Digest Journal of Nanomaterials and Biostructures Vol. 19, No. 4, October-December 2024, p. 1459-1469

The synthesis, characterization, and thermal properties of a titanium (III) amidinate compound and its potential as a single chemical vapor deposition precursor for N/C-doped TiO_2 film

Y. Zhang [a*], Z. Ju [a], C. Yao [a], L. Liu [a], X. Zhang [a], J. Xing [a], L. Cheng [b]
[a] *Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan Province, Institute of Surface Micro and Nano Materials, College of Chemical and Materials Engineering, Xuchang University, Xuchang, 461000, China*
[b] *Hefei ADChem Semi-Tech.Co.,Ltd., Hefei, 230000, China*

A titanium(III) amidinate compound had been successfully obtained using a salt elimination reaction between $TiCl_3$(3THF) and [Li(^{i}Pr-^{n}BuAMD)] in a 65% yield, and the characterization of the compound was conducted using various characterization methods. The reported compound's thermal performances were studied through thermal gravimetric analysis (TGA), and the result indicated that the reported titanium(III) amidinate compound exhibited a suitable volatility, high thermal stability, and sufficient vapor pressure. Furthermore, film material deposit was performed in a CVD reactor under low pressure, and a N/C-doped TiO_2 film was successfully deposited.

(Received August 8, 2024; Accepted October 8, 2024)

Keywords: Synthesis, Titanium(III) amidinate, CVD, Precursor, N/C-doped TiO_2 film

1. Introduction

TiO_2 film exhibits widespread applications in various fields—such as photocatalysis [1], photoelectrochemical [2], and solar cells [3] owing to its excellent physical and chemical properties. However, the pure TiO_2 can only absorb UV light (< 387 nm), which has seriously hindered its large-scale application [4,5]. To solve this problem, numerous methods are put into practice to enhance the photoactivity of TiO_2 at range of visible light for utilizing solar light more efficiently [6-10]. Among these, doping N or N/C elements have been considered as an effective way which can enhance visible light photochemical activities of TiO_2 through broadening its light absorption range [11-13].

So far, there are several methods used for preparing N or N/C-doped TiO_2 films, for instance, sputtering [14], sol-gel [15], chemical vapor deposition (CVD) [16], as well as atomic layer deposition (ALD) [17] *etc*. Especially, CVD attracts more and more attention owing to its distinct advantages in efficiency, uniformity, and durability of film deposition [18,19].

*Corresponding author: yxzhang@xcu.edu.cn
https://doi.org/10.15251/DJNB.2024.194.1459

Based on the basic of CVD process, it is found that metal precursor plays a key role in a CVD process and a suitable CVD precursor determines the success or failure of the deposition process [19]. So far, Several CVD precursors have been reported for preparing N- or N/C-doped TiO_2 films, such as $Ti(NMe_2)_4$ [20], $TiCl_4$ [21], $Ti(O^iPr)_4$ [22], $Ti(NMe_2)_3(Me_2NC(^iPrN)_2)_2$ [23], as well as $Ti(O^nBu)_4$ [12], *etc*. However, although these compounds have been successfully used to prepare N- or N/C-doped TiO_2 film, designing new type Ti precursor is still necessary; this is not only because different type precursors will greatly influence the attributes and performances of deposited materials, but also because that there are several drawbacks existed in the majority of reported Ti precursors and the corresponding film deposition process, such as low thermal stability [23], corrosive gas generation [21], as well as hazardous N source [24-26], *etc*. These circumstances encouraged us to design new Ti precursor for CVD of N- or N/C-doped TiO_2 films.

Generally, conjugated system is helpful in improving the stability of a metal compound, and the Ti precursor may be possessed high thermal stability if all its ligands are conjugated. However, almost all reported CVD Ti precursors so far are tetravalent and are difficult to form all conjugated ligand system Ti(IV) compound due to the all conjugated system Ti(IV) compound's large steric hindrance. Under this mind, an all conjugated ligand system Ti(III) amidinate compound was designed, synthesized, and characterized in this study. The synthesized compound exhibits the following advantages: high thermal stability, no corrosive gas generation, and as a single CVD precursor for preparing N- or N/C-doped TiO_2 films.

