Photocatalytic H$_2$ Evolution: Dealloying as Efficient Tool for the Fabrication of Rh-decorated TiO$_2$ Nanotubes

Mohsen Sheikhzadeh,[a, b] Seyedsina Hejazi,[a] Shiva Mohajernia,[a] Ondrej Tomanc,[c] Mohamed Mokhtar,[d] Abdulmohsen Alshehri,[d] Sohrab Sanjabi,[b] Radek Zboril,[c] and Patrik Schmuki*[a, c]

In this work, we report on a facile and novel method for decorating titanium dioxide (TiO$_2$) nanotubes with Rh nanoparticle-nanowires networks that act as co-catalysts in photocatalytic H$_2$ evolution. In a first step, a Ti–Rh (0.2 at%) alloy is etched in Kroll’s solution leading to a dealloyed surface decorated with a Rh nanoparticle-network of adjustable geometry and loading. By subsequent anodization of the alloy samples, Rh/TiO$_2$ nanotubes can be grown where the tube mouths are strongly decorated with the Rh nanoparticle network (RhNW). As evident from X-ray photoelectron spectroscopy (XPS) analysis, these Rh oxide Nws are converted to metallic Rh under UV irradiation. As a result, with time a steady increase of the H$_2$ evolution from the RhNW decorated TiO$_2$ nanotubes is observed. Nanotubes carrying RhNW yield in photocatalytic experiments a 5-times higher H$_2$ evolution activity in comparison with nanotubes decorated by conventional Rh-sputtering (the same loading), and show a 228 times higher activity than pristine TiO$_2$ nanotubes.

Introduction

Nowadays green energy sources have attracted great attention due to the environmental concerns arising from burning fossil fuels,[5, 11] One of the most promising clean energy sources is hydrogen.[3, 4] Hydrogen carries a high chemical potential energy, which can be converted to electricity or momentum while reacting with oxygen and produce water as a by-product.[10] While currently most hydrogen is generated by steam reforming, a much greener way would be the photocatalytic splitting of water or other suitable H$_2$ sources on an illuminated semiconductor.[6–12]

Titanium dioxide is one of the most studied semiconductors for photocatalysis due to its unique properties such as high photocorrosion resistivity, nontoxicity, low cost, and most importantly a suitable conduction band position for H$_2$ formation from aqueous environments. TiO$_2$ can be used in different nanostructures, namely nano-wires, nano-rods, nano-powders. Anodic TiO$_2$ nanotubes (TNs) offer some superior features such as high surface area, orthogonal charge separation, directional charge transfer and an excellent back contact for the nanostructures.[13–15]

Despite unique properties of TNs, the hydrogen evolution reaction (HER) from water on a TiO$_2$ surface is kinetically hampered.[16–18] This is due to the fact that charge transfer at the TiO$_2$/water interface is naturally sluggish. To tackle this problem, TNs are often modified with suitable noble metal co-catalysts, particularly Au, Ru and Pt, which allow a faster extraction of the excited electron from TiO$_2$ conduction band to the noble metal, and subsequently transfer it to the solution. This consequently results in a significantly enhanced photocatalytic hydrogen evolution.[19–21]

Several modification approaches with a suitable co-catalyst have been reported in the last years.[22–25] Typically these co-catalytic metals are decorated uniformly on TiO$_2$ nanotubes with common deposition methods such as chemical deposition,[26] electrochemical deposition,[27] and sputter-deposition.[28]

Previously it was shown that selective top decoration of nanotubes, particularly by noble metals nanoparticles (NPs), show a more efficient H$_2$ production (for the same loading) than uniformly decorated TNs.[29] Additionally it was previously reported that porous co-catalysts formed by dealloying could significantly improve electrocatalytic and photocatalytic reactions, as they provide a higher surface area for the catalytic reactions.[30–32] Therefore, combination of dealloying and site-selective decoration is a promising approach to improve effectiveness and at a same time minimize the loading of noble metal decoration to achieve a more efficient photocatalytic H$_2$ evolution.

