PAPER

Highly photocatalytic TiO₂ interconnected porous powder fabricated by sponge-templated atomic layer deposition

To cite this article: Shengqiang Pan et al 2015 Nanotechnology 26 364001

View the article online for updates and enhancements.

Related content

- Atomic layer deposition: an enabling technology for the growth of functional nanoscale semiconductors Necmi Biyikli and Ali Haider
- <u>Significant photocatalytic performance</u> <u>enhancement of TiO2 by CeO2 atomic</u> <u>layer deposition</u> Xiaofeng Wang, Ye Jin and Xinhua Liang
- <u>Mechanism of strong visible light</u> photocatalysis by Ag2O-nanoparticledecorated monoclinic TiO2(B) porous nanorods Kamal Kumar Paul, Ramesh Ghosh and P K Giri

Recent citations

- <u>Assembly and Self-Assembly of</u> <u>Nanomembrane Materials-From 2D to 3D</u> Gaoshan Huang and Yongfeng Mei
- Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review Mika Sillanpää *et al*
- <u>Printable inorganic nanomaterials for</u> <u>flexible transparent electrodes: from</u> <u>synthesis to application</u> Dingrun Wang *et al*



LIVE WEBINAR

NanoRaman: Correlated Tip-Enhanced Optical Spectroscopy and Scanning Probe Microscopy

Thursday 8 March 15.00 GMT

REGISTER NOW!

physicsworld.com

Nanotechnology 26 (2015) 364001 (6pp)

Highly photocatalytic TiO₂ interconnected porous powder fabricated by sponge-templated atomic layer deposition

Shengqiang Pan^{1,6}, Yuting Zhao^{1,6}, Gaoshan Huang^{1,2}, Jiao Wang³, Stefan Baunack⁴, Thomas Gemming⁵, Menglin Li¹, Lirong Zheng³, Oliver G Schmidt⁴ and Yongfeng Mei¹

¹ Department of Materials Science, Fudan University, Shanghai 200433, People's Republic of China ² Key Laboratory of Inorganic Coating Materials, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

³ School of Information Science & Engineering, Fudan University, Shanghai 200433, People's Republic of China

⁴Institute for Integrative Nanosciences, IFW Dresden, Helmholtzstr. 20, D-01069 Dresden, Germany

⁵ Institute for Complex Materials, IFW Dresden, Helmholtzstr. 20, D-01069 Dresden, Germany

E-mail: gshuang@fudan.edu.cn

Received 4 May 2015, revised 8 June 2015 Accepted for publication 22 June 2015 Published 17 August 2015



Abstract

A titanium dioxide (TiO_2) interconnected porous structure has been fabricated by means of atomic layer deposition of TiO_2 onto a reticular sponge template. The obtained freestanding TiO_2 with large surface area can be easily taken out of the water to solve a complex separation procedure. A compact and conformal nanocoating was evidenced by morphologic characterization. A phase transition, as well as production of oxygen vacancies with increasing annealing temperature, was detected by x-ray diffraction and x-ray photoelectron spectroscopy, respectively. The photocatalytic experimental results demonstrated that the powder with appropriate annealing treatment possessed excellent photocatalytic ability due to the co-action of high surface area, oxygen vacancies and the optimal crystal structure.

S Online supplementary data available from stacks.iop.org/NANO/26/364001/mmedia

Keywords: TiO₂, atomic layer deposition, photocatalysis

(Some figures may appear in colour only in the online journal)

1. Introduction

Today's society is suffering from worsening environmental pollution and it is highly in demand to develop efficient methods to decompose toxic pollutants. In this case, photocatalytic degradation of the toxic pollutants from semiconductors is a promising solution to address the urgent problem [1]. TiO₂, because of its chemical stability, nontoxicity and favorable energy band structure, has been proven to be the most suitable photocatalyst [2, 3]. However, on the one hand, using TiO₂ in efficient photocatalytic degradation of toxic chemicals is still challenging, in terms of efficient charge separation channels [4, 5], high surface area [4, 6, 7], and optimal crystalline structure [7, 8]. One of the strategies to improve the efficiency stresses tailoring the size, shape and structure of TiO₂ particles [9–12]. TiO₂ porous structures have especially drawn much attention because of their excellent performance in photocatalytic systems [13]. Porous structures are advantageous for the enhanced surface-tovolume ratio, which allows a robust interaction with solvent and also for their reduced diffusion path length [14, 15]. On the other hand, although the suspended photocatalyst for elimination of pollutants has often been reported, the complex separation procedure of photocatalyst from purified water and

⁶ These authors contributed equally.