2. Experimental

2.1. General synthesis

All processes were accomplished in a nitrogen system using standard Schlenk technique or glovebox. All the used solvents were water- and oxygen-free. N,N'-diisopropylcarbodiimide and *n*-butyllithium (2.5 M in hexane) were used directly, which got from Meryer. $TiCl_3(THF)$ was synthesized as described in the literature [27].

Tris(N,N'-Diisopropylpentanamidinate) Titanium(III) [$Ti(^iPr\text{-}^nBuAMD)_3$] 1. 0.11 mol of *n*-Butyllithium was slowly added to 40 mL of tetrahydrofuran (THF) containing N,N'-diisopropyl-carbodiimide (13.88 g, 0.11 mol) at -78 °C, and the produced light-yellow solution was stirred overnight at room temperature. Then the resulted mixture was added to 50 mL of THF containing $TiCl_3(3THF)$ (13.34 g, 0.036 mol) and stirred for 24 h. All volatiles were removed under vacuo, and then extracted by 50 mL of *n*-hexane. The hexane extract was filtrated, and the obtained filtrate was concentrated and then cooled to -29 ºC for 2 days to afford dark green crystals (13.77 g, Melting point: 80.3-84.4 ºC, 65% yield). ^1H NMR: δ = -13.58 (br, 2H, CH_2), -0.09-0.33 (br, 2H, CH_2), 0.66 (br, 6H, $(CH_3)_2$), 1.47-1.57 (br, 11H, $(CH_3)_2$, CH_2CH_3), 13.71(br, 1H, CH), 26.06 (br, 1H, CH). C33H69N6Ti (597.8): Calcd. C 66.30, H 11.63; N 14.06; Found: C 66.04; H 11.25, N 14.47.

2.2. Thermogravimetric analysis and film growth

The TGA curve was measured by an STA449F3 apparatus under continuous argon flowing, and the rate of temperature rise was 10 K/min. The vapor pressure was obtained based on TGA data using method mentioned in the literature [28].

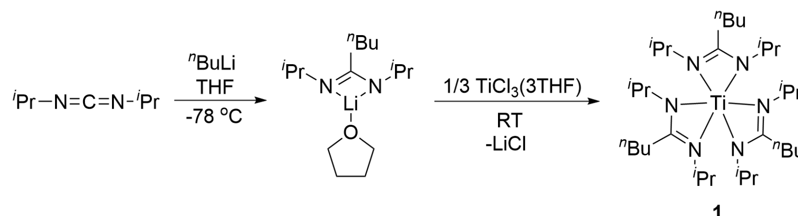
The film was deposited on quartz substrate (20 mm×20 mm×1 mm) at 300 ºC for 30 min through CVD technique, and the CVD equipment was described in the literature [29]. Pure TiO_2 film was selected as a reference and synthesized by sol-gel method [30]. The synthesized compound was heated to 230 ºC and transported to the reactor chamber through a N_2 flow (120 mL/min). O_2 was selected as an oxidant with 50 mL/min gas flow. The deposition pressure was set to 10 Torr.

2.3. Characterization

Diffraction data were obtained by X-ray single crystal diffractometer using Mo-Kα. The ^{1}H NMR was recorded through a Bruker ACF-400 apparatus at 25 ºC using C_6D_6 as solvent. The morphology and composition of the deposited film analyzed through atomic force microscopy (AFM), scanning electron microscope (SEM), and energy dispersive spectrometer (EDS), respectively. The light absorption performance of the deposited film was measured by UV-vis spectrophotometer.

3. Results and discussions

Scheme 1 showed that complex **1** was obtained by a simple LiCl elimination reaction between $TiCl_3$(3THF) and lithium amidinate ([Li(^{i}Pr-^{n}BuAMD)]) in THF, and the stoichiometric ratio was 1/3. Pure dark green products were isolated through recrystallization at -29 ºC in hexane with a moderate yield (65%). After testing, it was found that the designed complex was sensitive to oxygen and moisture.