[caption]M. Sheikhzadeh, S. Hejazi, S. Mohajernia, Prof. Dr. P. Schmuki
Department of Materials Science
University of Erlangen-Nuremberg
Institute for Surface Science and Corrosion WW4-LXO
Martensstraße 7, 91058 Erlangen (Germany)
E-mail: Schmuki@ww.uni-erlangen.de
[b] M. Sheikhzadeh, Prof. Dr. S. Sanjabi
Department of Materials Science, Nanomaterials Group
Tarbiat Modares University
P.O. Box: 14115–143, Tehran (Iran)
[c] O. Tomanec, Prof. Dr. R. Zboril, Prof. Dr. P. Schmuki
Regional Centre of Advanced Technologies and Materials
Palacky University Olomouc
Listopadu 50 A, 772 07 Olomouc (Czech Republic)
[d] Prof. Dr. M. Mokhtar, Prof. Dr. A. Alshehri
Chemistry Department, Faculty of Sciences
King Abdul-Aziz University
80203 Jeddah (Saudi Arabia)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.201901183

This manuscript is part of the Special Issue “Photocatalysis: From Solar Power to Sustainable Chemical Production”, which is part of the wider project “Building A New Economy with Catalysis”.

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.
Generally, co-catalysts such as Pt or Rh are most efficient in promoting H\(_2\) generation – they are located at the peak of the volcano diagram of electrocatalytic H\(_2\) production. This means that not only Pt requires low activation energy to transform H\(^+\) to atomic absorbed hydrogen but also have predominantly low barriers for surface recombination of adsorbed atomic hydrogen to H\(_2\).[33]

In the present work, we introduce a new strategy for top decorating TiO\(_2\) nanotubes with Rh NPs in the form of optimized coherent networks. We show that by suitable dealloying of a Ti–Rh alloy a self-organizing Rh-NC network can be formed on the surface of a Ti-alloy. After subsequent anodization, this network remains on the anodically formed tube’s mouth. This results in a TiO\(_2\) nanotubular structure decorated at the tube top by Rh oxide nano-networks. Moreover, we find that Rh-oxide in the RhNw under UV irradiation is increasingly converted to metallic Rh. This in turn leads to a steady increase of the H\(_2\) evolution during the photocatalytic process. Optimized Rh loading can achieve a significantly higher photocatalytic H\(_2\) evolution efficiency than the same amount of Rh loaded by conventional approaches.

Results and Discussion

In the present work, we used sheets of Ti and Ti–Rh 0.2 at.% with surfaces that were mirror polished and treated in Kroll solution. Figure 1a–c and Figure S1a–c in the Supporting Information show the SEM images of the titanium mirror polished and dealloyed surfaces of the Ti–Rh 0.2 at.% alloys after different treatment times in Kroll solution. As anticipated, by this treatment Ti is dissolved selectively and mainly a metallic RhNw remains on the surface that in an ideal case forms fully interconnected structures. Figure 1d–f and Figure S1d-i show the SEM images of top and cross sections of the pristine TiO\(_2\) nanotubes, TNs decorated with Rh nano-networks after dealloying for different times from 30 s to 480 s. SEM images show that RhNw mainly cover the nanotube’s mouth – the procedure is shown in Scheme S1 in the Supporting Information. The SEM images together with EDX result in Figure S2 in the Supporting Information reveal that by increasing dealloying time from 30 s to 480 s, the amount of RhNw increases, and after 120 s, the nano-networks tend to agglomerate and form an interconnected network on the surface of the nanotubes. The nanotubular structure under these conditions consists of tubes with an inner diameter of 120 nm and a length of ~7 μm.

Figure 2a shows the EDS elemental map in the cross sectional view of the 120 s dealloyed TiRh nanotubes (DTiRh120-TNs). The EDS map confirms the SEM results and shows that the Rh nano-networks are mainly located at the TiO\(_2\) nanotube’s mouth. Also the high-angle annular dark-field imaging (HAADF) shows the presence and accumulation of RhNw on the nanotube mouths (see inset Figure 2a). The high resolution TEM (HR-TEM) images of DTiRh120-TNs from the nanotube mouth in Figure 2b confirm the development of RhNw in form of nano-networks and NPs with an average size of ~7 nm. The SAED pattern of the same position in Figure 2c shows scattering rings corresponding to anatase and Rh.

Figure 1. SEM image of (a) titanium polished surface, (b) TiRh alloy after 120 s of dealloying, and (c) TiRh alloy after 240 s of dealloying; (d) top view of TNs, (e) top view of DTiRh120 TNs, (f) top view of DTiRh240 TNs.

