A Comparative Study Structural Models, Lattice Planes, and Patterson Densities in Three Polymorphs of Titanium Dioxide

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ABSTRACT

Titanium dioxide, TiO_2, is one of the most important bio-compatible material and photocatalytic material that exist as three main polymorphs anatase, rutile, and brookite. The presence one or all of these polymorphs phases can significantly affect the overall performance of the material. In current study, we explore the main difference structural models, lattice parameters, and Patterson densities of all three polymorphs using Visualization for Electronic and Structural Analysis (VESTA) theoretical tool. An illustration of the intense Lattice planes that appear in five different TiO2 polymorphs is also presented. The Patterson densities were analyzed by using model electron densities and model nuclear densities and constructed structure models are attributed to various phases of TiO_2 polymorphs.

1. INTRODUCTION:

In the last few decades, Titanium dioxide which is also known as Titania, attracts the attention of numerous researchers due to its capability to work as a photocatalyst and help in many technological and eco-friendly applications. Titanium dioxide has a diverse application area including hydrogen generate, treating air and water pollution, blocking pigments as well as biological areas and display and sensor technologies, photocatalytic, photocatalysis, light-energy conversion systems, paints, papers, sunscreen, and ultraviolet (UV) [1-3]. Various structures of TiO_2 such as mesoporous nanorods, nanotubes, and core-shell structures with the hybrid materials have also been established in particular appropriate for solar cell electrode capability and photocatalysis [4]. Over the existing fourteen polymorphs of TiO_2 the anatase, rutile, and brookite phases have been extensively studied. The crystallographic structure of TiO_2 observed to occur in different phases called transition polymorphs. The cell volume of brookite-TiO_2 is bigger as compared anatase or rutile-TiO_2, having eight TiO_2 groups in one unit cell in comparison to four for anatase-TiO_2 and two for rutile-TiO_2. The rutile-TiO_2 exhibit furthermost refractive indices in visible region of electromagnetic spectrum in comparison to other known crystal, which makes it a potential candidate for specific optical instrument based on polarization optics with working range longer visible and infrared region [5-8]. The phase-dependent crystallographic study on polymorphs of TiO_2 is, therefore, essential to understanding the coordination environments as well as the distribution of electrons and nucleons. Numerous theoretical approaches for predicting the crystal structure have been established but they are not suitable for displaying inter-atomic distances and bond angles. To analyze the variation in band gap for anatase, brookite, and rutile-

TiO_2 polymorphs, it is necessary to visualize their fundamental structures and geometrical structure factors. The current research work aims to distinguish between the three main polymorphs of titanium dioxide.

2. COMPUTATIONAL DETAIL

The investigation of crystallographic information in language of structure models, lattice planes, ranges of fractional coordinates, and Patterson densities form model electron densities and model nuclear densities of TiO_2 polymorphs, in particular anatase, brookite, and rutile is performed by VESTA software theoretical tool using the available observed values (as Listed in Table.1).

3. RESULTS AND DISCUSSIONS

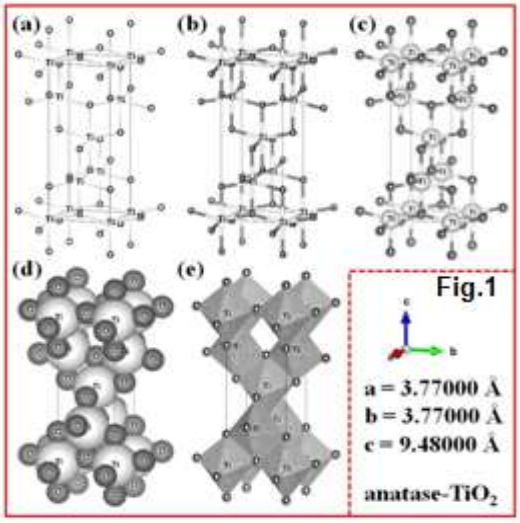
The anatase, rutile and brookite phases of TiO_2 are selected from numerous polymorphs for the comparative investigation of crystallographic parameters using structure models, lattice planes, ranges of fractional coordinates and analysis of Patterson densities by applying concept of model electron densities and model nuclear densities.

