



Field Emission Characteristics of Double Walled TiO₂ Nanotubes

Girish P. Patil,^{1,2} Sachin R. Rondiya,³ Vivekanand S. Bagal,⁴ Sugam Shivhare,⁴ Russell W. Cross,³ Nelson Y. Dzade,³ Sandesh R. Jadkar⁵ and Padmakar. G. Chavan^{1,*}

Abstract

Double walled TiO₂ nanotubes have been synthesized by two probe anodization method on highly pure Titanium (Ti) substrate. FESEM and XRD analyses revealed the morphological and structural properties of the as-synthesized double walled TiO₂ nanotubes. Investigation of their field emission characteristics in a planar diode configuration at a base pressure of 1×10^{-8} mbar has been done. The turn-on field defined for the emission current density of $10 \mu\text{A}/\text{cm}^2$ is found to be $2.1 \text{ V}/\mu\text{m}$. As the field is increased further to $2.95 \text{ V}/\mu\text{m}$ maximum, a current density of $890 \mu\text{A}/\text{cm}^2$ is achieved. Current-time (I-t) measurement at a preset value of $1 \mu\text{A}$ emission current for the duration of 3 h demonstrates a robust emission current stability. The observed low turn-on field and stable electron emission makes the double walled TiO₂ nanotubes a suitable emitter for various electronics devices applications.

Keywords: TiO₂; Double walled nanotubes; Density functional theory; Current stability; Field emission.

Received date: 25 November 2020; Accepted date: 17 January 2021.

Article type: Research article.

1. Introduction

One-Dimensional (1D) nanostructures have attracted significant research interest in the last few decades.^[1] 1D nanostructures proved themselves as potential candidate for various materials science applications due to promising electrical, mechanical and optical properties.^[2] Anodic oxidation is simple and low cost method to synthesized self-organized 1D nanostructures.^[3] Particularly, the formation of self-aligned and organized titanium dioxide (TiO₂) nanotube arrays is possible by using two probe anodic oxidation method.^[4] TiO₂ is an inorganic semiconductor material with large band gap of 3.2 eV.^[5] It exhibits a wide range of application as electrochromic material,^[6] biomedical devices,^[7]

gas sensors,^[8] photocatalysis,^[9] photo-electrochemistry,^[10] dye-sensitized solar cells,^[11] and field emission.^[12] In recent times, the tremendous efforts have been made by scientific community to synthesis various TiO₂ nanostructures such as, nanowires,^[13] nanotubes,^[14] nanosheets,^[15] and nanorods^[16] etc. Field emission is quantum mechanical tunneling phenomenon in which electron from the materials has been extracted under the action of strong electrostatic field.^[12] Various applications such as X-ray generation techniques, space research, electronic displays, electron microscopes and medical devices depends on electron emitter source of field emission technology.^[17] Field emission is highly geometry dependent and a surface-sensitive phenomenon. Emitter materials that possess a high areal density, good electrical conductivity, low work function, very fine tip radius and sharp-edged nanostructures generally show superior field emission characteristics material.^[3] TiO₂ nanotubes array possess geometrical/morphological features similar to highly aligned CNTs. They can also be made as a tightly adherent layer on the surface of Ti substrate by simple anodization process, which makes them suitable as electron percolation pathways for free electron transfer between interfaces. Aligned TiO₂ nanotubes array with high packing density can significantly enhance the field emission properties of the materials, so it can become one of the ideal candidates for field emission applications.^[3] In the present work, double walled TiO₂ nanotubes were synthesized by simple and economic method of anodization. The structural, morphological, and field

¹ Department of Physics, School of Physical Sciences, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon, 425001.

² The State Key Laboratory of Refractories and Metallurgy, Institute of Advance Materials and Nanotechnology, College of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, P. R. China.

³ School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, Wales, United Kingdom.

⁴ Department of Applied Sciences & Humanities, SVKM's NMIMS, Mukesh Patel School of Technology Management and Engineering, Shirpur Campus, 425405, India.

⁵ Department of Physics, Savitribai Phule Pune University, Pune 411007, India.

*E-mail: dpgchavan@nmu.ac.in (P. G. Chavan)

emission properties of the as-synthesized double walled TiO₂ nanotubes were systematically characterized and discussed.