Figure 2. (a) TEM image of the cross section of DTiRh120-TNs; (b) Top view TEM image of DTiRh120-TNs; (c) SAED pattern of the DTiRh120-TNs sample; EDX map of (d) Ti, (e) O and (f) Ti–O–Rh in DTiRh120-TNs sample.
-- the latter indicates the metallic nature of the decorated nanonetworks. Figure 2d-f show the TEM-EDS elemental maps of Ti, O and mixture of Ti, O and Rh of the DTiRh120-TNs nanotube’s mouth.

In order to characterize the phase composition, X-ray diffraction (XRD) was performed on the pristine TNs, TiRh-TNs and DTiRh120-TNs layers (Figure 3a). The diffraction peaks at 25.3° and 37.8° confirm the formation of anatase phase (JCPDS Card no. 21-1272). The signals from the Ti metal substrate show a hexagonal close packed (hcp) crystal α phase structure, and the position of the XRD reflections corresponds well to data in the literature (JCPDS card no. 44-1294). No signals can be attributed to Rh as the amount of Rh is probably below the detection limit of XRD.

To investigate the effect of UV illumination on the chemical composition of Rh in DTiRh120-TNs, X-ray photoelectron spectroscopy (XPS) was employed and the results are presented in Figure 3b-c. The XPS surveys of pristine TiO$_2$, TiRh TNs and DTiRh120-TNs (Figure 3b) show that all the structures are composed of Ti, O, and small traces of adventitious carbon. For the DTiRh120-TNs sample Rh and F (due to dealloying in a fluoride rich solution) are also evident. Figure 3c shows the high resolution XPS spectra of Rh 3d for the Rh decorated tube before and after UV illumination. From the XPS result, one can see a clear shift towards higher binding energy for the illuminated sample. The main peaks at 307.40 eV and 312.18 eV in the illuminated sample correspond to Rh$^{5/2}$ 3d$_{3/2}$ and Rh$^{3/2}$ 3d$_{5/2}$ while the peaks at 308.58 eV and 313.41 eV in the non-illuminated sample are related to Rh$^{3+}$ 3d$_{3/2}$ and Rh$^{2+}$ 3d$_{5/2}$ respectively. XPS results show that after illumination a tiny amount of surface rhodium oxide (Figure 2e) is reduced to metallic nanonetworks.

To determine the role of visible light in photocatalytic performance of the samples, IPCE was measured for pristine TiO$_2$, TiRh TNs and DTiRh120-TNs samples and the data are presented in Figure 3d. The results show a higher IPCE value in the UV range and a negligible IPCE value in visible range for the DTiRh120-TNs and TiRh-TNs samples. Additionally, in the present work the band gap remains unchanged and shows a value of 3.12 eV for both structures (see Figure 3e and Table S4). It has been reported previously that anodization of Ti–X alloys can result in the formation of X doped TNs. Therefore, formation of Rh doped TiO$_2$ via anodization of Ti–Rh alloy is likely. Doping Rh in low content (below 0.1 at. %) in TiO$_2$ results in formation of oxygen vacancies and as a result enhanced conductivity, and doping in high content (above 0.1 at.% ) introduces Rh$^{1+}$ 3d states in the band gap of TiO$_2$ and significantly enhanced visible light absorption.$^{34,35}$ In the present work, the amount of Rh in the oxide is 0.05 at.%, and based on the negligible visible response in IPCE data, it can be concluded that Rh doping in TNs leads to enhanced conductivity which results in higher IPCE in UV region. Mott Schottky measurements were done and the result are presented in in Figure S3 in the Supporting Information and flat band potential are listed in Table S1. The presented results show accordingly a very small negative shift of the flat band potential for the de-alloyed samples compared with the pristine titanium oxide.

Electrochemical impedance spectroscopy and intensity modulated photocurrent spectroscopy under UV were carried out and the results are reported in Figure S4a,b in the Supporting Information. The results indicate similar photo impedance spectra and overall charge transfer resistance in the low frequency range for the doped and pristine TiO$_2$ nanotube layers and a slightly lower charge transfer resistance for the decorated sample, and this further confirms differences in IPCE results for the mentioned samples. IMPS results also similarly confirm that the TNs, which grow on Ti–Rh alloys, benefit from lower electron transfer coefficient.