Scheme 1. Fabrication of TiO_2 interconnected porous structure. (a) The reticular sponge is used as raw material. (b) TiO_2 is deposited onto the sponge template. (c) After ALD, the sponge is coated by conformal TiO_2 nanocoating. (d) The sponge is thermally removed and the TiO_2 porous structure/powder can be obtained.

reuse of the photocatalyst are considered drawbacks. An immobilized mode such as a solid membrane is proposed as an alternative, although membranes are generally 2D and have reduced surface areas [16, 17]. For these reasons, the need for a freestanding structure with large surface area which can be easily separated from water should be solved simultaneously.

Atomic layer deposition (ALD) is a thin-film growth technique with the capability of conformal coverage of a three-dimensional structure with high aspect ratio based on sequential, self-limiting surface reactions [18–21]. There have been several reports on ALD of photocatalytic TiO₂. Different templates have been used for ALD of TiO₂. Ahn et al produced three-dimensional nanoshell titania with high uniformity by ALD on a polymer template prepared by proximity field nanopatterning [18]; Tan et al prepared photocatalytic well-aligned TiO₂ nanotube arrays via ALD of TiO₂ onto porous anodic alumina template [22]; Verbruggen et al fabricated photocatalytic spacious TiO₂ film by ALD on supported carbonaceous sacrificial template [14]; and Kim et al fabricated pure anatase TiO₂ submicrotube using electrospun poly(vinyl pyrrolidone) (PVP) fiber as a soft template [23]. However, some templates such as supramolecular nanotemplate [15] and electrospun polymer fiber template [23] require additional complex fabrication or surface modification processes [24]. This complex procedure sometimes makes it hard for up-scaled industrial production. Thus it remains challenging to find easily obtained and directly usable templates.

In this work, we used a commercially available and directly usable sponge as the template for TiO_2 deposition. Several precursors have been successfully used for ALD of TiO_2 . Titanium tetrachloride ($TiCl_4$) is widely invested as an inorganic precursor; however, its drawbacks include the corrosive by-product HCl and chlorine residues [25, 26]. Titanium alkoxides, such as titanium isopropoxide, are halide-free and non-corrosive, and therefore have been used as alternative precursors. One of the essential properties for the ALD precursor is a high reactivity with counter-reactants to reduce the cycle time [25]. The lesser reactivity of water

owing to the fact that a metal-halide bond is greater stronger than metal-nitrogen bond, metal amide compounds have significantly higher reactivity with water [25]. Therefore, titanium isopropoxide (TDMAT) and H₂O have been adopted for our current ALD processes. A compact and uniform layer of TiO₂ was coated on the reticular framework. After removal of sponge by post-annealing, a freestanding, interconnected porous structure was achieved. Moreover, the monolithic TiO₂ can be separated easily from the water and this freestanding behavior has promise for saving the complex separation procedure. Detailed structural properties were characterized and the results show a phase transition from pure anatase to a mixture phase of anatase and rutile with increasing annealing temperature, as well as production of oxygen vacancies. Photocatalytic abilities of the samples were studied by methyl orange (MO) decomposition under UV light, and obvious increasing photocatalytic ability was observed with increasing annealing temperature.

with titanium isoproposides has been reported [27], and

2. Experimental details

2.1. Preparation of TiO₂ porous powder

An illustration of the process for preparing TiO₂ porous powder is shown in scheme 1. Deposition was carried out at 150 °C in a homemade reactor. The template used here is commercially available reticular sponge which was cut into $2 \times 2 \times 0.5$ cm pieces and put into the pre-heated chamber (see figure S1 in the supplementary data). Tetrakis(dimethylamido) titanium (TDMAT) and water were used as precursors. Nitrogen (N₂) gas served as both carrier and purge gas. The flow rate of the carrier gas was 20 sccm and the deposition for TiO₂ nanocoating on sponge was conducted at ~20 Pa. A typical coating cycle used the following sequence: TDMAT pulse (200 ms), N₂ purge (20 000 ms), H₂O pulse (15 ms), N₂ purge (20 000 ms). After ALD process, the samples were calcinated at 500 °C and 550 °C for 3 h under a flow of 400 mL min⁻¹ O₂. The sponges were removed during this thermal treatment and TiO₂ interconnected porous structure was simultaneously formed, which is proved by the colour change from yellow (TiO₂ nanocoating on sponge, figure S1 (a)) to white (pure TiO₂ film, figure S1(b)).