2. Synthesis

The double walled TiO₂ nanotubes were synthesised by the anodization method as per previous report.^[1] In brief, prior to anodization, a high purity titanium foil (99.7% purity, 0.25 mm thickness, Sigma Aldrich) was cleaned in an ultrasonic bath for 10 min with ethanol and 10 min with acetone sequentially. By taking titanium foil (1 cm × 2 cm) as the working electrode and platinum foil (1 cm × 2 cm) as the counter electrode, anodization was performed in a two-electrode configuration under constant potential at room temperature (25 °C). The reaction was carried out by adding 0.1 M of NH₄F and 1 M of H₂O in 50 ml of Ethylene glycol. During reaction constant voltage of 30 V was applied for 30 min. Finally, the as-anodized Ti foil was rinsed in deionized water and used for further characterization. Annealing of the Ti foil was carried out at 530 °C for 3 h in air. A double layer oxide, which is double walled TiO₂ is formed over the Ti metal substrate due to the coupling of cation and anion migration during oxide growth. For tube formation of the double layer finally turns into an outer- and inner-shell in morphology. The anodic potential causes oxidation of the metal.^[1]

3. Characterizations

Field Emission Scanning Electron Microscope (FESEM) (Model Hitachi S-4800) was used to study surface morphology of the doubled walled TiO₂ nanotubes and X-ray diffraction (XRD) by D8 Advance, Bruker instrument was used for phase identification of the double walled TiO₂ nanotubes. Field emission characteristics have been investigated in a planar diode configuration at the base pressure of 1×10^{-8} mbar. Further details of the field emission measurement is given in reference.^[18] The density functional theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP).^[19] The interactions between the core and valence electrons were described using the Project Augmented Wave (PAW) method.^[20] An energy cut-off of 600 eV, and $7 \times 7 \times 3$ Monkhorst-Pack k -point mesh,^[21] was used to sample the sample the Brillouin zone of bulk anatase TiO₂, whereas the (001) and (101) surfaces were modelled using $5 \times 5 \times 1$ and $5 \times 3 \times 1$ k -point meshes, respectively. All calculations were deemed to be converged when the forces on all atoms were less than 0.001 eV/Å. For accurate determination the electronic structure and bandgap, the screened hybrid functional (HSE06)^[22] was employed with the exact exchange value of 25% and a screening parameter of $\mu = 0.2 \text{ \AA}^{-1}$. The (001) and (101) surfaces of TiO₂ were created from the optimized bulk material using the METADISE code.^[23] In order to align the energies to the vacuum level, a slab-gap model was constructed and the corresponding electrostatic potential was averaged along the c -direction, using the Macro Density package.^[24] The work function (Φ) was calculated as

$\Phi = V_{\text{vacuum}} - E_F$, where E_{vacuum} is the V_{vacuum} level and E_F is the Fermi level.

4. Results and discussion

4.1 Crystal structure and morphological analyses

XRD pattern of the annealed doubled walled TiO₂ shown in Fig. 1 reveals the polycrystalline nature of predominant anatase TiO₂ peak centred at 2θ value of 25.32. In present study the lattice constants have been evaluated from (h k l) planes by using the following equation of interplaner spacing for a tetragonal unit cell as,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

Where, h , k and l are the miller indices, d is interplaner spacing, a and c are the lattice constant of unit cell. The reflections due to the TiO₂ peaks can be indexed to anatase TiO₂ with lattice constants $a = 3.7884 \text{ \AA}$ and $c = 9.5190 \text{ \AA}$, which is consistent with the literature (JCPDS Card No. 84-1286). The other peaks are related to the Ti substrate and are assigned as T. Fig. 2 shows the FESEM images of the doubled walled TiO₂ nanotubes. The doubled walled TiO₂ nanotubes have an average inner tube diameter of 46 nm, an outer tube diameter of 74 nm, and areal density of $29 \times 10^9 / \text{cm}^2$ (see Fig. 2a). The average tube length is calculated at 1.3 μm (Fig. 2b).