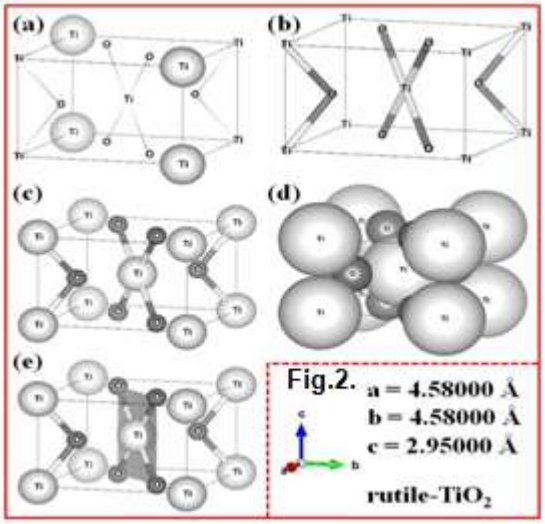
3.1.STRUCTURE MODELS

An organized investigation for the crystallographic information using structure models of three polymorphs of TiO_2 (especially anatase, rutile, and brookite) in five different styles are compared and explored by using VESTA theoretical tool and demonstrated in Fig.1. Both anatase and rutile have a tetragonal crystal system while brookite having orthorhombic. The values of lattice parameters a and b increase while that of c observed to decreases as we move in order anatase rutile and brookite respectively.

Table.1. Polymorphs-TiO_2 structure with their crystallographic parameters

Polymorphs TiO_2	**Crystal system**	**Space group (No.)**	**Lattice parameters**			**Unit cell volume ($Å^3$)**
			a (Å)	**b (Å)**	**c (Å)**	
anatase-TiO_2	tetragonal	$I4_1/amd$ (141)	3.77	3.77	9.48	134.73
brookite-TiO_2	orthorhombic	Pbca (61)	9.19	5.46	5.15	258.41
rutile-TiO_2	tetragonal	$P4_2/mnm$ (136)	4.58	4.58	2.95	61.88





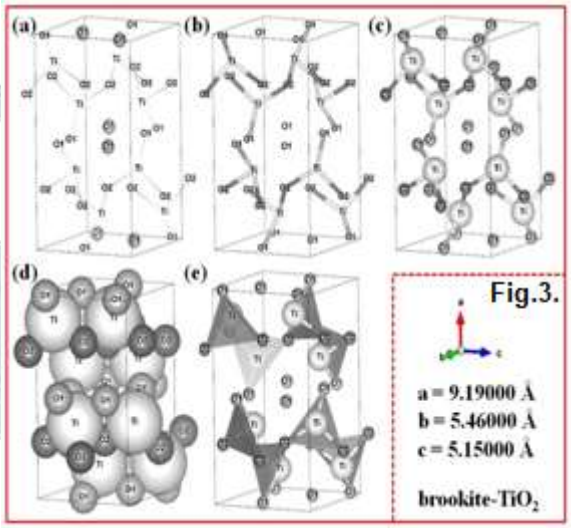


Fig. 1-3. Crystallographic representation: anatase, rutile and brookite(a) wire-frame, (b) stick, (c) ball stick, (d) space-filling (e) polyhedral structural models of Anatase, Rutile, and Brookite respectively. Colour code: gray and small spheres indicate oxygen (O) atoms; white and large spheres point out the titanium (Ti) atoms, polyhedra are showing in gray color.

3.2. LATTICE PLANES

The wireframe structure models of dominant lattice planes appear in various phases; particularly anatase, rutile, and brookite phase of TiO_2 polymorphs from a crystallographic perspective are shown and discussed in Fig.2. (a-c) provides the crystallographic representation of dominant lattice planes (101) and (200) that appear in anatase-TiO_2 polymorphs structure. The densest lattice planes (210) and (321) observed in brookite-TiO_2 polymorphs are displayed in Fig. 2(b). Fig. 2(c) illustrates the crystallographic demonstration of the intense lattice planes (110) and (211) observed in rutile-TiO_2 polymorphs structure [9-12].