2.2. Characterizations of morphology, crystallization and valence states

The morphology of the sample has been investigated by means of scanning electron microscopy (SEM, JEOL JSM-6701F) and transmission electron microscopy (TEM, Tecnai F30), The crystallinity and the phase composition of the samples have been characterized by x-ray diffraction (XRD) analysis on a Bruker D8 x-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). X-ray photoelectron spectroscopy (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer).

2.3. Photocatalytic performance evaluation

The photocatalytic activity of TiO₂ porous powder was monitored by immersing the powder with 1.5 cm^3 volume (weight: ~1.5 mg) into a borosilicate glass dish containing 6 mL methyl orange (MO) solution with an initial concentration of 10 mg L⁻¹. The photocatalyst concentration is thus 0.25 mg mL⁻¹. UV light irradiation is achieved with a 200 W xenon lamp (Lanpu, China), which is 50 cm away from the MO solution. The powder–MO suspension is allowed to equilibrate for 30 min prior to illumination. The variation in MO concentration is determined by measuring the change of light absorbance at 464 nm, which is the maximum absorption wavelengths of MO, using a Shimadzu UV-2550 spectrometer.

2.4. Surface area measurement

Nitrogen sorption isotherms were measured at 77 K with a QuadraSorb SI MP Station: 1. The samples were degassed in a vacuum at $250 \,^{\circ}$ C for 3 h before measurement.

3. Results and discussion

3.1. Structural characterizations

SEM images of the TiO₂ interconnected porous powder that are obtained by annealing TiO₂-coated (1000 ALD cycles) sponge at 550 °C are shown in figures 1(a) and (b). Figure 1(a) displays the top view of the TiO₂ interconnected porous powder with low magnification. One can easily see the porous structure with interconnected geometry. The diameter of the pores is roughly estimated to be 300 μ m, with large fluctuation. We compared the morphologies of the sample before and after annealing and found that TiO₂ film well duplicated the frame structure of the original sponge. This is understandable because of the conformity of the ALD technique. This advantage is also reflected by the homogeneous thickness of the TiO₂ nanocoating. A typical lateral views taken at the edge of the TiO_2 film with high magnification is displayed in figure 1(b), which proves that the TiO_2 film is compact, with a thickness of about 110 nm.

To check the structure of the TiO₂ nanocoating after annealing in more detail, TEM was carried out on the same sample. Prior to TEM observation, the sample was subjected to ultrasonic vibration for several seconds and the fragments were fished out using Cu grids to perform TEM characterization. The obtained TEM image in figure 1(c) further proves the uniformity of the TiO_2 film. In addition, the small thickness makes the TiO₂ film soft and folding of the film can be observed in the TEM image (deep black areas at edge in figure 1(c)). The high-resolution TEM image in figure 1(d)indicates that the TiO_2 is crystalline and the distance of the lattice fringes is determined to be 0.35 nm, corresponding to the (101) planes of anatase TiO_2 . The electron diffraction pattern (see figure S2 in the supplementary data) demonstrates that the TiO₂ possesses the tetragonal phase with space group 141 (see figure S3 in the supplementary data). We also noticed that a small amount of Ca can be detected by composition analysis during TEM, which was considered to be due to residual sponge after calcinations.

The compositions and the valence states of the TiO₂ porous powder were investigated by XPS as shown in figure 2. Figure 2(a) is the high-resolution XPS spectra of O1s, which shows that all spectra have a major peak at around 529.7 eV with a shoulder at higher bonding energy, indicating two different kinds of O species in the sample. The peak at 529.7 eV is ascribed to O^{2-} in crystal structure while the shoulder peak at higher bending energy is ascribed to oxygen vacancies [28]. The peak density of the shoulder peak turned stronger with the annealing temperature increasing from 500 to 550 °C, revealing an effect of the annealing temperature on the oxygen vacancy concentration. The high-resolution XPS spectrum of O1s of the as-deposited sample is shown in figure S4 in the supplementary data. It has been reported that the oxygen vacancy states have a direct effect on the electronic structure of TiO₂ by forming a donor level below the conduction band which will affect photocatalytic activities (see discussion below) [29]. Figure 2(b) shows the highresolution XPS spectra of Ti 2p. The peaks of $Ti^{4+}(2p_{3/2})$ and $Ti^{4+}(2p_{1/2})$ were confirmed with binding energy of 458.5 and 464.2 eV for the $\rm TiO_2$ annealed at 500 $^{\circ}\rm C$ and 458.3 eV and 464.1 eV for the TiO₂ annealed at 550 °C [30, 31]. It should be noted that both of $Ti^{4+}(2p_{3/2})$ and $Ti^{4+}(2p_{1/2})$ have a gradual red shift with increasing annealing temperature compared with the standard values from previous literature [32]. This phenomenon should be mainly attributed to the existence of Ti³⁺ located with lower binding energy, formed by the interaction of the electrons left in the oxygen vacancies and the adjacent Ti⁴⁺ [29]. This also proves the existence of oxygen vacancy in our TiO₂ porous samples.