*Scheme 1. Synthetic process of **1**.*

As described in experimental, several methods were used to observe the chemical structure of **1**. The measured compound's element content was in agreement with the proposed structure, which demonstrated a high purity of obtained compound. The ^{1}H NMR result (Fig. 1) revealed that the number of peaks and corresponding H atoms of **1** agreed with the target structure. The peaks at 26.06, 13.71, and -13.58 ppm corresponded to the *α*-H atoms of ^{i}Pr and ^{n}Bu group in the proposed structure, respectively. The α-H resonances of ^{i}Pr and ^{n}Bu group were shifted to lower and higher field respectively compared with those in Ti(IV) amidinate compound (2.95-3.77 ppm for ^{i}Pr group and 1.66-2.09 ppm for ^{n}Bu group) [31-33]; this difference can be attribute to the magnetism of the synthesized compound due to the single electron of titanium spins in 3d orbit.

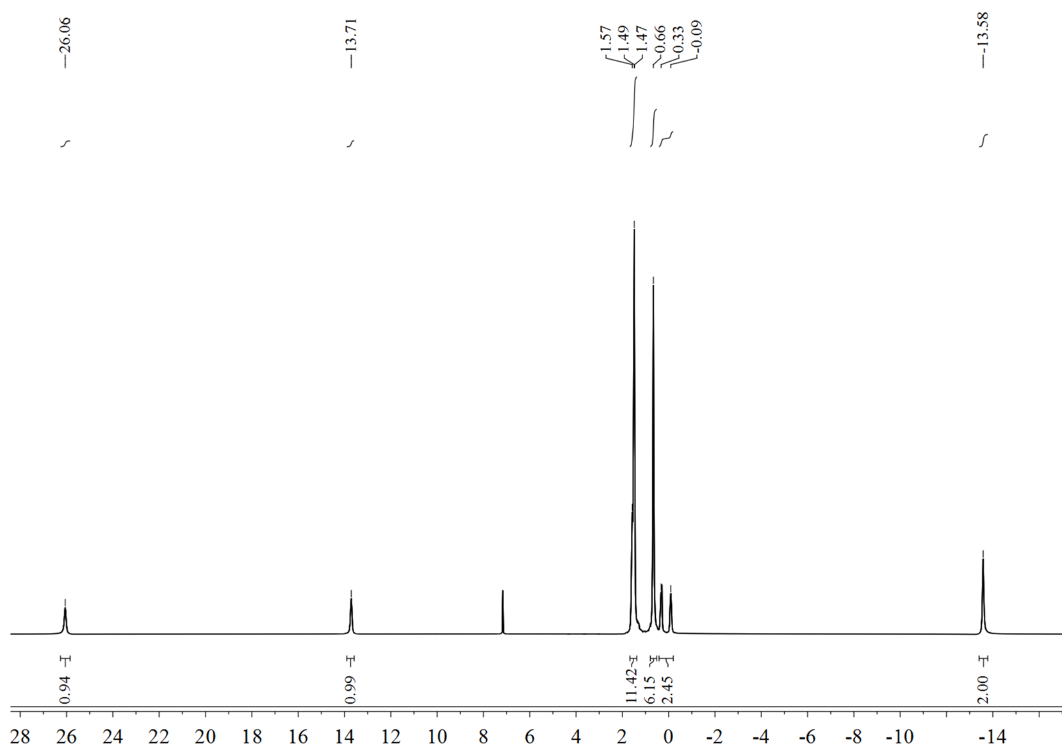


*Fig. 1. ^{1}H NMR spectrum of **1**.*

An intuitive single crystal structure diagram and crucial bond lengths [Å] and angles [deg] data of **1** are presented in Fig. 2 and its caption, respectively, and crystallographic parameters are presented in Table 1. It is found that the synthesized compound exhibited a monomeric structure and its titanium center was surrounded by six nitrogen atoms from the three η^2-coordinated amidinate ligands in a strongly disturbed octahedral geometry. The Ti-N bond length average was 2.14 Å (range of 2.106(3)-2.176(3) Å), similar to those in the reported Ti(III) amidinate complex [$(CyNC(H)NCy)_4Ti_2Cl_2 \cdot 2THF$] [34]. All of N-Ti-N angle within the chelate rings of **1** were ~62°, and the coordination geometry was consistent with other TiL_3 (L= bidentate ligand) complexes [35,36]. All these results demonstrated the reasonability of the proposed structure of **1**.