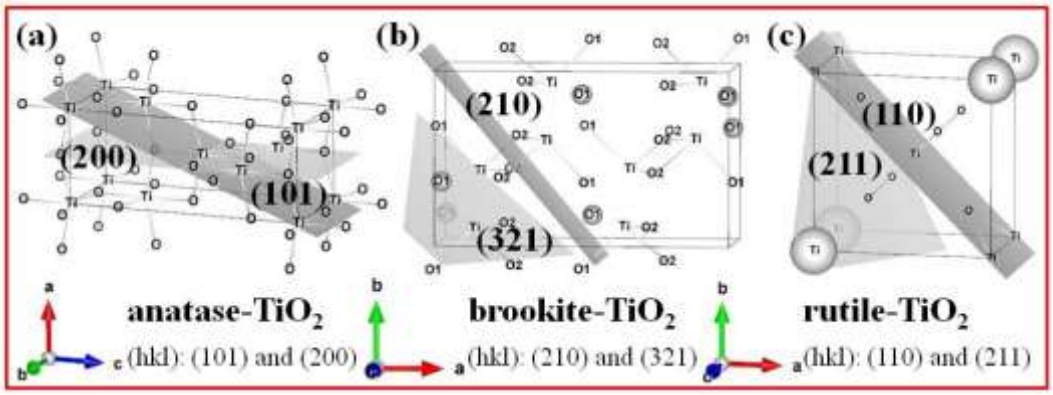


Fig.2.(a-c) Crystallographic representation of the intense Lattice Planes in TiO_2 polymorphs: (a) anatase-TiO_2, (b) brookite-TiO_2 and (c) rutile-TiO_2. All the lattice planes are described by a set of integer Miller indices (hkl). The representative unit cell is enveloped using thin solid lines in the wireframe structure model.

3.3.Lattice Planes and Ranges of Fractional Coordinates

A comparative study on the visualization of lattice planes family and ranges of fractional coordinates of different polymorphs of TiO_2; in particular anatase, rutile and brookite TiO_2 polymorphs is performed and displayed in Fig. 3-5.

The dissimilar lattice planes of anatase phase of TiO_2 are shown by Fig.3. (a-c) confirms using by different set Miller indices (hkl). Fig. 3.(a) explore the lattice planes along the z-direction *i.e.*(001), (002) and (003), whereas the lattice planes along the y-direction *i.e.*(010), (020) and (030) are demonstrated in Fig.3.(b) and (100), (200) and (300) lattice planes along the x-direction are displayed in Fig.3.(c). Fig.3. (d-g) reveals the fractional coordinates ranges of anatase. Fig.3. (d) x = y = z = 1, hence it's have one unit cell, even as Fig.3. (e) Demonstrate y = z = 1, x = 2presenting one extra unit cell in x-direction. Likewise in Fig.3 (f) x = z = 1, y = 2 indicating one extral unit cell along y-direction and Fig.3. (g), y = z = 1, x = 2 also observed to have one extra unit cell along z-direction [13-15].

Fig.4.(a-g) grant the visualization of the various lattice planes for rutile-phase of TiO_2 having dissimilar Miller indices (hkl) values. The lattice plane shown in Fig.4 (a) are (100), (110) and (120) in Fig.4. (b) (010), (011) and (012) and (100), (101) and (102) sketching in Fig.4. (c) For rutile-TiO_2. Fig.4. (d-g) also explores the fractional coordinates ranges. Fig.4.(d) indicate the wireframe structure model having position x = y = z = 1, providing only one unit cell of rutile TiO_2, while Fig.4. (e) Reveals y = z = 1 and x = 2 referring one extra unit cell along x-direction. Same way the Fig. 4.(f), showing position x = z=1 but y = 2, also one extra unit cell but along y-direction and finally Fig.4.(g) with x = y = 1 but z = 2 [16-19], showing one extra unit cell in z-direction.

