Formation of rod-like nanostructure by aggregation of TiO₂ nanoparticles with improved performances

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Abstract. To improve the performance of titanium dioxide (TiO₂)-based devices, many efforts have been made to prepare nanostructures with composite of TiO₂ nanoparticles and nanorods. In this work, a novel rod-like TiO₂ nanostructure was obtained via a controllable hydrolysis process. Morphology and structure analysis showed that the rod-like nanostructure was a well-aligned aggregate of nearly spherical TiO₂ nanoparticles. Rod-like TiO₂ nanoparticle aggregates were fabricated on a primary TiO₂ nanoparticle-based layer without the use of template, and formed a hierarchical TiO₂ composite film together. The photocatalytic activity of the TiO₂ film with rod-like nanoparticle aggregates was evaluated by the degradation of methylene blue. The antibacterial activity of fabricated hierarchical TiO₂ film was assessed against *Staphylococcus aureus*. The photoelectrochemical property of this film as the photoanode in assemble dye-sensitized solar cell was also tested. Compared with randomly distributed nanoparticle-based TiO₂ film, the hierarchical TiO₂ film exhibited improved performance of photocatalysis, antibacterial activity and photoelectric conversion.

Keywords. Rod-like nanostructure; aligned nanoparticle aggregates; photocatalytic activity; antibacterial activity; dye-sensitized solar cell.

1. Introduction

Titanium dioxide (TiO₂) nanostructures have drawn great interest because of their unique performance in optical, bioactive and electrical properties by effective utilization of light. Further TiO₂ nanostructures have been investigated for many promising applications in many fields ranging from environmental protection as photocatalysis^{1,2} and healthcare as antibiosis^{3,4} to renewable energy development as photovoltaic cells.^{5,6} The nanostructured TiO₂ has been proven to be a kind of excellent photocatalysis materials to break down most organic compounds with highly efficient degradation and no secondary pollution. TiO₂ nanomaterials, one of the most studied inorganic antibacterial agents due to its strong inhibition power to bacteria and nontoxicity to human body, have been used in some fields for antimicrobial health applications, such as textiles, coating and footwear.⁷ Dye-sensitized solar cell (DSSC) has been considered as the

most potential photovoltaic cells due to relatively high-power conversion efficiencies and low cost.⁸ And the most critical component of a DSSC is the nanostructured TiO₂ photoelectrode, in which the majority of the photoinduced energy transfer and conversion steps take place.

Much attention has been focused on the preparation of nanostructured TiO₂ materials, including nearly spherical nanoparticles, nanorods, nanofibres, nanosheets and so on. Among them, the nearly spherical nanoparticles have relatively higher surface-to-volume ratio. The reaction mainly occurs on the surface or at the interface and strongly depends on the surface area of the TiO₂ nanomaterials.⁹ Hence high specific surface area is beneficial to many TiO₂-based devices, such as larger surface area for more effective degradation of organic molecular in photocatalytic process, for extended contact with microorganism as antimicrobial nanomaterials, and for absorption of more photosensitive dyes in DSSC. Compared with spherical nanoparticles, TiO₂ nanorods can decrease interfacial collision and provide direct electrical pathway for photogenerated charger carrier. And the rod geometry may not only decrease the carrier recombination probability due to specified directionality, but also present more efficient light scattering ability.^{10,11}

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In order to take advantages of both of the high surface area of TiO₂ spherical nanoparticles and effective transport pathway of TiO₂ nanorods, the optimizational morphology of composite nanostructure is important to improve the performance. In recent times, some efforts have been devoted to the preparation of nanoparticles/nanorods composite TiO₂ nanostructure. Saji and Pyo¹² synthesized titania nanorods and nanoparticles, and described the changes of the DSSC performance with the variation of the nanoparticles/nanorods composites of photoanodes. Liu *et al*¹³ prepared spherical particles formed by aggregating of TiO₂ nanorods. Hong *et al*¹⁴ also fabricated a composite of TiO₂ nanoparticles and nanorods, and the nanorods were obtained by using the electrospinning technique.

In this work, rod-like TiO₂ nanostructures by a controllable slow hydrolysis process was successfully synthesized. More importantly and unlike other traditional nanorods, as-prepared rod-like nanostructure was made up of TiO₂ nanoparticles, a well-aligned aggregate of random nanoparticles. Those rod-like TiO₂ nanoparticle aggregates were fabricated directly on TiO₂ nanoparticle-based layer with no use of any template during the formation process. The performance of nanomaterials was closely related to the morphology of nanostructures. Thus, the photocatalytic activity, antibacterial activity and photoelectrochemical property as electrode in DSSC of TiO₂ film with this novel rod-like aggregate nanostructure were preliminarily evaluated.