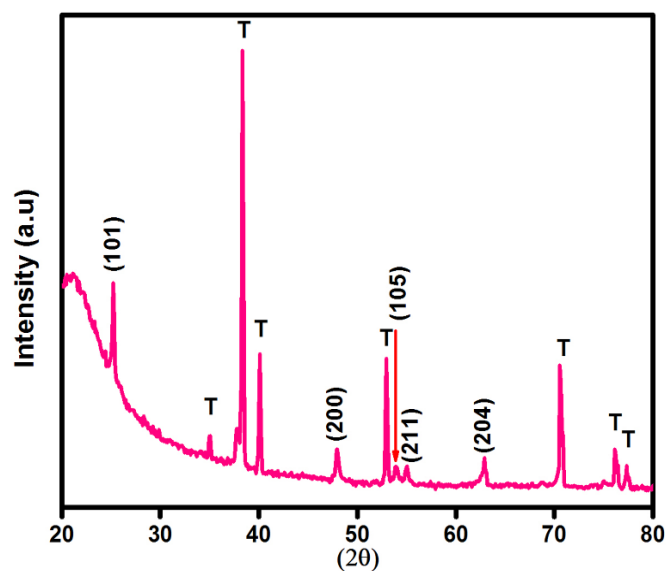


Fig. 1 XRD pattern of doubled walled TiO₂ nanotubes.

4.2 Field emission studies

Fig. 3 (a) shows the current density-electric field (J-E) plot of the double walled TiO₂ nanotubes. The turn-on field defined at a current density of $10 \mu\text{A}/\text{cm}^2$ is found to be 2.1 V/ μm . Compared to other TiO₂ nanostructures reported in the literature (as summarized in Table 1),^[25-28] the observed low turn on field of the double walled TiO₂ nanotubes is found to be superior. The observed low turn-on field for the double walled TiO₂ nanotubes may be attributed to the well-aligned nature, nanometric size, and high density of the double walled TiO₂ nanotubes. High emission current density of $890 \mu\text{A}/\text{cm}^2$

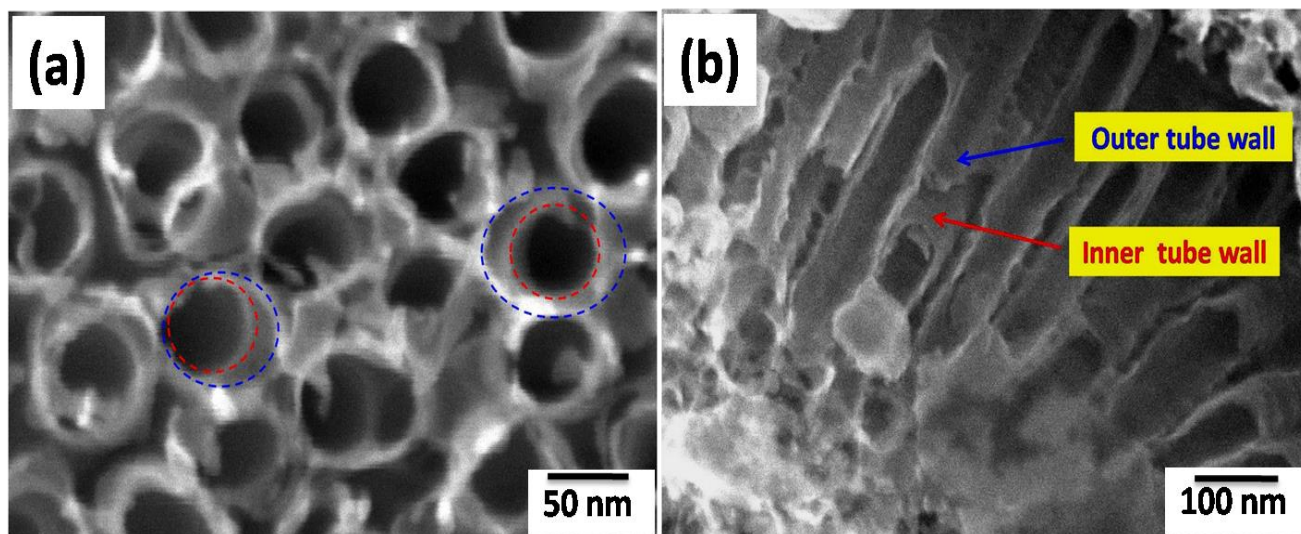


Fig. 2 (a) and (b) FESEM image of doubled walled TiO₂ nanotubes.

Table 1 Turn-on field values of the TiO₂ nanostructures reported in the literature.