Further insights on the nature of the formed TiO₂ porous powder are obtained from the XRD patterns as shown in figure 3. It shows that the as-deposited titania have no crystal structure (curve (a)). After being annealed at 500 °C in an O₂ atmosphere (curve (b)), intense and narrow diffraction peaks from the TiO₂ anatase phase are observed at $2\theta = 25.326^{\circ}$



Figure 1. Morphology of the TiO₂ interconnected porous powder: (a) SEM image with low magnification. (b) SEM image of the TiO₂ film with thickness of 110 nm from the lateral view. (c) TEM image of powder flakes prepared from the porous sample. (d) High-resolution TEM image showing the lattice fringe of the TiO₂ crystal.

(101), 37.831° (004), 48.08° (200), 53.941° (105) and 62.168° (213). When further increasing the temperature to 550 °C, represented by curve (c), another peak at $2\theta = 27.461^{\circ}$ appears, which is associated with (110) lattice plane of rutile TiO₂ phase, indicting a mixture of anatase and rutile phases. This result suggests a titania phase transformation from anatase to rutile at elevated temperature. The crystal phase discrepancy caused by thermal treatment could influence the photocatalytic performance (see discussion below).

3.2. Photocatalytic activities of samples

The photocatalytic activities of the samples in the degradation of MO were assessed by detecting the decomposition of 10 mg L^{-1} MO solution under UV irradiation with the same amount of photocatalysts (1.5 mg). Figure 4 shows the degradation of MO solutions as a function of irradiation time by calculating the absorbance of MO molecules at the peak featured at 464 nm. The concentration compensation has been taken into account in the calculation. As can be seen from figure 4, the annealed samples show far better photocatalytic activity than the unannealed sample. The sample annealed at 550 °C (curve (c)) leads to a 94.5% degradation after 120 min of UV illumination, and the values for samples annealed at 500 °C (curve (b)) and the unannealed sample (curve (a)) are 73.7% and 13.3%, respectively. This remarkable enhancement can be attributed to two factors. Firstly, we have proven the existence of oxygen vacancies in our sample. The oxygen vacancies can not only serve as positive charge centers with

which to trap the electron and inhibit the recombination of charge carriers, but they also favor the adsorption of O₂ on the surface and reduce absorbed O_2 by the trapped electrons to generate superoxide radicals, which play a key role in the oxidation of organics [33]. Moreover the presence of the oxygen vacancies in TiO₂ can efficiently expand the light absorption from the UV to the visible light by forming a donor level below the conduction band [29]. According to XPS spectra results, TiO₂ annealed at 550 °C have a stronger shoulder peak, demonstrating a large amount of oxygen vacancy in the sample annealed at 550 °C. Thus, TiO₂ annealed at 550 °C shows improved photocatalytic activity compared to the other samples. Secondly, the crystal phase discrepancy caused by thermal treatment may influence the photocatalytic performance. As disclosed by the aforementioned XRD results, after annealing at 500 °C, the amorphous TiO₂ nanocoating on the sponge template is converted to pure anatase, and annealing at 550 °C leads to a mixture of anatase and rutile phases. The enhanced photocatalysis in curve (c) agrees closely with many studies that pure anatase can lead to better photocatalysis than rutile or amorphous [34] and the addition of the relatively inactive rutile phase can significantly improve the photocatalytic activity of pure anatase [33], because the synergy between anatase and rutile leads to spatial charge separation and hinders recombination [35]. Thus, the oxygen vacancies and crystal phase discrepancy can significantly influence the photocatalytic performance. One thing to notice is that both factors arose from the change in annealing temperature. That is, there is a collaboration effect



Figure 2. XPS spectra of the TiO₂ powders annealed at 550 °C and 550 °C in O₂ atmosphere: (a) O1s and (b) Ti2p.