Figure 4a shows the open circuit photocatalytic H$_2$ evolution results of the TiO$_2$ nanotubes with different loading of Rh as a function of dealloying time as well as pristine TNs and conventionally Rh decorated TNs. The tubes were intentionally prepared with the same concentration as the optimized sample to show the advantage of the decorating dealloying treatment. The results show that by increasing the dealloying time up to 120 s, H$_2$ evolution rate is enhanced. However, further increasing the dealloying time has a detrimental effect on the H$_2$ evolution rate. This can be ascribed to the agglomeration of nanonetworks in higher loading, which not only decreases the active surface area for H$_2$ evolution but also the agglomerated nanonetworks can interfere with the light absorption on the surface of TiO$_2$. The enhancement in H$_2$ evolution rate for the Rh decorated tubes can be mainly attributed to the metallic nature of the Rh. The metallic Rh forms localized Rh/TiO$_2$ Schottky junctions along the TiO$_2$ NT mouth. The Rh co-catalytic centers can act as electron-traps for...
TiO₂ CB electrons, thereby facilitating charge separation, and also as an electron transfer mediator by transferring electrons to the electrolyte for H₂ evolution reaction. By this approach, electron-hole recombination in TiO₂ can be limited, consequently leading to enhanced photocatalytic performances.²⁶,²⁷

In order to additionally evaluate the visible light contribution in open circuit H₂ evolution rate of the Rh decorated TiO₂ nanotubes, the samples were irradiated by UV and visible light sources, separately. The result in Figure 4b shows that the effect of visible light absorption on the enhanced H₂ evolution rate is negligible, as for the sample irradiated by 520 nm laser there was no detectable H₂ and for the 400 nm irradiated sample very little H₂ was found, which is in line with IPCE results. Figure 4c shows the time dependent trend of H₂ evolution rate of DTRh120-TNs for 6 hours. The time dependent results indicate that the H₂ evolution rate is slower at the first 2 hours and it increases with time until it reaches a constant value in longer illumination times (slope in Figure 4c represents H₂ evolution rate). Figure 4d shows the reusability result of the Rh decorated sample. It is evident that in the beginning of the illumination (first 1 h), the H₂ evolution rate is slow, which is due to the conversion of Rh oxide to metallic Rh with higher catalytic activity. By further illumination, H₂ evolution rate is enhanced by a constant rate and no sign of inactivity can be observed in H₂ evolution.

Electrochemical impedance spectroscopy was measured for the dealloyed layers. The Bode plot and the corresponding extracted surface areas are shown in Figure S5 and Table S2 in the Supporting Information. The extracted specific surface areas are well in line with the H₂ evolution results. This further illustrates the importance of the porous structure of the de-alloyed nanoparticles.

Conclusions

In conclusion, we demonstrate a facile and novel method for decorating titanium dioxide (TiO₂) nanotubes with Rh nanonetworks using dealloying followed by anodization for photocatalytic applications. The TiO₂ nanotubes decorated with Rh nanonetworks show a superior photocatalytic activity which is 5-times higher than the conventional Rh decorated TiO₂ nanotubes, and 228 times higher than pristine TiO₂ nanotubes. The key is the porous structure of the dealloyed nanonetworks, which can provide a high active surface area. A secondary key for an efficient H₂ evolution is the reduction of Rh oxide to Rh metal under UV irradiation. Moreover, the dealloyed Rh decorated TiO₂ nanotubes are stable and the high rate of hydrogen evolution under UV irradiation is maintained over a time period of 6 hours.

Experimental Section

The samples were denoted as “DTRhX-TNs”, where “D” stands for “Dealloying”, and “X” stands for the dealloying time in seconds. Ti–Rh alloy (0.2 at%) was fabricated by Hauner Metallische Werkstoffe of Germany. The samples were degreased by sonicating in acetone, ethanol, and deionized water followed by drying in N₂ stream. The dealloying solution consists of 3 mL HF, 6 mL HNO₃, and 100 mL water. The TiRh substrates were immersed in the dealloying solution and then washed with deionized water. The dealloying times were varied from 30 s to 480 s.

The dealloyed Ti–Rh alloy served as an anode and a Pt sheet was used as a cathode. The anodizing of the samples was performed by applying a potential of 60 V for 20 min using a DC power supply (VSP 2653HE). After anodization, the samples were rinsed with ethanol and dried under N₂ stream. To obtain a crystalline structure the samples were annealed at 450 °C in tube furnace under air condition. This annealing temperature was used, as it does not result in doping of the noble metals from decorated material into the TiO₂ structure.⁴⁰–⁴⁲

One of the conventional processes for deposition is sputtering. For comparison of the hydrogen production, some samples were Rh-decorated with the same atomic concentration as for the optimum sample by sputter-deposition. The sputter-deposition of Rh on the anodic TiO₂ films was carried out using a high vacuum sputter coater (Leica-EM SCDS00). The sputtered Rh decorated TiO₂ samples were air annealed at 450 °C.