Materials	Turn-on field (V/μm) (for J= 10 μA/cm ²)	Reference
Double walled TiO ₂ nanotubes	2.1	Present Work
Aligned TiO ₂ nanotubes	7.8	25
TiO ₂ nanowires	5.7	26
N ₂ doped TiO ₂	11.2	27
TiO ₂ nanotubes	23.8	28

has been achieved upon the application of an applied electric field of 2.95 V/μm. The field emission characteristic is further analyzed by the Fowler–Nordheim (F-N) plot, *i.e.* ln(J/E²) versus (1/E), derived from the observed J–E characteristic as shown in Fig. 3b. The F–N plot shows a non-linear behavior

for the doubled walled TiO₂ nanotubes. The stability of the emission current of the doubled walled TiO₂ nanotubes was ascertained from the current-time (I-t) plot at a preset value of 1 μA emission current for the duration of 3 h as shown in Fig. 4. The emission current remained fairly stable for the entire duration of measurement with only small instabilities/fluctuations in the form of “spikes”. The observed fluctuations in the emission current may occurs due to adsorption, desorption of the residual gas molecules and phenomenon of ion bombardment.^[29]

4.3 Density functional theory

The field emission characteristics are influenced by the work function (Φ) of the emitter material, we have carried out density functional theory calculations to gain atomic-level insight into the electronic structure bulk anatase TiO₂ and predict the work function of the two most stable and commonly observed (001) and (101) surfaces of TiO₂

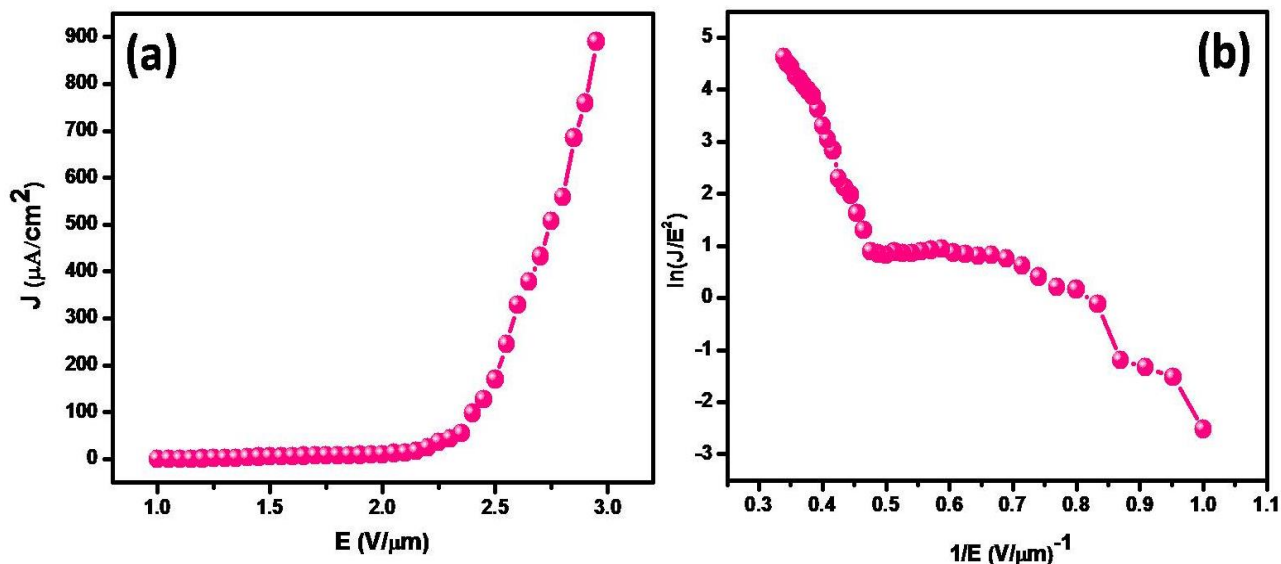


Fig. 3 (a) J–E plot and (b) corresponding F–N plot of doubled walled TiO₂ nanotubes.