The various kinds of lattice planes of brookite-polymorphs of TiO_2 are shown by Fig.5(a-g) with diverse set of Miller indices (hkl) values. Fig.5. (a-c) explore the different sets of lattice planes (100), (200) and (400), Fig.5. (b) (010), (020) and (040) and Fig.5.(c). (001), (002) and (004) lattice planes are illustrated in Fig.5.(d-g) explore the ranges of fractional coordinates of brookite-polymorphs of TiO_2. Fig.5. (d) with positional parameters x = y = z = 1 having single unit cell while Fig.5.(e) shows x =z= 1 but y = 2 have one extra unit

cell along y-direction. In same manner, Fig.5.(f) having positional parameters x = y = 1 but z = 2, clearly indicating one extra unit cell along z-direction and Fig.5.(g) owing position y = z = 1 but x = 2 also revealing one extra unit cell in x-direction [20-21].

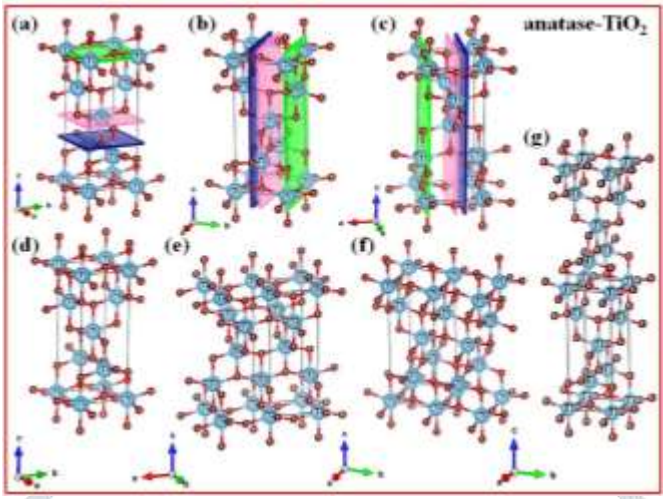


Fig.3(a-g) Crystallographic representation Anatase TiO_2

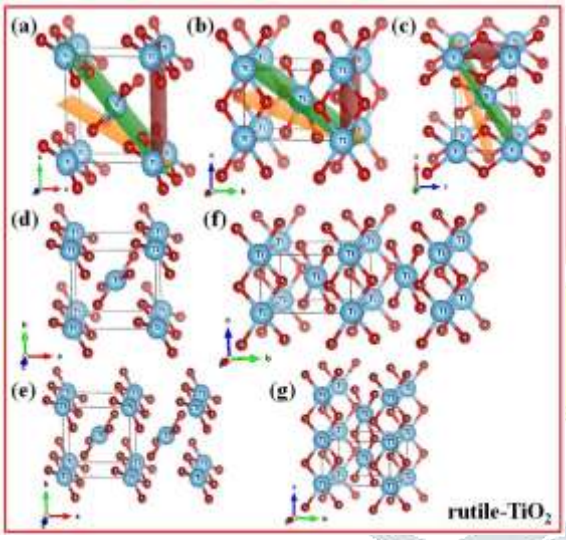


Fig.4(a-g) Crystallographic representation Rutile TiO_2

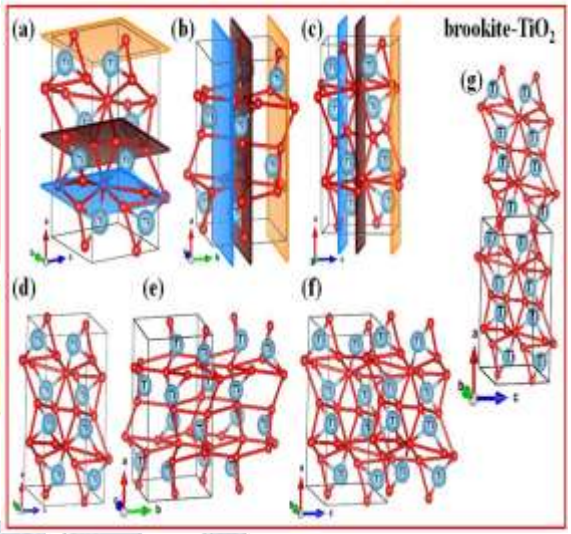


Fig.5(a-g) Crystallographic representation Brookite Ti

3.4.PATTERSON DENSITIES

An organized investigation on the crystallographic data for Patterson densities from model electron densities and model nuclear densities of three polymorphs ofTiO_2 (especially anatase, rutile, and brookite) is compared and established using VESTA theoretical tool, as shown in Fig.6.(A-C). The crystallographic structural characteristics of anatase-$TiO_2$are represented in Fig.6.A.(a-c). The wireframe structure model of anatase TiO_2 was observed to crystallize in a tetragonal crystal system. The isolated TiO_2 molecule is evident in Fig.6.A.(a), where each oxygen (O) atom is shared with three titanium (Ti) atoms and each Ti atom shared with six oxygen atoms further confirming the formation of the anatase-TiO_2. The bond length between Ti and O atoms is 1.9795 Å, which corresponds to the standard bond-length of metal and oxygen atoms.