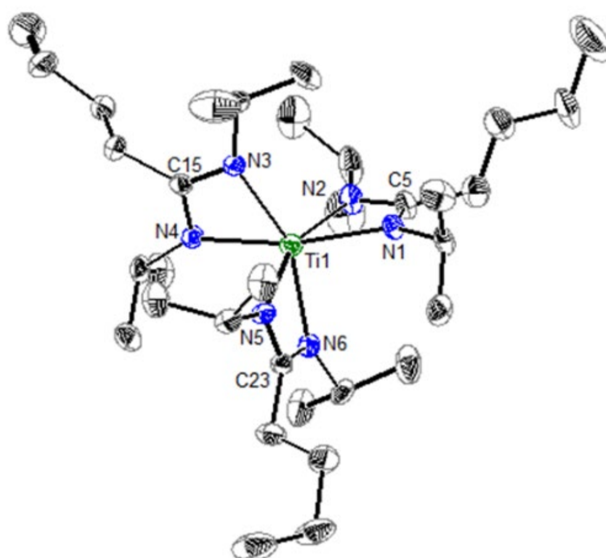


*Fig. 2. Single crystal structure diagram of **1**. Ti(1)-N(1) 2.176(3), Ti(1)-N(2) 2.106(3), Ti(1)-N(3) 2.115(3), Ti(1)-N(4) 2.162(4), Ti(1)-N(5) 2.144(3), Ti(1)-N(6) 2.146(3), N(1)-C(5) 1.315(6), N(2)-C(5) 1.343(6), N(3)-C(15) 1.338(5), N(4)-C(15) 1.321(5), N(5)-C(23) 1.336(5), N(6)-C(23) 1.330(5), N(2)-Ti(1)-N(1) 62.43(13), N(3)-Ti(1)-N(4) 62.38(13), N(5)-Ti(1)-N(6) 62.24(12), N(1)-C(5)-N(2) 113.3(4), N(4)-C(15)-N(3) 112.8(4), N(6)-C(23)-N(5) 112.6(3).*

*Table 1. Crystallographic parameters of **1**.*

Formula	$C_{33}H_{69}N_6Ti$	a/Å	10.4283(4)
Mw	597.84	b/Å	16.9927(5)
Temperature (K)	150.15	c/Å	42.4288(16)
Crystal system	Orthorhombic	α/°	90
Space group	P2(1)2(1)2(1)	β/°	90
Wavelength Mo Kα (Å)	0.71073	γ/°	90
D_x/g cm^{-3}	1.056	V/Å^3	7518.6(5)
2θ range/°	2.176-25.406	Z	8
R, wR_2 (I > 2σ(I))	0.0537, 0.1176	Absorption coefficient, mm^{-1}	0.255
R, wR_2 (all data)	0.0749, 0.1270	CCDC number	1584852

The thermal performance of **1** was evaluated by TGA. As shown in Fig. 3, the synthesized compound vaporized in a single step weight loss with a low residue (3.07%), and the termination vaporization temperature was observed at 310 °C. This result demonstrated that compound **1** possessed an excellent thermal stability. Moreover, the start vaporization temperature of compound **1** was observed at 200 °C, indicated that compound **1** exhibited a sufficient volatility.

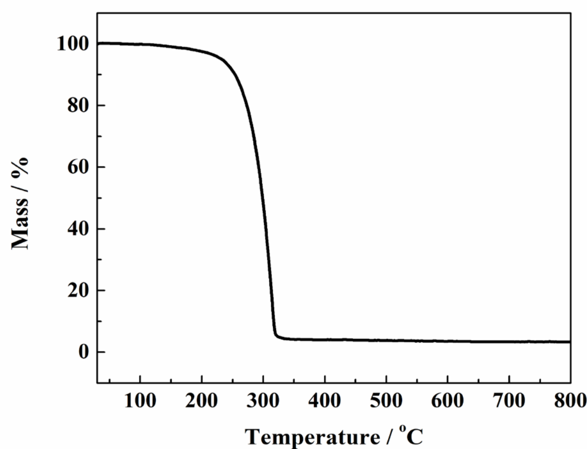


*Fig. 3. Thermal gravimetric analysis of **1**.*

Vapor pressure-temperature plot was measured to further study the thermal properties of compound **1**. As shown in Fig. 4, compound **1** provided a vapor pressure (1.3 Torr) at 230 ºC, and this pressure is sufficient for a CVD precursor [19]. From above results, it was certainly that the designed compound satisfies CVD precursors' requirements.