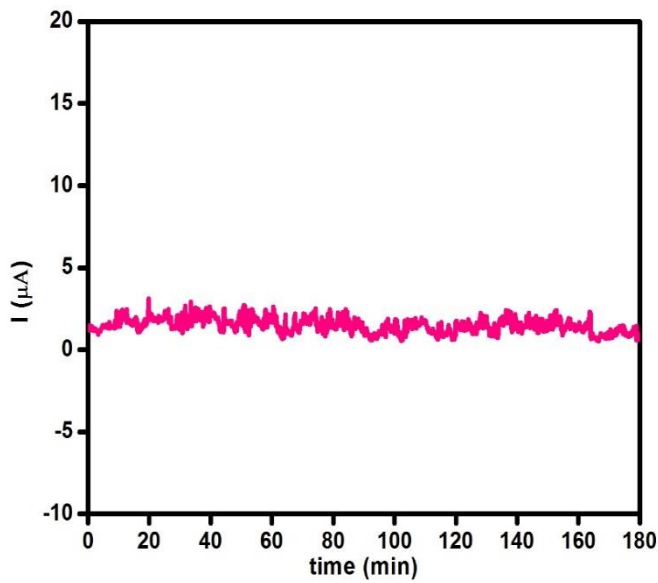


Fig. 4 I-t plot of doubled walled TiO₂ nanotubes.

nanocrystals.^[30, 31] The optimized lattice constants of the bulk anatase TiO₂ (Fig. 5a) were obtained at $a=b=3.803 \text{ \AA}$, $c=9.517 \text{ \AA}$, in good agreement with the experimental lattice constants ($a=b=3.782 \text{ \AA}$ and $c=9.502 \text{ \AA}$). The electronic band gap of anatase TiO₂ is predicted at 3.21 eV (Fig. 5b), in good agreement with experimental estimate of 2.23 eV. The valence band edge consists mainly of O-*p* states whereas the conduction band edge is dominated by Ti-*d* states. The (001) facet has a higher surface energy predicted at 0.88 Jm^{-2} than the (101) surface, which has a lower surface energy of 0.45 Jm^{-2} . These results are consistent with previous theoretical calculations.^[31] We have also consistently predicted a lower work function for the most stable (101) surface at 5.10 eV than for the less stable (001) surface at 5.52 eV. The lower work function for the most stable (101) surface is promising for the field emission applications, as it favours efficient electron emission capability of the TiO₂ material.

