/I$_2$ (each electrolyte contain 0.60 M of KI): (a) KI/I$_2$ = 0.60/0, (b) (b) KI/I$_2$ = 0.60/0.06, and (c) KI/I$_2$ = 0.60/0.075.

Figure 4 Effect of the concentration of redox couple (KI + I_2) on conductivity for the cross-linked PEG-1000 electrolyte (the molar ratio of KI to I_2 is 10 : 1; the temperature is at 30°C).

polymer electrolytes were presented in Figure 3. When KI and I_2 added in the polymer, a stronger Raman peak was observed at 114 cm^{-1}, which was attributed to the Raman spectrum band of I_3^-.[25] And, a weaker Raman peak was observed at 143 cm^{-1}, which was attributed to the Raman spectrum band of I_{2n+3}^- ($n = 1, 2, 3, \ldots$)[26] and enhanced with the increase of the concentration of I_2 (comparison between curve b and curve c). Moreover, the band attributed to vibration of molecular iodine around 180–200 cm^{-1} was not observed, confirming the complete dissolution of I_2 in the polymer electrolytes.[27,28]

Ionic conductivity of the cross-linked PEG electrolyte

Generally, the overall light-to-electricity conversion efficiency of DSSCs is heavily dependent upon the mobility of the redox couple (I^-/I_3^-) and consequently on the ionic conductivity of the electrolyte.[29] In this regard, the ionic conductivity of the polymer electrolyte was studied.

The influence of the concentration of redox couple triiodide/iodide on the conductivity of the cross-linked PEG-1000 electrolyte is shown in Figure 4. With the increase of the concentration of the redox couple, the conductivity of the electrolyte increases and then decreases slightly after reaching a maximum conductivity of 3.12 mS cm^{-1} with 0.60 M KI and 0.06 M I_2. This is due to that the ionic conductivity is a function of the number of charge carriers in the polymer gel electrolyte. However, with the increase of the concentration of the redox couple, the conductivity of electrolyte decreases slightly after reaching a maximum conductivity. It is well-known

that the alkali-metal cation binds with the ether oxygens of the polyether molecules and that the viscosity increases with increasing salt concentration[30] and a high salt concentration can reduce the segmental motion of the polymer chains.[31] And the larger ionic radius of I_{2n+3}^- ($n = 1, 2, 3, \ldots$) reduces the mobility of ions. So the ionic conductivity decreases.
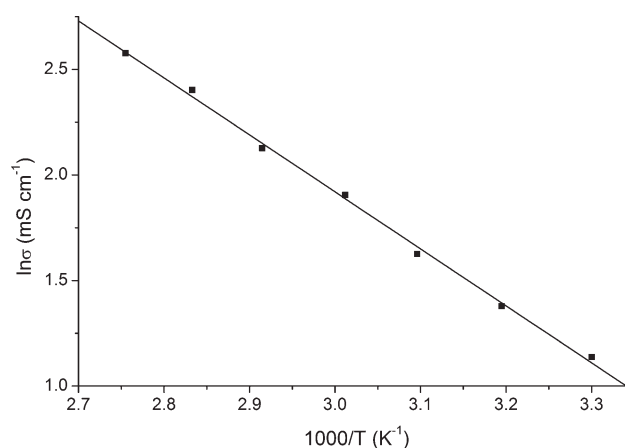
Figure 5 shows temperature dependence of the ionic conductivity for the cross-linked PEG-1000 electrolyte (contain KI 0.60 M and I_2 0.06 M). Mechanistically, when an ionic transport process involves an intermolecular ion hopping, the conductivity will be determined by the thermal hopping frequency, which leads to an Arrhenius conductivity-temperature behavior [eq. (1)].[32] As is apparent from Figure 5, the conductivity data of all membranes showed a typical positive curvature in Arrhenius plots.