Field-emission scanning electron microscope (FE-SEM, Hitachi S4800) and high resolution transmission electron microscope (HRTEM, FEI TITAN G2 60-300) were used to study the morphology of samples. The chemical composition was characterized using X-ray photoelectron spectroscopy (XPS, PHI 5600, US) and peak positions were calibrated on the C 1s peak at 284.8 eV. The crystallographic properties of materials were examined by X-ray diffraction (XRD) with an X'pert Philips MPD (equipped with a Panalytical X'celerator detector).

To evaluate the produced hydrogen rate, a quartz cell was used where the sample was placed inside the cell and filled with methanol/water (50/50 vol%). The cell was deaerated with N₂ for 20 min. The enclosure was completely sealed and placed in front of the light sources with
Acknowledgements

The authors would like to acknowledge the ERC, the DFG and the Operational program research, Development and education (European regional development Fund, Project No. CZ.02.1.01/0.0/0.0/15_003/0000416 of the ministry of education, youth and sports of the Czech Republic) for this project. This work was in part funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant no. RG-25-130-40. The authors, therefore, acknowledge with thanks DSR technical and financial support. The authors would also like to express their sincere thanks to Dr. Narasimharao Katabathini for his technical help.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: photocatalytic properties · titanium oxide nanotube · Rhodium oxide · anodizing · Ti-Rh alloy