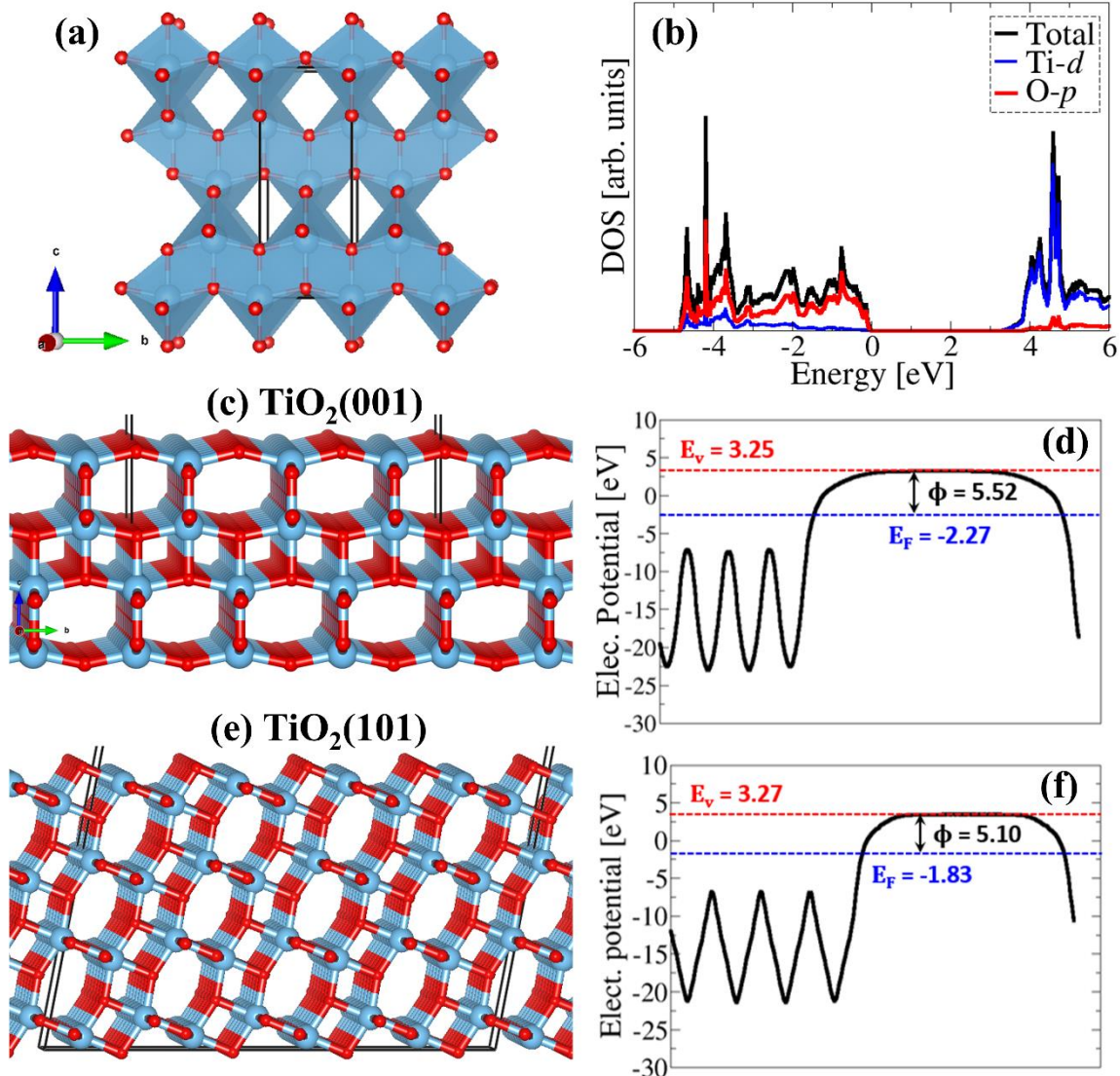


Fig. 5 (a) Crystal structure (b) the HSE06 partial density of states (PDOS) of anatase TiO₂. The structure of the (c) (001) and (e) (101) TiO₂ surfaces and their electrostatic potentials (d) and (f), respectively. The red and blue dashed lines represent the vacuum (E_{vac}) and the Fermi (E_F) levels, respectively, and the Φ is the work function.

5. Conclusions

In summary, we have successfully synthesized doubled walled TiO₂ nanotubes by a simple anodization method. FESEM analysis confirmed the formation of doubled walled TiO₂ nanotubes with an average inner and outer tube diameter of 46 nm and 74 nm, respectively. The doubled walled TiO₂ nanotubes show promising field emission behavior in terms of low turn-on field and stable field emission current. A low work function of 5.10 eV is predicted to the most stable TiO₂ (101) surface from first-principles DFT calculations, making it suitable to attain good field emission characteristics. These results demonstrate that doubled walled TiO₂ nanotubes are promising next generation field emission electron sources.

Acknowledgements

P.G.C. acknowledges the Consortium for Scientific Research (CSR) Indore, India for financial support (CSR project - CSR-IC-MSRSR-19/CRS-227/2017-2018/1308). V.S.B. is thankful to SVKM's NMIMS Deemed-to-be University for financial assistance. S.R.R., R.W.C., and N.Y.D. acknowledge the UK Engineering and Physical Sciences Research Council (EPSRC) for funding (Grant No. EP/S001395/1). This work has also used the computational facilities of the Advanced Research Computing at Cardiff (ARCCA) Division, Cardiff University, and HPC Wales. This work also made use of the facilities of ARCHER (<http://www.archer.ac.uk>), the UK's national supercomputing service via the membership of the UK's HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202).