between two factors. Moreover, we compared the photocatalytic efficiencies of our samples to those reported in the literature, Yang et al for example, got a 50% degradation of MO by using a larger photocatalyst concentration of 1 mg ml⁻¹ in around 120 min [36]; Roy *et al* achieved a close degradation rate in 120 min with photocatalyst concentration around 0.4 mg ml^{-1} [37], which proves the better performance of our samples, even if the others were treated with more catalyst. We also noticed that for the TiO₂ annealed at the same temperature (550 °C), the TiO₂ interconnected porous powder shows better photocatalytic performance than flat TiO₂ film on Si substrate with the same photocatalyst amount: the degradation ability of the latter catalyst (94.5% at 120 min) is larger than that of the former (84.5% at 120 min) (see figure S5 in the supplementary data). The films in both cases possess anatase structure and therefore the enhancement cannot originate from the crystal structures. Considering the



Figure 3. XRD patterns of (a) as-deposited TiO_2 and TiO_2 annealed at (b) 500 °C and (c) 550 °C, respectively.



Figure 4. Photodegradation of MO by the ALD-deposited TiO_2 under UV light irradiation. All the TiO_2 interconnected porous powders (curves (a), (b) and (c)) were deposited with 1000 ALD cycles, and a photcatalyst concentration of 0.25 mg mL⁻¹ was used in the experiment. Curve (a) represents as-deposited TiO_2 film on sponge. Curve (b) represents TiO_2 interconnected porous powder annealed at 500 °C. Curve (c) represents TiO_2 interconnected porous powder annealed at 550 °C. Curve (d) represents photoactivity performance of TiO_2 in reference [36] (with photocatalyst concentration of 1 mg mL⁻¹).

morphological difference, we think the enhancement indicates that the sponge acting as template greatly enhanced the surface area ($106 \text{ m}^2 \text{ g}^{-1}$, figure S6) and TiO₂ for degradation. The larger contact area between the TiO₂ and MO solution can be conducive to trap more photons with the irradiation of the UV light and then more electrons and holes are generated and consequently contribute to promoted photocatalytic activity. However, detailed quantitative analysis shows that the surface area of the interconnected porous powder is 52 times larger than that of the flat film and the enhancement in photocatalytic activity is obviously moderate. It is possible that the high aspect ratio of the powder does not allow for efficient diffusion of the MO dye and the degradation products (no stirring was used in the experiment) [38]. Insufficient penetration of the light all the way to the bottom of the pores is another possible reason that it produces such inconsistencies [38]. On the other hand, in the case of the flat TiO_2 film, the thin solution layer can guarantee sufficient light penetration and solution/film contact. As a result, the detected enhancement of photocatalytic activity is less than expected.

4. Conclusions

We have demonstrated here a simple method to prepare high surface area, mixed-phase TiO_2 interconnected porous powder by depositing TiO_2 nanocoating on sponge template using ALD technique. The high surface areas of TiO_2 interconnected porous powder, the oxygen vacancies, and the mixture of anatase and rutile phases associated with thermal treatment result in significantly enhanced photocatalytic activity, as evidenced by the degradation of MO under UV light illumination. The method introduced in this paper for fabricating an efficient TiO_2 photocatalyst is straightforward and believed to be applicable to waste treatment, or even for other applications, such as sensors and solar cells.

Acknowledgments

This work is supported by the Natural Science Foundation of China (nos. 51322201 and 51102049), Project Based Personnel Exchange Program with CSC and DAAD, Specialized Research Fund for the Doctoral Program of Higher Education (no. 201100711200095), Science and Technology Commission of Shanghai Municipality (nos. 12520706300 and 12PJ1400500), and Key Laboratory of Inorganic Coating Materials, Chinese Academy of Sciences.

References

- [1] Tong H, Ouyang S X and Bi Y P 2014 Adv. Mater. 24 229
- Maness P C, Smolinski S, Blake D M, Huang Z, Wolfrum E J and Jacoby W A 1999 *Appl. Environ. Microbiol.* 65 4094
- [3] Byrne J A, Eggins B R, Brown N M D, McKinnery B and Rouse M 1999 Appl. Catal. B 17 25
- [4] Regan B O and Grätzel M 1991 Nature 353 737
- [5] Snaith H J, Zakeeruddin S M, Schmidt-Mende L, Klein C and Grätzel M 2005 Angew. Chem. Int. Ed. 44 6413
- [6] Martinson A B F, Hamann T W, Pellin M J and Hupp J T 2008 Chem. Eur. J. 14 4458