[1] J. Hansen, M. Sato, R. Ruedy, A. Lacis, V. Oinas, Proc. Natl. Acad. Sci. USA 2000, 97, 9875–9880.
[2] A. A. Leisnerowitz, Risk Anal. 2005, 25, 1433–1442.
[3] A. G. Stern, Int. J. Hydrogen Energy 2018, 43, 4244–4255.
[4] B. Rohland, J. Nitsch, H. Wendt, J. Power Sources 1992, 37, 271–277.
[5] J. D. Holladay, J. Hu, D. L. King, Y. Wang, Catal. Today 2009, 139, 244–260.
[6] D. Gao, X. Wu, P. Wang, Y. Xu, H. Yu, J. Yu, ACS Sustainable Chem. Eng. 2019, 7, 10084–10094.
[7] Y. Kojima, M. Fukui, A. Tanaka, K. Hashimoto, H. Kominami, ChemCatChem 2018, 10, 3605–3611.
[8] H. Yu, W. Liu, X. Wang, F. Wang, Appl. Catal. B 2018, 225, 415–423.
[9] H. Cho, W. Dong Kim, J. Yu, S. Lee, D. C. Lee, ChemCatChem 2018, 10, 5679–5688.
[10] E. Borgarello, J. Kiwi, M. Grätzel, E. Pelizzetti, M. Visca, J. Am. Chem. Soc. 1982, 104, 2996–3002.
[11] M. Kitano, M. Matsuoka, M. Ueshima, M. Anpo, Appl. Catal. A 2007, 325, 1–14.
[12] G. N. Schrauzer, T. D. Guth, J. Am. Chem. Soc. 1977, 99, 7189–7193.
[13] I. Paramasivam, H. Jha, N. Liu, P. Schmuki, Small 2012, 8, 3073–3080.
[14] P. Roy, S. Berger, P. Schmuki, Angew. Chem. Int. Ed. 2011, 50, 2904–2939; Angew. Chem. 2011, 123, 2956–2995.
[15] K. Lee, A. Mazare, P. Schmuki, Chem. Rev. 2014, 114, 9385–9454.
[16] J. Low, B. Cheng, J. Yu, Appl. Surf. Sci. 2017, 392, 658–686.
[17] H. Bian, N. T. Nguyen, J. Yoo, S. Hejazi, S. Mohajerian, J. Müller, E. Spiecker, H. Tsuchiya, O. Tomanc, B. E. Sanabria-Arenas, ACS Appl. Mater. Interfaces 2018, 10, 18220–18226.
[18] S. Mohajerian, S. Hejazi, A. Mazare, N. T. Nguyen, P. Schmuki, Chem. Eur. J. 2017, 23, 12406–12411.
[19] S. Hejazi, M. Altomare, N. T. Nguyen, S. Mohajerian, M. Licklederer, P. Schmuki, Appl. Mater. Today 2019, 14, 118–125.
[20] T. Sreetawongs, S. Yoshikawa, Catal. Commun. 2005, 6, 661–668.
[21] J. Prakash, S. Sun, H. C. Swart, R. K. Gupta, Appl. Mater. Today 2018, 11, 82–135.
[22] C.-Y. Su, L.-C. Wang, W.-S. Liu, C.-C. Wang, T.-P. Peng, ACS Appl. Mater. Interfaces 2018, 10, 33287–33295.
[23] Y. Tan, Z. Shu, J. Zhou, T. Wang, Z. Zhao, Appl. Catal. B 2018, 230, 260–266.
[24] W. Y. Lim, H. Wu, Y.-F. Lim, G. W. Ho, J. Mater. Chem. A 2018, 6, 11416–11423.
[25] J. Xu, W.-M. Yang, S.-J. Huang, H. Yin, H. Zhang, P. Radianovic, Z.-L. Yang, Z.-Q. Tian, J.-F. Li, Nano Energy 2018, 49, 363–371.
[26] S. Mohajerian, S. Hejazi, A. Mazare, N. T. Nguyen, I. Hwang, S. Kment, G. Zoppellario, O. Tomanc, R. Zboril, P. Schmuki, Mater. Today 2017, 6, 46–52.
[27] N. Liu, K. Lee, P. Schmuki, Angew. Chem. Int. Ed. 2013, 52, 12381–12384; Angew. Chem. 2013, 125, 1260–1267.
[28] N. T. Nguyen, M. Altomare, J. Yoo, P. Schmuki, Adv. Mater. 2015, 27, 3308–3315.
[29] N. T. Nguyen, J. Yoo, M. Altomare, P. Schmuki, Chem. Commun. 2014, 50, 9653–9655.
[30] J. Li, F. Meng, H. Wang, X. Jiang, Y. Zhu, Electrochim. Acta 2016, 190, 852–861.
[31] J. Snyder, P. Asanithi, A. B. Dalton, J. Erlebacher, Adv. Mater. 2008, 20, 4883–4886.
[32] A. A. Vega, R. C. Newman, J. Appl. Electrochem. 2016, 46, 995–1010.
[33] P. Quaino, F. Juez, E. Santos, W. Schmickler, Beilstein J. Nanotechnol. 2014, 5, 846–854.
[34] J. Kunciewicz, B. Ohtani, RSC Adv. 2016, 6, 77201–77211.
[35] S. Ida, K. Sato, T. Nagata, H. Hagiwara, M. Watanabe, N. Kim, Y. Shiota, M. Koinuma, S. Takenaka, T. Sakai, Angew. Chem. Int. Ed. 2018, 57, 9073–9077; Angew. Chem. 2018, 130, 9211–9215.
[36] P. V. Kamat, J. Phys. Chem. B 2002, 106, 7729–7744.
[37] V. Subramanian, E. Wolf, P. V. Kamat, J. Phys. Chem. B 2008, 112, 105, 11439–11446.
[38] P. Roy, S. Berger, P. Schmuki, Angew. Chem. Int. Ed. 2011, 50, 2904–2939; Angew. Chem. 2011, 123, 2956–2959.
[39] J. R. Jennings, A. Ghicov, L. M. Peter, P. Schmuki, A. B. Walker, J. Am. Chem. Soc. 2008, 130, 13364–13372.
[40] J. García-Serrano, E. Gömez-Hernández, M. Ocampo-Fernández, U. Pal, Curr. Appl. Phys. 2009, 9, 1097–1105.
[41] M. Torrell, P. Machado, L. Cunha, N. M. Figueiredo, J. C. Oliveira, C. Louro, F. Vaz, Surf. Coat. Technol. 2010, 204, 1569–1575.
[42] J. Borges, T. Kubart, S. Kumar, K. Leifer, M. S. Rodrigues, N. Duarte, B. Martins, J. P. Dias, A. Cavaleiro, F. Vaz, Thin Solid Films 2015, 580, 77–88.
[43] J. Yoo, M. Altomare, M. Mokhtar, A. Alshehri, S. A. Al-Thabaiti, A. Mazare, P. Schmuki, J. Phys. Chem. C 2016, 120, 15884–15892.