$$\sigma[T] = A\left[-\frac{E_a}{RT}\right], \qquad (1)$$

where E_a is the activation energy, R is the molar gas constant, A is a constant, and T is absolute temperature.
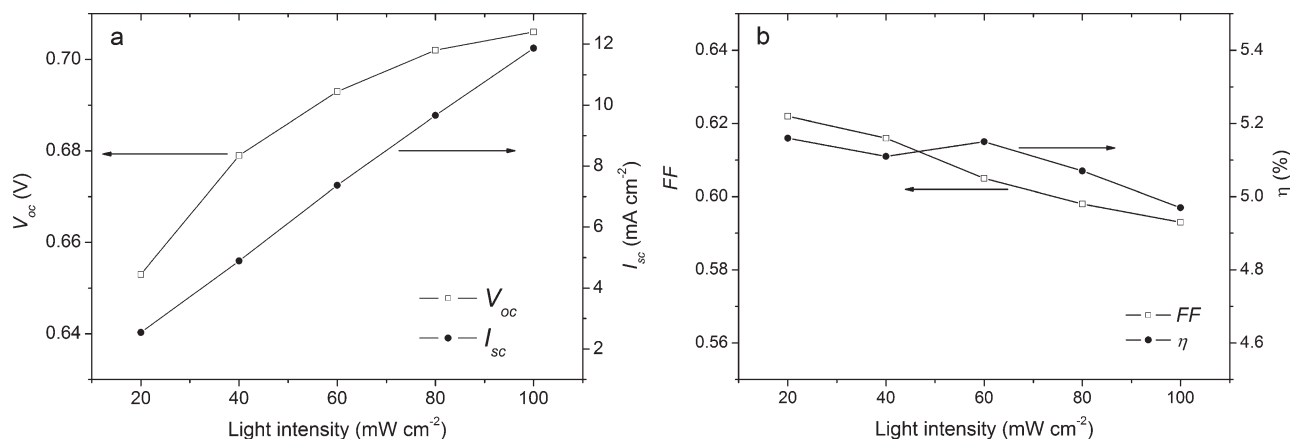
Photovoltaic performance of QS-DSSCs based on the cross-linked PEG electrolyte

Figure 6(a,b) show the effect of light intensity on the performance characteristics of QS-DSSCs. The open-circuit voltage and short-circuit current depend logarithmically and linearly on light flux, respectively. The fill factors fall off with increasing light intensity owing to the development of a large photo-shunt.[33] The curve of light-to-electricity energy conversion efficiency (η) results from the relation with the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}) and the fill factor (FF). The result is a

Figure 5 Temperature dependence of the ionic conductivity (σ) for the cross-linked PEG-1000 polymer electrolyte.
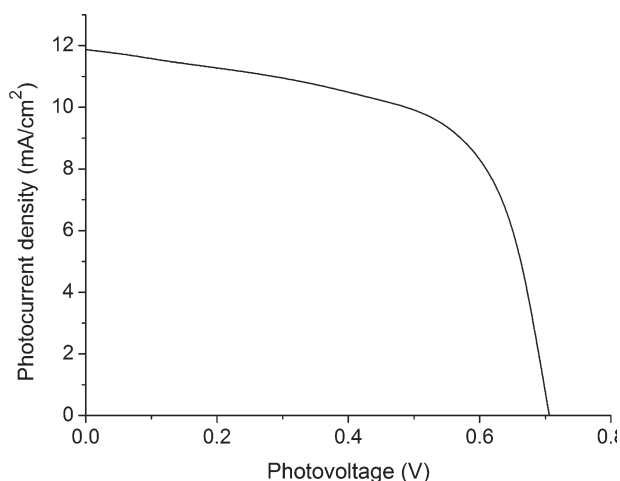
Figure 6 The effect of light intensity on the performance characteristics of QS-DSSCs based on the cross-linked PEG electrolyte. (a) Dependence of the open circuit voltage (V_{oc}) and short-circuit current (I_{sc}) on light intensity. (b) Light-to-electricity conversion efficiency (η) and the fill factor (FF) plotted as function of light intensity.

general behavior in QS-DSSCs employing solid polymer electrolytes.[10]

Figure 7 shows the photocurrent-photovoltage curve of the QS-DSSC fabricated with the cross-linked PEG electrolyte electrolyte (contain KI 0.60 M and I_2 0.06 M). The highest energy conversion efficiency of 4.97% (η) was obtained under light intensity of 100 mW cm^{-2}. This optimized polymer electrolyte composition achieved higher J_{sc} of 11.87 mA cm^2, V_{oc} of 0.706 V, and the fill factor of 0.593.

CONCLUSIONS

In this work, PEG-1000 was cross-linked with TEOS by condensation reaction. Crystallinity of PEG reduced significantly by the formation of cross-links. The higher ion conductivity of the optimum polymer electrolyte composition was 3.12 mS cm^{-1} at 30°C.

Using the optimized polymer electrolyte system to fabricate QS-DSSCs, a light-to-electricity conversion efficiency of 4.97% was achieved under AM 1.5 simulated solar light illumination.