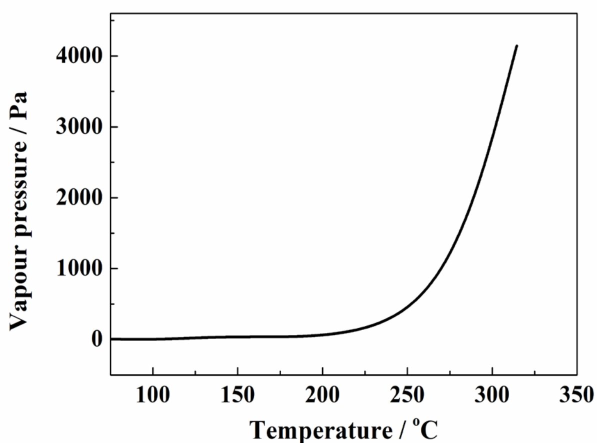


*Fig. 4. Vapour pressure-temperature diagram of **1**.*

Based on the research to above content, CVD film deposit under low-pressure was performed to confirming the potential of **1** as a single CVD precursor for preparing N/C-doped TiO_2 film. The film was deposited on quartz at 300 ºC of 30 min. The surface morphology of the deposited film was examined by SEM (Fig. 5a), and the result indicated that the prepared film was uniform and continuous. Fig. 5b presents the surface roughness of the deposited film, and the low value (1.15 nm) indicated that the deposited film had a smooth surface.

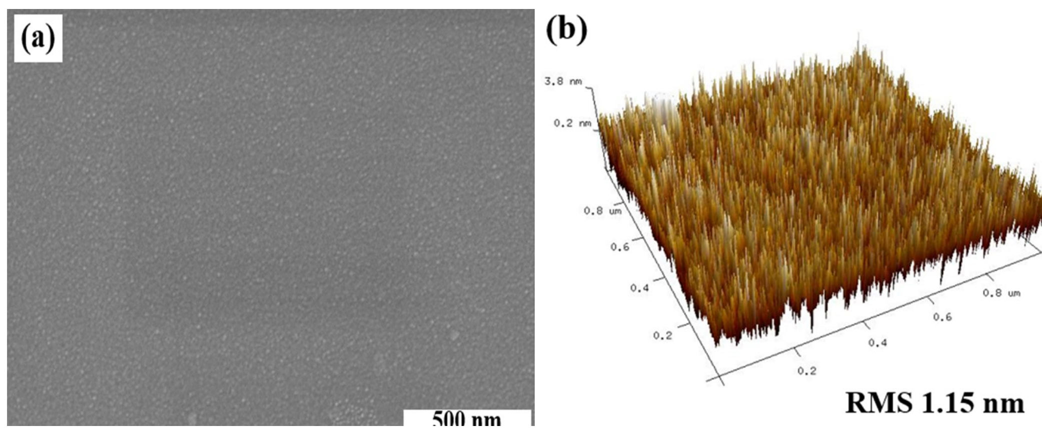
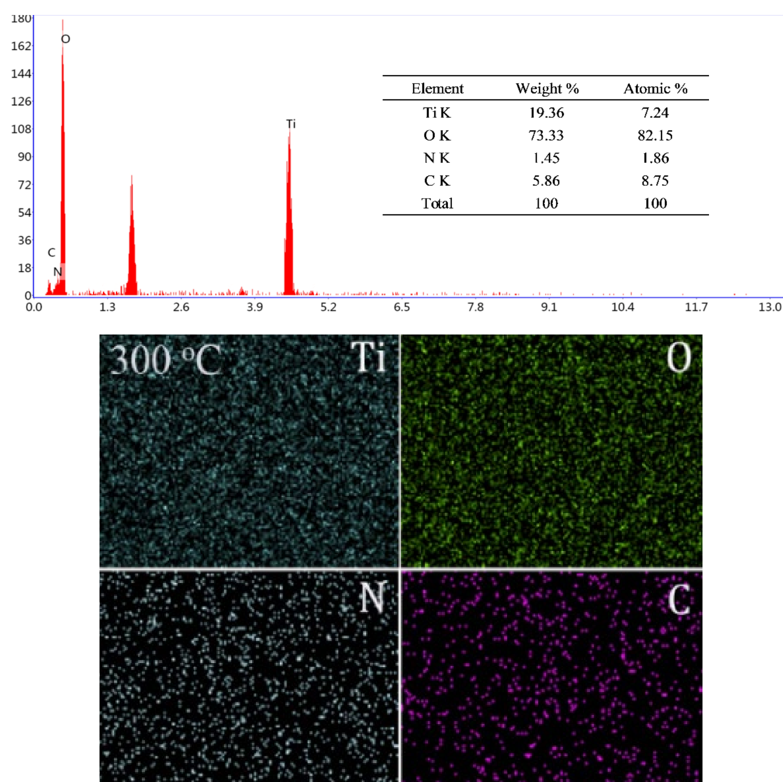