2. Experimental

2.1 Materials

Titanium butoxide (TBT: Ti(OBu)₄, Aladdin, 99%) was used as-received without further purification. Diethanolamine (DEA), ethylene glycol (EG) and oleic acid (OA) were obtained from Beijing Chemical Reagent Company (Beijing, China). All other chemicals and reagents used were of analytical grade.

2.2 Preparation of rod-like TiO₂ nanoparticle aggregates

The rod-like TiO₂ nanoparticle aggregates were based on a strategy of the slow hydrolysis synthesis method in mild conditions. The experimental process included two typical steps: in the first step, the TiO₂ nanoparticle-based layer was produced by dip coating the surface of cleaned FTO glass substrate with colloidal titanium coating solution, which was prepared according to the earlier work with slight modification.¹⁵ Briefly, the colloidal coating solution was prepared by TBT, DEA, ethanol, hydrochloric acid and deionized water. The molar ratio for the colloid solution was: TBT : DEA : EtOH : HCl : H₂O = 1 : 1 : 9 : 0.1 : 2. The thickness of resulted TiO₂ nanoparticle-based layer can be controlled by changing the repetition times of dip-coating process. In the second step, to fabricate the TiO₂ nanorod formed from TiO₂ nanoparticle, the above substrate with prepared TiO₂

nanoparticle-based layer was soon transferred into another dip-coating chamber containing a titanium precursor solution prepared by mixing TBT and EG with the volume ratio at 1 : 9. After this dip-coating process, a certain amount of dried OA was subsequently sprayed on the surface of coating under nitrogen flow. The finished substrate was placed in a sealed system and maintained at 90°C for 48 h to complete the growth of rod-like TiO₂ nanoparticle aggregates by a slow controlled hydrolysis process. The hydrolysis reaction of titanium precursor was induced by the water released slowly upon esterification of OA and EG. In the end, the substrate was heat treated at various temperature in an air stream by using a ramp rate of 2°C min⁻¹ to promote further crystallization of TiO₂ nanoparticles.

2.3 Performance measurements

The photocatalytic activities of TiO₂ films were evaluated by the photocatalytic oxidation of methylene blue (MB, [(CH₃)₂N]₂C₁₂H₆NS(Cl)) in aqueous solution under the irradiation of ultraviolet (UV) light. The photocatalytic degradation of MB as a function of irradiation time under the irradiation of a high-pressure-mercury lamp was monitored by a UV-vis spectrophotometer over the 200–900 nm range. The MB concentration in test cell was 0.025 mM, and the light intensity on the surface of the sample was about 1.5 mW cm⁻².

The antibacterial activity of synthesized TiO₂ films was assessed against *Staphylococcus aureus* (*S. aureus*, ATCC 6538), which is a fairly useful indicator as one of the most important organisms for infections.^{16,17} The test was conducted under 365 nm UVA light by the film contact method according to ISO 16187 standard with modification.¹⁸ Microorganism suspension was prepared in physiological saline solution with 1.0% nutrient broth with a microbial concentration of 10⁵ CFU ml⁻¹. The well-mixed bacterial suspension of 0.1 ml was dripped slowly onto the surface of each sample, and the cover film made of poly(ethylene terephthalate) (PET) was then spread to ensure uniform contact between the inoculums and samples. Immediately after the inoculation, half of specimens were eluted using SCDLP medium. Further the remaining samples were transferred to moisture chamber and subjected to UVA irradiation with the light intensity at 1.5 mW cm⁻². After the set irradiation time, the bacterial droplets were eluted following the same procedure. The antibacterial activity ratio (*R*) was calculated as follows:

$$R(\%) = (C_1 - T_1)/C_1 \times 100\%,$$

where *T*₁ refers to the average number of microorganism recovered from the test specimens and *C*₁ the number of bacteria recovered from the control specimens.