References

1. Grätzel, M. Nature 2001, 414, 338.
2. Hagfeldt, A.; Grätzel, M. Chem Rev 1995, 95, 49.
3. Smestad, G. Sol Energy Mater Sol Cells 2003, 76, 17.
4. O'Regan, B.; Lenzmann, F.; Muis, R.; Wienke, J. Chem Mater 2002, 14, 5023.
5. Bach, U.; Lupo, D.; Comte, P.; Grätzel, M. Nature 1998, 395, 583.
6. Nogueira, A. F.; Paoli, A. D.; Montanari, I. J Phys Chem B 2001, 105, 7517.
7. Cao, F.; Oskam, G.; Searson, P. C. J Phys Chem B 1995, 991, 17071.
8. Chatzivasiloglou, E.; Stergiopoulos, T.; Spyrellis, N.; Falaras, P. J Mater Process Tech 2005, 161, 234.
9. Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M. J Am Chem Soc 2003, 125, 1166.
10. Nogueira, A. F.; Durrant, J. R.; De Paoli, M. A. Adv Mater 2001, 13, 826.
11. Kang, M. G.; Kim, K. M.; Ryu, K. S.; Chang, S. H.; Park, N. G.; Hong, J. S.; Kim, K. J. J Electrochem Soc 2004, 151, E257.
12. Li, B.; Wang, L.; Kang, B.; Wang, P.; Qiu, Y. Sol Energy Mater Sol Cells 2006, 90, 549.
13. Wintersgill, M. C.; Fontanella, J. J.; Stallworth, P. E.; Newman, S. A.; Chung, S. H.; Greenbaum, S. G. Solid State Ionics 2000, 135, 155.
14. Marcinek, M.; Zalewska, A.; Zukowska, G.; Wieczorek, W. Solid State Ionics 2000, 136–137, 1175.
15. Wu, J. H.; Li, P. J.; Hao, S. C.; Yang, H. X. Electrochim Acta 2007, 52, 5334.
16. Wieczorek, W.; Lipka, P.; Zukowska, G.; Wycislik, H. J Phys Chem B 1998, 102, 6968.
17. Judeinstein, P.; Schmidt, H. J Sol-Gel Sci Technol 1994, 3, 189.
18. Judeinstein, P.; Titman, J.; Stamm, M.; Schmidt, H. Chem Mater 1994, 6, 127.
19. Lesot, P.; Chapuis, S.; Bayle, J. P.; Rault, J.; Lafontaine, E.; Campero, A.; Judeinstein, P. J Mater Chem 1998, 8, 147.
20. Grätzel, M. Prog Photovol Res Appl 2000, 8, 171.
21. Koo, J. N.; Kim, D. J Appl Polym Sci 2002, 86, 948.
22. Larhrib, H. Int J Pharm 1997, 147, 187.

Figure 7 Photocurrent density vs. photovoltage curve obtained for QS-DSSCs at 30°C.

23. Grätzel, M. Chem Lett 2005, 34.
24. Kubo W.; Murakoshi K.; Kitamura T.; Yoshida S.; Haruki M.; Hanabusa K.; Shirai H.; Wada Y.; Yanagida S. J Phys Chem B 2001, 105 12809.
25. Tadayyoni M.A.; Gao P. J Electroanal Chem Interfacial Electrochem 1986, 198, 125.
26. Loos K. R.; Jones A. C. J Chem Phys 1974, 78, 2306.
27. Kang M. S.; Kim J. H.; Won, J.; Kang Y. S. J Photochem Photobiol A 2006, 183, 15.
28. Klaeboe P. J Am Chem Soc 1967, 89, 3667.
29. Kubo, W.; Murakoshi, K.; Kitamura, T.; Yoshida, S.; Haruki, M.; Hanabusa, K.; Shirai, H.; Wada, Y.; Yanagida, S. J Phys Chem B 2001, 105, 12809.
30. Wixwat, W.; Fu, Y.; Stevens, J. R. Polymer 1990, 32, 1181.
31. Armand, M. Adv Mater 1990, 2, 278.
32. Wang, P.; Zakeeruddin, S. M.; Gratzel, M.; Kantlehner, W.; Mezger, J.; Stoyanov, E. V.; Scherr, O. Appl Phys A 2004, 79, 73.
33. Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. Nat Mater 2005, 4, 455.