Fig.6A.(b) stand for the model electron density of anatase-TiO_2, while green and red/orange shaded portion showing the electron density of Ti and O atoms, [22-25]. The shaded green segment is bigger than the red/orange shaded portion verifying the Ti atom has a bigger electron density as in comparison to O atom. Fig.6.A.(c) disclose the the anatase-TiO_2model nuclear density, where small shaded portions of Patterson density using model nuclear density are visible in this form of image.

Fig.6.B.(a-c) displays the representative wireframe structure model of the rutile-TiO_2 structure. To explain the crystal structure of rutile-TiO_2, the tetragonal unit cell is often more convenient containing titanium (Ti) and oxygen (O) atoms, where each O atom is shared with two Ti atoms and each Ti atom shared with four O atoms. The calculated bond-length between Ti and O atoms is about 1.9462 Å, which is well-matched with the established results. The Patterson densities observed from model electron density and model nuclear density are depicted in Fig.6.B.(a) to Fig.6.B. (c), respectively.

The crystallographic form in terms of structure model and Patterson densities of brookite-TiO_2 is shown in Fig.6(C).(a-c). Fig.6.C.(a) illustrates the wireframe representative structure model of brookite-TiO_2, corresponding to an orthorhombic crystal system. The isolated TiO_2 molecule is visible in Fig.6.C(b), where each titanium (Ti) atom is shared with two oxygen (O) atoms (O1 and O2) verifying the formation of the brookite-TiO_2. The bond-length between Ti and O atoms is about 1.9365 Å and 1.9246 Å for O1 and O2 atoms, respectively. The observed bond-lengths are well-matched with the established results [26-30]. Fig.6.C.(b) represents the model electron density of brookite-TiO_2. Fig6.C.(c) exhibit the model nuclear density of brookite-TiO_2. The oxygen atoms are linked with the other unit cell.