Fig. 5. The SEM (a) and AFM (b) image of film grown at 300 °C.

The chemical component of the deposited film was simply measured by EDS. the EDS spectrum (Fig. 6) shows that the deposited film was composed of Ti, O, N, and C; the detected Si element (unmarked) was originated from the quartz substrate. Moreover, the elements mappings pattern revealed that the detected elements were uniformly distributed in the deposited film. Clearly, the EDS results suggested that the deposited film was N/C-doped TiO_2 film.



Element	Weight %	Atomic %
Ti K	19.36	7.24
O K	73.33	82.15
N K	1.45	1.86
C K	5.86	8.75
Total	100	100

Fig. 6. EDS spectrum (left) and element mapping (right) of film grown at 300 °C.

The light absorption performance of the deposited film was evaluated by UV-vis absorption spectroscopy (Fig. 7). The result demonstrated that the absorption curve exhibited oscillation behavior due to the different refraction index between the substrate and layer [20]. Moreover, compared with pure TiO_2, the absorption edge of deposited film was red-shifted to 413 nm, which can be put down to the N/C-doped elements in the deposited film resulting in enhancement of visible light absorbing ability [12,13,37]. Obviously, all above results demonstrated the feasibility of 1 as a single CVD precursor for preparing N/C-TiO_2 film.

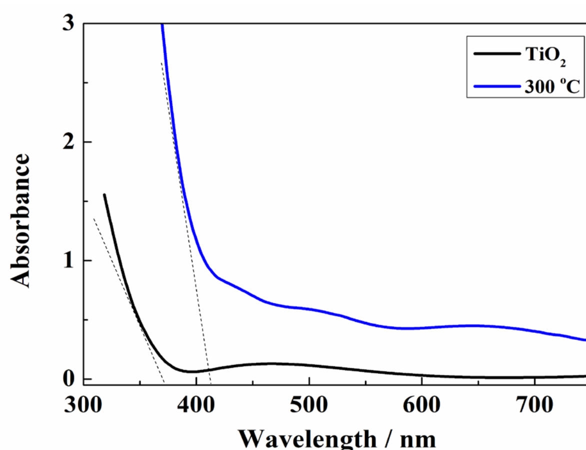


Fig. 7. UV-vis absorption spectrum of TiO_2 film (black line) and N/C-doped TiO_2 films (blue line)

4. Conclusions

In this study, a titanium(III) amidinate compound was successfully synthesized through the reaction of the lithium salt and $TiCl_3$(3THF) in 65% yield. The synthesized compound exhibited a monomeric structure, and possessed excellent thermal stability, sufficient volatility and vapor pressure. CVD film deposit was performed to confirming the practicability of the synthesized complex as a single CVD precursor, and a continuous, uniform, and smooth N/C-TiO_2 film was obtained. All the results verified the applicability of the synthesized complex used for CVD of N/C-TiO_2 film.