Then the photoelectrochemical experiments of TiO₂ films were conducted that were tested by assembling the DSSC. The resulting TiO₂ film with rod-like nanoparticle aggregates and prepared conventional TiO₂ film were applied with freshly diluted 0.5 M TiCl₄ solution for different times to fabricate photoanode with a same thickness of ~4 μm.¹⁹

The as-prepared electrodes were washed with distilled water, and immediately were annealed again at 500°C for 30 min in air. After cooling to 80–90°C, the TiO₂ electrodes were soaked in a 5×10^{-4} M solution of N719 in a mixture of acetonitrile and tert-butyl alcohol (v/v, 1 : 1), and kept overnight at room temperature. After completion of the dye adsorption, the electrodes were withdrawn from the solution and dried under a stream of nitrogen. The sandwich-type solar cell was assembled by placing directly a platinum-coated counter electrode on photoelectrode, and both electrodes were clamped tightly together. The redox electrolyte, composed of 0.6 M of 1-butyl-3-methylimidazolium iodide (BMII), 0.03 M of I₂, 0.1 M of guanidine thiocyanate and 0.5 M of 4-tert-butylpyridine in a mixture of acetonitrile and pentanenitrile (v/v, 85 : 15), was attracted into the inter-electrode space by capillary forces for testing.

3. Results and discussion

Figure 1 shows the SEM images of the FTO substrate, TiO₂ nanoparticle-based layer, resulting rod-like structures, and the isolated nanorods. It was observed that a rod-like morphology was the predominant structural feature. It should be noted especially that the rod-like structures were formed by TiO₂ nanoparticles, as observed in figure 1d of individual nanorods at higher magnification. Although there was clearly some variation in the diameters of the different rod-like structures, the diameter of the nanorods was relatively uniform throughout their length for each nanorod, as shown in figure 1c. It could be seen that the distribution of rod-like structures was generally uniform throughout the substrate. However, it is also found from figure 1c that there is less uniformity in the orientation of the different rod-like structures. Both the uniformity of bottom layer surface roughness and the rate of hydrolysis reaction were responsible for the morphology and orientation of rod-like TiO₂ nanoparticle

aggregates.^{15,20} It was known that the uniformity of bottom layer surface roughness had strong impact on the driving and distribution of nucleation sites for TiO₂.²¹ The hydrolysis reaction rate of titanium precursor played a key role in the size of TiO₂ nanoparticles during the formation of final rod-like structures. And this reaction rate was decided by the water content in the system. Thus, the less uniformity of diameter and growth orientation of the different rod-like TiO₂ nanoparticle aggregates could be resulted by both the relatively rough bottom layer and the difference in reaction rates.

Hydrolysis of titanium alkoxides was a typical synthesis method to prepare TiO₂ nanoparticles. The size and shape of TiO₂ nanoparticles were manipulated by means of strategies, depending on the chemical modification of the titanium precursor and the suitable content of water to control reaction rate.²² In this experimental system, titanium alkoxides were chemically modified with ethylene glycols to form a precursor with a glycolate structure. Moreover, extra glycols in mixed system would be employed as stabilizing solvent to greatly reduce the hydrolytic reaction rates of titanium alkoxides.²³ And the water as the driving force of hydrolytic reaction was provided by the esterification reaction between hydroxyl of EG and carboxylic of OA. After water was slowly released *in-situ* upon esterification, the titanium precursor can carry out hydrolysis and condensation reactions to form TiO₂. The detailed chemical reactions during the formation process of rod-like TiO₂ nanoparticle aggregates can be described as the following:

or

where $\text{R} = -(\text{CH}_2)_7-\text{CH}=\text{CH}(\text{CH}_2)_7-\text{CH}_3$.

That was, alkoxide of titanium alkoxide was firstly substituted by ethylene glycol to form a titanium glycolated precursor $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ (equation (1)); subsequently, $\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_2$ reacted with low concentration water (equation (2)) provided by slow esterification of EG and OA, and produced unstable $\text{Ti}(\text{OH})_{2x}(\text{OCH}_2\text{CH}_2\text{O})_{2-2x}$

Figure 1. SEM images of (a) original glass substrate; (b) coated TiO₂ nanoparticle-based layer; (c) formed rod-like TiO₂ nanostructures; and (d) isolated rod-like TiO₂ nanostructures at higher magnification.

Figure 2. Schematic illustration of gradual formation of the rod-like TiO_2 nanostructure by the stacking of nanoparticles without template.

in mild conditions (equation (3)); then further hydrolysis and polycondensation reactions followed via oxolation leading to an extensive Ti-O-Ti network (equation (4)). Finally, the product was TiO_2 nanoparticle after a series of reactions and processing.