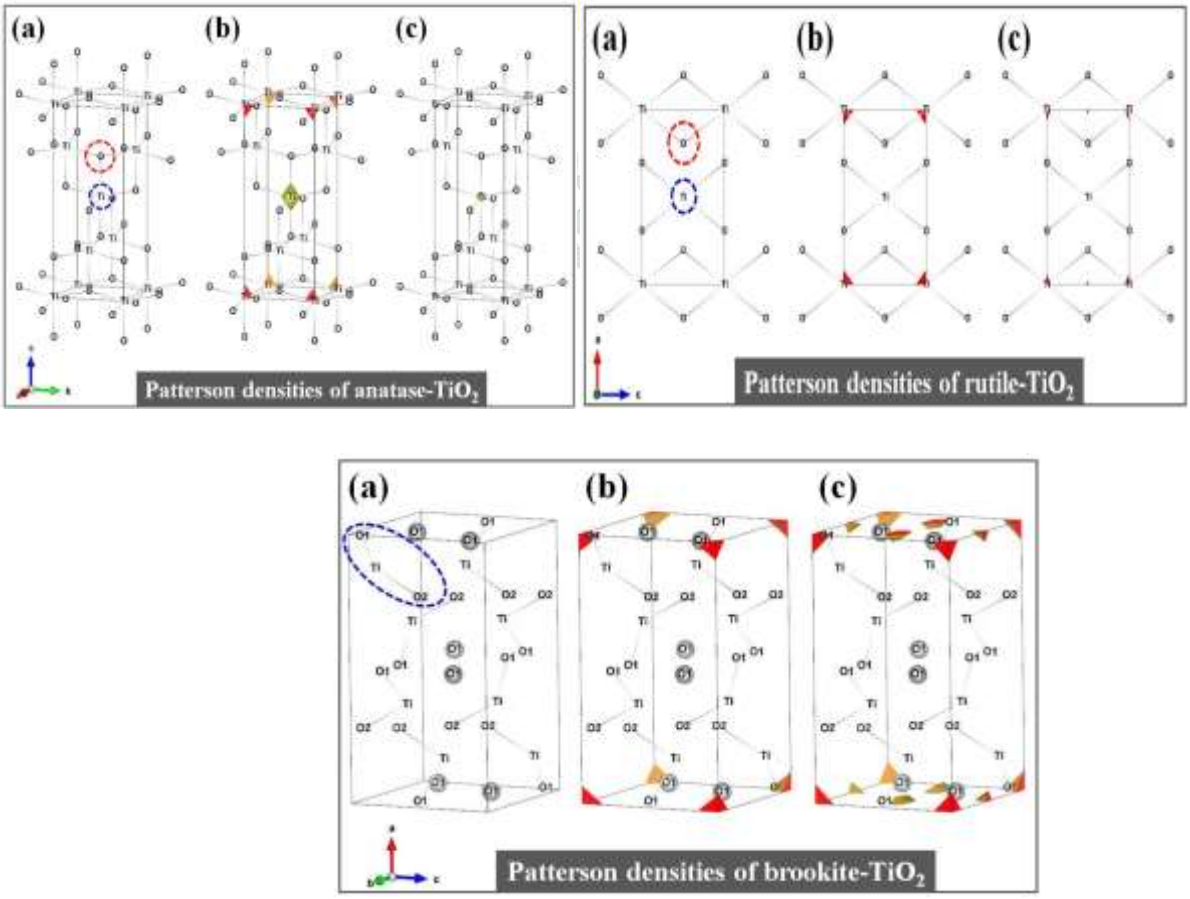


Fig.6(A-C) Crystallographic representation of Anatase,Rutile and Brookite-TiO_2

Table.2. The atomic position of Titanium and Oxygen atoms in Anatase, Rutile and Brookite -TiO_2

TiO_2 Polymorphs	Atom	X	y	z	bond length (Å)
anatase-TiO_2	titanium (Ti)	0.000	0.000	0.000	Ti-O →1.979
	oxygen (O)	0.000	0.000	0.208	
brookite-TiO_2	titanium (Ti)	0.128	0.098	0.862	Ti-O1 → 1.936
	oxygen (O1)	0.011	0.147	0.182	Ti-O2 → 1.938
	oxygen (O2)	0.229	0.108	0.534	
rutile-TiO_2	titanium (Ti)	0.000	0.000	0.000	Ti-O →1.946
	oxygen (O)	0.305	0.305	0.000	

4. Conclusions

The investigation of different lattice and structural parameters inclding lattice planes, ranges of fractional co-ordinates and Patterson densities from model electron densities and model nuclear densities for different TiO_2 polymorphs structures are successfully done. By using VESTA theoretical tool, the bond lengths of titanium atoms with oxygen atoms for different polymorphs TiO_2 structures are calculated. The two important Patterson densities, especially model electron density and model nuclear density, are compared and visualized through VESTA theoretical tool on three titania polymorphs structures. The investigation of phase-dependent Patterson densitiy suggests the general importance of anatase, rutile, and brookite TiO_2 in both fundamental and application-oriented research.