Appendix A. Supplementary Material

CCDC 1584852 contains the supplementary crystallographic data for 1. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This work was supported by Henan Provincial Science and Technology Research Project (No. 222102230083) and Key Scientific Research Project of Henan Provincial Institution of Higher Learning (No. 23B530003).

References

[1] L. He, D. R. T. Zahn, T. I. Madeira, Materials 16(15), 5494 (2023); https://doi.org/10.3390/ma16155494

[2] M.-J. Kim, J.-S. Bae, M.-J. Jung, E. Jeon, Y. Park, H. Khan, S.-H. Kwon, ACS Appl. Mater. Interfaces 15(39), 45732 (2023); https://doi.org/10.1021/acsami.3c06780

[3] R. Agarwal, C. Himanshu, C. Ameta, M. S. Dhaka, J. Mater. Sci.: Mater. Electron. 34(28), 1974 (2023); https://doi.org/10.1007/s10854-023-11307-8

[4] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293(5528), 269 (2001); https://doi.org/10.1126/science.1061051

[5] X. Pan, M.-Q. Yang, X. Fu, N. Zhang, Y.-J. Xu, Nanoscale 5(9), 3601 (2013); https://doi.org/10.1039/c3nr00476g

[6] S. Liu, N. Zhang, Z.-R. Tang, Y.-J. Xu, ACS Appl. Mater. Interfaces 4(11), 6378 (2012); https://doi.org/10.1021/am302074p

[7] H. Tada, T. Kiyonaga, S.-I. Naya. Chem. Soc. Rev. 38(7), 1849 (2009); https://doi.org/10.1039/b822385h

[8] D. Li, Z. Chen, Y. Chen, W. Li, H. Huang, Y. He, X. Fu, Environ. Sci. Technol. 42(6), 2130 (2008); https://doi.org/10.1021/es702465g

[9] Y. Zhang, Z.-R. Tang, X. Fu, Y.-J. Xu, ACS Nano 5(9), 7426 (2011); https://doi.org/10.1021/nn202519j

[10] Z. Li, F. Wang, A. Kvit, X. Wang, J. Phys. Chem. C 119(8), 4397 (2015); https://doi.org/10.1021/jp512622j

[11] R. Quesada-Cabrera, C. Sotelo-Vazquez, J. A. Darr, I. P. Parkin, Appl. Catal., B 160-161, 582 (2014); https://doi.org/10.1016/j.apcatb.2014.06.010

[12] G. Wu, T. Nishikawa, B. Ohtani, A. Chen, Chem. Mater. 19(18), 4530 (2007); https://doi.org/10.1021/cm071244m

[13] S. Liu, L. Yang, S. Xu, S. Luo, Q. Cai, Electrochem. Commun. 11(9), 1748 (2009); https://doi.org/10.1016/j.elecom.2009.07.007

[14] M. Rahman, B. H. Q. Dang, K. McDonnell, J. M. D. MacElroy, D. P. Dowling, J. Nanosci. Nanotechnol. 12(6), 4729 (2012); https://doi.org/10.1166/jnn.2012.4897

[15] Y. Dou, Y. Chang, X. Duan, L. Fan, B. Yang, J. Lv, Int. J. Environ. Res. Public Health 19(23), 15721 (2022); https://doi.org/10.3390/ijerph192315721

[16] H. Rasoulnezhad, G. Hosseinzadeh, R. Hosseinzadeh, N. Ghasemian, J. Adv. Ceram. 7(3), 185 (2018); https://doi.org/10.1007/s40145-018-0270-8

[17] M. Zafar, J.-Y. Yun, D.-H. Kim, Korean J. Chem. Eng. 35(2), 567 (2018);

https://doi.org/10.1007/s11814-017-0285-9

[18] N. Chankhunthod, P. Junploy, S. Suthirakun, L. Ngamwongwan, C. Phromma, N. Ruchusartsawat, A. Siyasukh, P. Yanu, P. Kijjanapanich, S. Yimklan, A. Rujiwatra, R. Drummond-Brydson, Y. Chimupala, Environ. Res. 239, 117347 (2023); https://doi.org/10.1016/j.envres.2023.117347