According to the above experiment observation and formation mechanism of nearly spherical TiO_2 nanoparticles, a simple schematic diagram was performed to illustrate the process steps. We propose a ‘stacking growth’ model containing three steps to explain the formation mechanism of rod-like TiO_2 nanoparticle aggregates, as shown in figure 2. In the initial step, titanium alkoxides were chemically modified to a precursor with a glycolates structure, which were coated on the surface of substrate. In the second step, the esterification reaction between alcohol and carboxylic provided the driving force of hydrolysis reaction. The completion of *in-situ* esterification of EG and OA was really slow, so the esterification rate decided the generation rate of TiO_2 nanoparticles. The TiO_2 nanoparticle only grew to a certain size before falling down below the interface of EG and OA in which next nanoparticle would begin generating. The final step was that the lately generated TiO_2 nanoparticles deposited to previously generated. Meanwhile, the deposition of nanoparticles lifted up the reaction system within the size of OA droplets, which resulted in continue stacking of TiO_2 nanoparticles. The rod-like TiO_2 nanoparticle aggregates gradually formed in shape until the reaction was stopped.

Figure 3 shows the XRD patterns of the as-synthesized rod-like TiO_2 nanoparticle aggregates before and after annealing at various temperatures. The TiO_2 nanoparticles before annealing did not show any well-defined diffraction peak but a large reflex in the XRD pattern (figure 3a), suggesting the nanoparticles were amorphous nature in structure. After the TiO_2 nanoparticles were annealed at 550°C , the XRD pattern (figure 3b) presented several diffraction peaks and these assignments (h, k, l) of 2θ values could be clearly attributed to the anatase phase of titanium dioxide. No other phases such as rutile phase diffraction peak could be detected, which indicated the formation of the pure anatase phase without any secondary phase at 550°C . The phase transformation from anatase to rutile phase for TiO_2 nanoparticles was occurred at 700°C , where diffraction peaks assigned to the rutile phase of TiO_2 were clearly observed after annealing at this temperature for 2 h (figure 3c).^{23,24}

To explore the possible application in potential fields, some performances of the nanostructured TiO_2 film with well-aligned rod-like nanoparticle aggregates were evaluated. Figure 4a shows the overview of the hierarchical TiO_2 film and the distribution of rod-like TiO_2 nanoparticle aggregates

Figure 3. XRD patterns of the rod-like TiO_2 nanoparticle aggregates (a) without heat treatment and after annealing at (b) 550°C and (c) 700°C for 2 h.

was uniform throughout the film. For the comparative study, the general TiO_2 films were also fabricated using commercial P25 nanoparticles by the screen printing method in the present investigation, as displayed in figure 4b and c. The magnified images revealed the disordered nanoparticles of conventional TiO_2 film.

The as-synthesized TiO_2 film with rod-like nanoparticle aggregates on a primary TiO_2 nanoparticle-based layer after annealing at 550°C was measured by degradation of MB to investigate the effect of the morphology on the photocatalytic activity, and conventional TiO_2 film composed of anatase TiO_2 nanoparticles was used as a comparison. Figure 5 shows the change of MB concentration over irradiation time in the absence of photocatalyst, and in the presence of conventional TiO_2 film and prepared TiO_2 films with rod-like nanostructures, respectively. Typically, the variation of maximum absorption around 664 nm in UV-vis absorption spectroscopy was applied to identify the change of MB concentration.²⁵ Control experiments indicated that MB hardly self-degraded in the absence of TiO_2 photocatalyst within irradiation period, as shown in figure 5a. From figure 5 curves b and c, it could be clearly seen that the photocatalytic activity of the TiO_2 film with rod-like nanostructures was much higher than that of conventional TiO_2 film. In addition, the typical linear correlation between $\ln(C_0/C)$ and irradiation time illustrated that the photodegradation kinetics were first-order reactions for all of the samples. The photocatalytic degradation reaction rate constants of MB on the TiO_2 film with rod-like

Figure 4. SEM images of (a) overview of the nanostructured TiO₂ film with rod-like nanoparticle aggregates; (b) and (c) prepared conventional TiO₂ film at different magnifications.