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable

References

- [1] N. Liu, H. Mirabolghasemi, K. Lee, S. P. Albu, A. Tighineanu, M. Altomarea and P. Schmuki, *Faraday Discuss.*, 2013, **164**, 107-116, doi: 10.1039/C3FD00020F.
- [2] I. Paramasivam, H. Jha, N. Liu and P. Schmuki, *Small*, 2012, **8**, 3073-3103, doi: 10.1002/sml.201200564.
- [3] G. P. Patil, V. S. Bagal, S. R. Suryawanshi, D. J. Late, M. A. More and P. G. Chavan, *Appl. Phys. A*, 2016, **122**, 560, doi: 10.1007/s00339-016-0090-z.
- [4] G. P. Patil, V. S. Bagal, C. R. Mahajan, V. R. Chaudhari, S. R. Suryavanshi, M. A. More and P. G. Chavan, *Vacuum*, 2016, **123**, 167-174, doi: 10.1016/j.vacuum.2015.10.028.
- [5] X. S. Fang, Y. Bando, G. Z. Shen, C. H. Ye, U. K. Gautam, P. M. F. J. Costa, C. Y. Zhi, C. C. Tang and D. Golberg, *Adv. Mater.*, 2007, **19**, 2593-2596, doi: 10.1002/adma.200700078.
- [6] Y. Y. Song, Z. D. Gao, J. H. Wang, X. H. Xia and R. Lynch, *J. Adv. Funct. Mater.*, 2011, **21**, 1941-1946, doi: 10.1002/adfm.201002258.
- [7] D. V. Portan, A. A. Kroustalli, D. D. Deligianni and G. C. Papanicolaou, *J. Biomed. Mater. Res.*, 2012, **100A**, 2546-2553, doi: 10.1002/jbm.a.34188.
- [8] Y. Li, X. Yu and Q. Yang, *J. Sens.*, 2009, **402174**, 1-19, doi: 10.1155/2009/402174.
- [9] Y. Xie, D. Fu, *J. Appl. Electrochem.*, 2010, **40**, 1281-1291, doi: 10.1007/s10800-010-0077-y.
- [10] R. Asmatulu, A. Karthikeyan, D. C. Bell, S. Ramanathan and M. J. Aziz, *J. Mater. Sci.*, 2009, **44**, 4613-4616, doi: 10.1007/s10853-009-3703-5.
- [11] J. Y. Kim, T. Sekino and S. I. Tanaka, *J. Mater. Sci.*, 2011, **46**, 1749-1757, doi: 10.1007/s10853-010-4994-2.
- [12] G. P. Patil, A. B. Deore, V. S. Bagal, D. J. Late, M. A. More and P. G. Chavan, *Chem. Phys. Lett.*, 2016, **657**, 167-171, doi: 10.1016/j.cplett.2016.06.003.
- [13] Z. Gong, N. Yang, Z. Chen, B. Jiang, Y. Sun, X. Yang and L. Zhang, *Chem. Eng. J.* 2020, **380**, 122524, doi: 10.1016/j.cej.2019.122524.
- [14] X. Wang, M. Sun, M. Murugananthan, Y. Zhang and L. Zhang, *Appl. Catalys. B-Environ.*, 2020, **260**, 118205, doi: 10.1016/j.apcatb.2019.118205.
- [15] X. Lu, X. Li, F. Chen, Z. Chen, J. Qian and Q. Zhang, *J. Alloy. Compd.*, 2020, **815**, 152326, doi: 10.1016/j.jallcom.2019.152326.
- [16] B. Fu, Z. Wu, S. Cao, K. Guo and L. Piao, *Nanoscale*, 2020, **12**, 4895-4902, doi: 10.1039/C9NR10870J.
- [17] G. Mittal and I. Lahiri, *J. Phys. D Appl. Phys.*, 2014, **47**, 323001, doi: 10.1088/0022-3727/47/32/323001.
- [18] V. S. Bagal, G. P. Patil, A. B. Deore, P. K. Baviskar, S. R. Suryawanshi, M. A. More and P. G. Chavan, *Chem. Phys. Lett.*, 2016, **650**, 7-10, doi: 10.1016/j.cplett.2016.02.052.
- [19] G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775, doi: 10.1103/PhysRevB.59.1758.
- [20] P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953, doi: 10.1103/PhysRevB.50.17953.
- [21] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188, doi: 10.1103/PhysRevB.13.5188.
- [22] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 224106, doi: 10.1063/1.2404663.
- [23] G. W. Watson, E. T. Kelsey, N. H. de Leeuw, D. J. Harris and S. C. Parker, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 433-438, doi: 10.1039/FT9969200433.
- [24] A. M. Ganose, K. T. Butler, A. Walsh, D. O. Scanlon, *J. Mater. Chem. A*, 2016, **4**, 2060-2068, doi: 10.1039/C5TA09612J.
- [25] J. B. Chen, C. W. Wang, B. H. Ma, Y. Li, J. Wang, R. S. Guo and W. M. Liu, *Thin Solid Films*, 2009, **517**, 4390-4393, doi: 10.1016/j.tsf.2009.01.088.
- [26] J. M. Wu, H. C. Shih and W. T. Wu, *Chem. Phys. Lett.*, 2005, **413**, 490-494, doi: 10.1016/j.cplett.2005.07.113.
- [27] G. Liu, F. Li, D. W. Wang, D. M. Tang, C. Liu, X. Ma, G. Q. Lu and H. M. Cheng, *Nanotechnology*, 2008, **19**, 025606, doi: 10.1088/0957-4484/19/02/025606.
- [28] X. Xu, C. Tang, H. Zeng, T. Zhai, S. Zhang, H. Zhao, Y. Bando and D. Golberg, *ACS Appl. Mater. Interfaces*, 2011, **3**, 1352-1358, doi: 10.1021/am200152b.