[19] A. C. Jones, M. L. Hitchman, Chemical Vapour Deposition: Precursors, Processes and Applications, Royal Society of Chemistry, London, p. 207, 2009; https://doi.org/10.1039/9781847558794

[20] P. Romero-Gómez, S. Hamad, J. C. González, A. Barranco, J. P. Espinós, J. Cotrino, A. R. González-Elipe, J. Phys. Chem. C 114(51), 22546 (2010); https://doi.org/10.1021/jp104634j

[21] R. Quesada-Cabrera, C. Sotelo-Vázquez, M. Quesada-González, E. P. Melián, N. Chadwick, I. P. Parkin, J. Photochem. Photobiol., A 333, 49 (2017); https://doi.org/10.1016/j.jphotochem.2016.10.013

[22] C. Sarantopoulos, A. N. Gleizes, F. Maury, Thin Solid Films 518(4), 1299 (2009); https://doi.org/10.1016/j.tsf.2009.04.070

[23] S. J. Kim, K. Xu, H. Parala, R. Beranek, M. Bledowski, K. Sliozberg, H.-W. Becker, D. Rogalla, D. Barreca, C. Maccato, C. Sada, W. Schuhmann, R. A. Fischer, A. Devi, Chem. Vap. Deposition 19(1-3), 45 (2013); https://doi.org/10.1002/cvde.201206996

[24] S. E. Alexandrov, M. V. Baryshnikova, L. A. Filatov, A. L. Shahmin, V. D. Andreeva, J. Nanosci. Nanotechnol. 11(9), 8274 (2011); https://doi.org/10.1166/jnn.2011.5072

[25] R.-D. Duminica, F. Maury, R. Hausbrand, Surf. Coat. Technol. 201(22-23), 9349 (2007); https://doi.org/10.1016/j.surfcoat.2007.04.061

[26] Y. Guo, X.-W. Zhang, W.-H. Weng, G.-R. Han, Thin Solid Films 515(18), 7117 (2007); https://doi.org/10.1016/j.tsf.2007.03.012

[27] N. A. Jones, S. T. Liddle, C. Wilson, P. L. Arnold, Organometallics 26(3), 755 (2007); https://doi.org/10.1021/om060486d

[28] S. F. Wright, D. Dollimore, J. G. Dunn, K. Alexander, Thermochim. Acta 421(1-2), 25 (2004); https://doi.org/10.1016/j.tca.2004.02.021

[29] Y. Zhang, C. Yao, Z. Ju, S. Zhang, H. Wang, W. Yin, N. Qin, X. Li, Y. Zhang, Inorg. Chem. Commun. 146, 110165 (2022); https://doi.org/10.1016/j.inoche.2022.110165

[30] K. A. Vorotilov, E. V. Orlova, V. I. Petrovsky, Thin Solid Films 207(1-2), 180 (1992); https://doi.org/10.1016/0040-6090(92)90120-Z

[31] L. R. Sita, J. R. Babcock, Organometallics 17(24), 5228 (1998); https://doi.org/10.1021/om980706q

[32] J.-F. Sun, S.-J. Chen, Y. Duan, Y.-Z. Li, X.-T. Chen, Z.-L. Xue, Organometallics 28(10), 3088 (2009); https://doi.org/10.1021/om900162b

[33] S. Ren, Z. Qiu, Z. Xie, Organometallics 32(15), 4292 (2013); https://doi.org/10.1021/om400458r

[34] S. K. Hao, K. Feghali, S. Gambarotta, Inorg. Chem. 36(9), 1745 (1997); https://doi.org/10.1021/ic961358s

[35] A. Spannenberg, A. Tillack, P. Arndt, R. Kirmse, R. Kempe, Polyhedron 17(5-6), 845 (1998); https://doi.org/10.1016/S0277-5387(97)00281-7

[36] D. P. Steinhuebel, S. J. Lippard, Inorg. Chem. 38(26), 6225 (1999); https://doi.org/10.1021/ic9909072

[37] P. G. Wu, C. H. Ma, J. K. Shang, Appl. Phys. A: Mater. Sci. Process. 81(7), 1411 (2005); https://doi.org/10.1007/s00339-004-3101-4