References:

1. J. Gangwar, B. K. Gupta, S. K. Tripathi and A. K. Srivastava, *Nanoscale* 7, 13313(2015).
2. M. Niu, F. Huang, L. Cui, P. Huang, Y. Yu, and Y. Wang, *ACS Nano***4**, 681 (2010).
3. C. C. Yang,and Y. W. Mai, *Mater. Sci. Eng. R***79**, 1 (2014).
4. M. I. Khan, *J. Solid State Chem.***152**, 105 (2000).
5. J. Gangwar, B. K. Gupta and A. K. Srivastava, *Defence Sci. J.***66**, 323-340 (2016).
6. Y. Li, M. Gecevicius, and J. Qiu, *Chem. Soc. Rev.***45**,2090 (2016).
7. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga,*Science***293**, 269 (2001).
8. K. K. Dey, D. Bhatnagar, A. K. Srivastava, M. Wan, S. Singh, R. R. Yadav, B. C. Yadav and, M. Deepa,*Nanoscale***7**, 6159 (2015).
9. S. Zhang, L. Ren, and S. Peng, *Cryst. Eng. Comm.***16**, 6195 (2014).
10. Q. J. Xiang, J. G. Yu, and M. Jaroniec, *Chem. Soc. Rev.***41**, 782 (2012).
11. S. Li, S. Xu, L. He, F. Xu, Y. Wang, and L. Zhang, *Polym.-Plast. Technol. Eng.***49**, 400 (2010).

12. J. Gangwar, K. K. Dey, S. K. Tripathi, M. Wan, R. R. Yadav, R. K. Singh, Samta and A. K. Srivastava,*Nanotechnology***24**, 415705 (2013).

13. M. Y. Xing, Y. M. Wu, J. L. Zhang, and F. Chen, *Nanoscale***2**, 1233 (2010).

14. C. Y. Flores, C. Diaz, A. Rubert, G. A. Benitez, M. S. Moreno,M. A. F. L. De Mele, R. C. Salvarezza, P. L. Schilardi, andC. Vericat, *J. Colloid Interface Sci.* 350, 402 (2010).

15. T. Froschl, U. Hormann, P. Kubiak, G. Kucherova, M. Pfanzelt, C. K. Weiss, R. J. Behm, N. Husing, U.Kaiser, K. Landfester and M. W. Mehrenes, Chem. Soc. Rev. 41, 5313-5360 (2012).

16. R. Verma, J. Gangwar, and A. K Srivastava, *RSC Adv.***7**, 44199 (2017).

17. Z. Ren, E. Kim, S. W. Pattinson, K. S. Subrahmanyam,C. N. R. Rao, A. K. Cheetham, and D. Eder, *Chem. Sci.***3**, 209 (2012).

18. J. F. Jacobs, L. V. de Poel, and P. Osseweijer, *Nanoethics***4**, 103 (2010).

19. H. Zhang and J. F. Banfield, Chem. Rev. 114, 9613-9644 (2014).

20. M. Gratzel, *Nature***414**, 338 (2001).

21. D. C. Sayle, J. A. Doig, S. A. Maicaneanu, and G. W. Watson, *Phys. Rev. B: Condens. Matter Mater. Phys.***65**,245414 (2002).

22. K. Liu, M. Cao, A. Fujishima, and L. Jiang, *Chem. Rev.***114**, 7740 (2014).

23. J. Yao, M. Yang and Y. Duan, Chem. Rev. 114, 6130-6178 (2014).

24. J. Gangwar, A. Chandran, T. Joshi, R. Verma, A. M. Biradar, S. K. Tripathi, B. K. Gupta, and A. K. Srivastava,*Mater. Res. Express***2**, 075013 (2015).

25. L. Poul, S. Ammar, N. Jouini, F. Fieovet, and F. Villain, *Solid State Sci.***3**, 31 (2001).

26. M. Cargnello, T. R. Gordon, and C. B. Murray, *Chem. Rev.***114**, 9319 (2014).

27. Ebelmen, *Ann. Chim. Phys. Ser*.**57**, 319 (1846).

28. S. Shang, K. Xue, D. Chen, and X. Jiao, *Cryst. Eng. Comm.***13**, 5094 (2011).

29. J. Gangwar, B. K. Gupta, P. Kumar, S. K. Tripathi, and A. K. Srivastava, *Dalton Trans.***43**, 17034(2014).

30. Y. Zhou, and M. Antonietti, *J. Am. Chem. Soc.***125**,14960 (2003).