Figure 5. Concentration changes of MB as a function of irradiation time using (a) no photocatalyst, (b) conventional TiO₂ film and (c) nanostructured TiO₂ film with rod-like nanoparticle aggregates as the photocatalyst, respectively.

nanostructures was about 0.01698 min^{-1} , which was nearly double that 0.00898 min^{-1} of conventional TiO₂ film. The TiO₂ film with rod-like nanostructures showed better results in photodegradation of MB under UV irradiation compared with the conventional TiO₂ film, so the photocatalytic properties of TiO₂ film were improved with the rod-like TiO₂ nanoparticle aggregates.

The test results of antibacterial activity of synthesized TiO₂ films are shown in figure 6. To rule out the biocidal effect of UV-ray itself, sterilized FTO glass substrate without coated TiO₂ was tested as control sample, and six repetitions of each type of sample were tested. As shown in figure 6, both the TiO₂ film with rod-like nanostructures and conventional TiO₂ film displayed antibacterial activity towards *S. aureus*, although to varying degrees. The bacterial colonies were enumerated by using plate count method. After 1 h of irradiation under UVA light, the TiO₂ film with rod-like aggregates proved to be 73.26% effective against *S. aureus*. While the antibacterial activity value only reached 52.05% on conventional TiO₂ film. The prepared TiO₂ film with rod-like aggregates exhibited an improvement in the antibacterial

Figure 6. Antibacterial effect of (a) control, (b) conventional TiO₂ film and (c) nanostructured TiO₂ film with rod-like nanoparticle aggregates against *S. aureus* after UV exposure (orange refers to 0 h; olive refers to 1 h).

activity. These results indicated that the rod-like TiO₂ nanoparticle aggregates played an important role in promoting the antimicrobial activity of TiO₂ film.

Figure 7A shows the photocurrent–voltage (*J*–*V*) curves measured from the two cells using as-synthesized TiO₂ film with rod-like nanoparticle aggregates and prepared conventional TiO₂ film as photoelectrodes, respectively. The details of photovoltaic data are listed in table 1. For the conventional TiO₂ film-based solar cell the generated photocurrent (*J*_{sc}) was 6.73 mA cm^{-2} , while the *J*_{sc} response of the as-prepared TiO₂ film with rod-like nanoparticle aggregate-based cell was 9.03 mA cm^{-2} . The achieved high photocurrent suggested that the rod-like TiO₂ nanoparticle aggregates improved the electron transportation. This result was consistent with the incident monochromatic photo-to-current conversion efficiency (IPCE) spectra as shown in figure 8. IPCE was defined as the number of electrons in the external circuit divided by the number of incident photons. The TiO₂ film with rod-like nanoparticle aggregate-based cell presented not only higher efficiency but also wider wavelength range than the conventional TiO₂ film-based solar cell. Taking the main

Figure 7. (A) Photocurrent–voltage curves of the DSSCs based on (a) the nanostructured TiO₂ film with rod-like nanoparticle aggregates and (b) prepared conventional TiO₂ film under simulated AM 1.5G sunlight illumination; (B) Proposed electron transport path in the rod-like TiO₂ nanoparticle aggregates.

Table 1. Photovoltaic performance of the DSSCs based on different photoanodes.

Photoanodes	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)
Rod-like TiO ₂ nanoparticle aggregates	9.03	605	0.51	2.75
Disordered TiO ₂ nanoparticles	6.73	609	0.61	2.44

Figure 8. Photocurrent action spectra of the DSSCs based on (a) the nanostructured TiO₂ film with rod-like nanoparticle aggregates and (b) prepared conventional TiO₂ film.

structure features of the rod-like TiO₂ nanoparticle aggregates into account, as shown in figure 7B, the rod-like TiO₂ nanoparticles aggregate provided a direct transport path for electron, which not only enhanced the electron transfer efficiency but also led to the reduction of charge recombination.

In addition, this improvement was partially ascribable to the fast electron transport, and partially attributed to the dye loading capability. The as-prepared rod-like nanostructure was a well-aligned aggregate of nearly spherical TiO₂ nanoparticles, so it can take advantage of the high surface area of nanoparticles. The maximum IPCE value for TiO₂ film with rod-like nanoparticle aggregates is about 59%, which indicated that further improvement should be achievable through increasing the thickness of film. Attributed to this enhanced photocurrent, the overall conversion efficiency (η) of the TiO₂ film with rod-like nanoparticle aggregate-based DSSC was higher than that of the conventional TiO₂ film-based DSSC.