- [29] K. Dewangan, G. P. Patil, R. V. Kashid, V. S. Bagal, M. A. More, D. S. Joag, N. S. Gajbhiye and P. G. Chavan, *Vacuum*, 2014, **109**, 223-229, doi: 10.1016/j.vacuum.2014.07.027.
- [30] S. Yang, N. Huang, Y. M. Jin, H. Q. Zhang, Y. H. Su and H. G. Yang, *Cryst. Eng. Comm.*, 2015, **17**, 6617–6631, doi: 10.1039/C5CE00804B.
- [31] M. Lazzeri, A. Vittadini and A. Selloni, *Physica B*, 2001, **63**, 155409, doi: 10.1103/PhysRevB.63.155409.

Author information



Girish P. Patil received the M.Sc. (Physics) degree with specialization in material science from the Department of Physics, School of Physical Sciences, Kavayitri Bahinabai Chaudhari North Maharashtra University Jalgaon, Maharashtra, India, in 2013. He is currently working toward the Ph.D. degree in materials science and engineering with the Wuhan University of Science and Technology, Wuhan, China. He has authored or co-authored 24 publications. His research interest includes synthesis of nanomaterials of inorganic semiconducting materials toward Field emission, supercapacitors and device grade lithium-sulfur battery developments.



Vivekanand S. Bagal received the M. Sc. (Physics) degree with specialization in material science from the department of Physics, School of Physical Sciences, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon, Maharashtra, India, in 2006. He also Ph. D. degree in Physics from the department of Physics, School of Physical Sciences, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon, Maharashtra, India, in 2019. He is currently working as Assistant Professor in SVKM's NMIMS University, Shirpur Campus, District: Dhule, Maharashtra, India. He has authored or co-authored 18 publications in various reputed journals. His research interest includes synthesis of various nanostructures and nano-heterostructures for the applications of field emission and supercapacitors.



Sugam J Shivhare received the M. Sc. (Applied Chemistry) with specialization in organic chemistry from School of Chemical Sciences, Devi Ahaliya Vishwavidyalaya, Indore, Madhya Pradesh, India in 2001. He received his doctorate in chemistry on Polarographic and Voltammetric Study on some Heterocyclic Compounds containing Nitrogen with life Essential Elements" from Govt. Holkar Sc. College, Devi Ahaliya Vishwavidyalaya, Indore,

Madhya Pradesh, India in 2014. He is currently working as Assistant Professor in SVKM's NMIMS University, Shirpur Campus, Dhule, Maharashtra, India. He has authored or co-authored 20 publications in various reputed journals. His research interest includes synthesis of various nanostructures for the applications of supercapacitors and batteries.



Padmakar G. Chavan received his masters in subject Physics from Department of Physics, School of Physical Sciences, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon, Maharashtra, India, in 2006. He completed his Ph. D. in 2012 from Department of Physics, Savitribai Phule Pune University, Pune, Maharashtra, India. He is working as Assistant Professor at Department of Physics, Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon since 2012. He has published 51 research papers in the journal of International repute. His research interest includes synthesis of various nanostructures for field emission applications.



Russell W. Cross is a graduate from Cardiff University, where he gained MSc in Catalysis and a BSc in Chemistry degrees. Russell's PhD research involves computer-aided design of transition metal phosphides for efficient hydrogen evolution reaction. He is also working on the rational design of bimetallic Ni-based catalyst for direct hydrazine fuel cell (DHFC) technology.

Publisher's Note Engineered Science Publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.