- [7] Kim Y J, Lee M H, Kim H J, Lim G, Choi Y S, Park N G, Kim K and Lee W I 2009 Adv. Mater. 21 3668
- [8] Lee J S, You K H and Park C B 2012 Adv. Mater. 24 1084
- [9] Chen X and Mao S S 2007 Chem. Rev. 107 2891
- [10] Kitano M, Takeuchi M, Matsuoka M, Thomas J M and Anpo M 2005 Chem. Lett. 34 616
- [11] Kamat P V 2007 J. Phys. Chem. C 111 2834
- [12] Usseglio S, Damin A, Scarano D, Bordiga S, Zecchina A and Lamberti C 2007 J. Am. Chem. Soc. 129 2822
- [13] Li W, Wu Z X, Wang J X, Elzatahry A A and Zhao D Y 2014 Chem. Mater. 26 287
- [14] Verbruggen S W, Deng S, Kurttepeli M, Cott D J,
 Vereecken P M, Bals S, Martens J A, Detavernier C and Lenaerts S 2014 Appl. Catal. B 160 204
- [15] Ceylan H, Ozgit-Akgun C, Erkal T S, Donmez I, Garifullin R, Tekinay A B, Usta H, Biyikli N and Guler M O 2013 Sci. Rep. 3 2306
- [16] An S, Lee M W, Joshi B N, Jo A, Jung J and Yoon S S 2014 Ceram. Int. 40 3305
- [17] Yu J C, Ho W, Lin J and Yip H 2003 Environ. Sci. Technol. 37 2296
- [18] Ahn C, Park J, Kim D and Jeon S 2013 Nanoscale 5 10384
- [19] Kemell M, Pore V, Ritala M, Leskelä M and Lindén M 2005 J. Am. Chem. Soc. 127 14178
- [20] Puurunen R L 2005 J. Appl. Phys. 97 121301
- [21] Johnson R W, Hultqvist A and Bent S F 2014 Mater. Today 17 236
- [22] Tan L K, Kumar M K, An W W and Gao H 2010 ACS Appl. Mater. Interfaces 2 498
- [23] Kim G M, Lee S M, Michler G H, Roggendorf H, Gosele U and Knez M 2008 Chem. Mater. 20 3085
- [24] Cavanagh A S, Wilson C A, Weimer A W and George S M 2009 Nanotechnology 20 255602
- [25] Lim G T and Kim D H 2006 Thin Solid Films 498 254
- [26] Reiners M, Xu K, Aslam N, Devi A, Waser R and
- Hoffmann-Eifert S 2013 *Chem. Mater.* **25** 2934 [27] Xie Q, Jiang Y L, Detavernier C, Deduytsche D, Von Mairhagehe P L, Pu C P, Li P, Z and Ou X L
- Van Meirhaeghe R L, Ru G P, Li B Z and Qu X P 2007 J. Appl. Phys. **102** 083521
- [28] Fang W Z, Xing M Y and Zhang J L 2014 Appl. Catal. B 160 240
- [29] Pan X Y, Yang M Q, Zhang N and Xu Y J 2013 Nanoscale 5 3601
- [30] Zhang X B, Tian H M, Wang X Y, Xue G G, Tian Z P, Zhang J Y, Yuan S K, Yu T and Zou Z G 2013 Mater. Lett. 100 51
- [31] Ren Y Q, Li J P and Yu J 2014 Electrochim. Acta 138 41
- [32] Li M L, Huang G S, Wang D X, Zhang J, Shi J J and Mei Y F 2013 Nanotechnology 24 305706
- [33] Zhang Z, Wang W Z, Gao E P, Shang M and Xu J H 2011 J. Hazard. Mater. 196 255
- [34] Sohn Y S, Smith Y R, Misra M and Subramanian V 2008 Appl. Catal. B 84 372
- [35] Fresno F, Coronado J A, Tudela D and Soria J 2005 Appl. Catal. B 55 159
- [36] Yang H, Zhang K, Shi R R, Li X W, Dong X D and Yu Y M 2006 J. Alloys Compd. 413 302
- [37] Roy N, Park Y, Sohn Y, Leung K T and Pradhan D 2014 ACS Appl. Mater. Interfaces 6 16498
- [38] Kemell M, Pore V, Tupala J, Ritala M and Leskelä M 2007 Chem. Mater. 19 1816