4. Conclusions

In summary, the novel rod-like crystalline TiO₂ nanostructure in the form of well-aligned nanoparticles aggregate has been prepared using a slow hydrolysis method with no use of template. The detailed chemical reactions were performed to explain the formation process. A ‘stacking growth’ schematic model including three steps of substitution, hydrolysis and stacking was performed to explain the formation process of TiO₂ film with rod-like nanoparticle aggregates. Compared with traditional nanoparticle-based TiO₂ film, the hierarchical TiO₂ film exhibited a higher photocatalytic activity in degradation of MB. Attribution of rod-like nanoparticle aggregates on the surface enhanced the antibacterial efficiency towards *S. aureus*. As photoanode in DSSC, the hierarchical TiO₂ film greatly increased the photocurrent and finally resulted in more conversion efficiency. These improved performances were believed to be attributed to the rod-like TiO₂ nanoparticle aggregates. Furthermore, the application of the slow hydrolysis growth method to other substrates for preparation of nanostructures should be available, and this new

class of well-aligned rod-like TiO₂ nanoparticle aggregate could find great promise for application in various fields.

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References

- Ojeda M L, Velasquez C, Renteria V, Campero A, García-Sánchez M A and Rojas F 2015 *Bull. Mater. Sci.* **38** 29
- Chen S, Chu W, Huang Y Y, Liu X and Tong D G 2012 *Mater. Res. Bull.* **47** 4514
- Li J, Liu X, Qiao Y, Zhu H and Ding C 2014 *Colloid Surf. B* **113** 134
- Dalai S, Pakrashi S, Chakravarty S, Hussain S, Chandrasekaran N and Mukherjee A 2014 *Bull. Mater. Sci.* **37** 371
- Hwang D, Jo S M, Kim D Y, Armel V, MacFarlane D R and Jang S Y 2011 *ACS Appl. Mater. Interfaces* **3** 1521
- Manca M, Marco L, Giannuzzi R, Agosta R, Dwivedi C, Quattieri A, Cozzoli P D, Dutta V and Gigli G 2013 *Thin Solid Films* **568** 122
- Rodriguez C, Cara A, Renaud F N R, Freney J, Horvais N, Borel R, Puzenat E and Guillard C 2014 *Catal. Today* **230** 41
- Wu J J, Liao W P and Yoshimura M 2013 *Nano Energy* **2** 1354
- Chen X and Mao S S 2007 *Chem. Rev.* **107** 2891
- Liu J, Liu L, Bai H, Wang Y and Sun D D 2011 *Appl. Catal. B* **106** 76
- Thavasi V, Renugopalakrishnan V, Jose R and Ramakrishna S 2009 *Mater. Sci. Eng. R* **63** 81
- Saji V S and Pyo M 2010 *Thin Solid Films* **518** 6542
- Liu Z, Su X, Hou G, Bi S, Xiao Z and Jia H 2013 *J. Alloys Compd.* **555** 68
- Hong C K, Jung Y H, Kim H J and Park K H 2014 *Curr. Appl. Phys.* **14** 294
- Li Y, Guo M, Zhang M and Wang X 2009 *Mater. Res. Bull.* **44** 1232
- Page K, Palgrave R G, Parkin I P, Wilson M, Savin S L P and Chadwick A V 2007 *J. Mater. Chem.* **17** 95
- Bahloul W, Mélis F, Bounor-Legaré V and Cassagnau P 2012 *Mater. Chem. Phys.* **134** 399
- Anonymous 2013 *ISO 16187 Footwear and footwear components—Test method to assess antibacterial activity*
- Ai G, Sun W T, Zhang Y L and Peng L M 2011 *Chem. Commun.* **47** 6608
- Pal M, Serrano J G, Santiago P and Pal U 2007 *J. Phys. Chem. C* **111** 96
- Sedach P A, Gordon T J, Sayed S Y, Fürstehsupt T, Sui R, Baumgartner T and Berlinguette C P 2010 *J. Mater. Chem.* **20** 5063
- Cozzoli P D, Kornowski A and Weller H 2003 *J. Am. Chem. Soc.* **125** 14539
- Jiang X, Herricks T and Xia Y 2003 *Adv. Mater.* **15** 1205
- Jung J H, Shimizu T and Shinkai S 2005 *J. Mater. Chem.* **15** 3979
- Li X, Fu X and Yang H 2011 *Phys. Chem. Chem. Phys.* **13** 2809