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Theoretical Calculation of Surface Energy of Anatase TiO_2 (111) and ZrO_2(111): An Important Parameter for Osseointegrationof Dental Implants

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ABSTRACT
The characteristics of the materials that are used for dental implants are critical for the success of the implant process. Surface energies of the materials that are used for implant surgery are especially important for osseointegration of the implant and to prevent implant failure. In this study, we performed a theoretical analysis of the surface energies of two prominent materials. The surface energies of anatase TiO_2 (111) and ZrO_2 (111) were calculated with General Utility Lattice Program (GULP). Through analysis of surface energy values, usage of TiO_2 (111) and ZrO_2 (111) in dental implants is discussed in detail. Obtained theoretical results show that surface energy of TiO_2 (111) is greater than the surface energy of ZrO_2 (111) which is consistent with the literature.

Keywords: Dental Implants, Surface Energy, TiO_2, ZrO_2.

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I. INTRODUCTION

Materials may exert higher conductivity, higher surface area, and better biocompatibility characteristics atnanodimensions compared to their macro forms. Thus, studies in nanoscale contribute to the production of novel materials in different fields such as physics, chemistry, biology, medicine and dentistry [1-5]. One of the fields that nanotechnology is widely used in is nanodentistry. Advances innanomaterials, nanosurgery and nanodrugs will shape the future of clinicalnanodentistry [6]. These fields become more important especially for the success of dental implants [7].

One of the most common causes of failure in dental implants is the lack of osseointegration between the implant and the bone. Interactions between the cells and the material interface affect the attachment of blood and bone cells to the surface, and their proliferation and differentiation. This is an important factor for enhancing osteointegration and implant success [8-13]. Interactions between the biomaterials and the cells depend on the surface features of the biomaterials, such as surface topography, surface energy and physical and chemical characteristics [14]. Especially the surface feature of implants is very important in implant technology which increases the importance of nanodentistry. Although there are many studies investigating the role of surface topography of implants on biological response, the number of studies evaluating surface energy of dental implants is rather low [15].

Presence of a hydrophilic surface accelerates the interactions of the implant surface with blood, thereby enhancing wound healing and osseointegration, and is closely related to the surface energy of the biomaterial [16]. Different materials used in implant construction have different surface properties and different surface energies [17]. Implant surface energy is an important factor in the regulation of osteogenesis. Depending on the surface energy, the materials might have a hydrophilic or a hydrophobic surface [18]. Generally, when the implant surface is positively charged, the surface becomes hydrophilic and some of the plasma proteins required to create the initial osteogenic interactions areadsorbed to these surfaces [19]. This shows the importance of surface energy on osseointegration.
Titanium (Ti) and Ti-based alloys are widely used especially in dental implants due to their excellent biocompatibility and excellent mechanical properties [12]. These titanium-based implants have an unreactiveoxide layer on their surfaces that resists rusting and promotes osseointegrationof the surrounding bone tissue [23]. Increasing use of dental implants has led to the search for new materials to be used in orthopedic applications that would be an alternative to titanium implants. One of these materials is zirconium. When exposed to oxygen, zirconium is converted to the

biocompatible zirconium dioxide (ZO, chemically ZrO_2) [24]. Zirconium dioxide has been shown to enhance the osseointegration of the surface [12].

Previously, theoretical and experimental studies have been performed that analyze the surface energies of titanium dioxide and zirconium dioxide [23-26]. However, theoretical studies on the investigation of surface energies in dental practice are lacking. Since surface energy has been shown to effect osseointegration, the aim of this study was to theoretically calculate and compare the surface energy of two different implant surfaces, TiO_2 and ZrO_2, by using General Utility Lattice Program (GULP), which is a forcefield based program.

II. METHODS

Total Lattice Energy of TiO_2 (Bulk), ZrO_2 (Bulk), anatase TiO_2 (111) and ZrO_2 (111) were obtained by GULP [27-28]. GULP is designed to perform a variety of tasks based on force field methods. Dreiding force field method was used for TiO_2 surface [29], and Lewis force field method was used for ZrO_2 surface. For both systems, P1 symmetry was adopted. Surface energy of the surfaces was obtained by using the following formula;

$$\Delta U_{SE} = \frac{U_{surf} - U_{Bulk}}{A} \quad (1)$$

where ΔU_{SE} is surface energy, U_{surf} is the total lattice energy of the (111) surface, U_{Bulk} is the total lattice energy of the bulk system and A is the surface area. We have cleaved the surfaces along Y (u) and XY (v) planes for both TiO_2 and ZrO_2.

For TiO_2 (111), u is 5.34 Å, v is 10.21 Å and contact angle is 105°. The surface thickness for TiO_2 (111) surface was set to 15.42 Å. For bulk TiO_2, lattice parameters are a = 3,776, b = 3,776 and c = 9,486 Å, respectively.

For ZrO_2 (111), u and v are 3.58 Å and contact angle is 120°. The surface thickness for ZrO_2 (111) was set to 11.71 Å. For bulk ZrO_2, lattice parameters are a = b = c = 5,070 Å.

III. RESULTS AND DISCUSSION

This study presents the calculation and comparison of the surface energies of two different implant materials which were previously proven to be successful as dental implants.

Utilizationof dental implants in completely or partially edentulous patients is a scientifically accepted and well documented treatment method [30]. Titanium and titanium alloys have become gold standard for implant surgery in dentistry due totheirexcellentbiocompatibility,appropriatemechanical properties and proven success as dental implants [20] (Fig. 1a). The titanium dioxide layer that is formed when the titanium surface contacts with oxygen forms the basis of its biocompatibility. The characteristics of the titanium dioxide layer on the surface are very important for its biological activity during implant-bone osseointegration [21]. However, some aesthetic concerns regarding the titanium implants have led researchers to search for new alternative biocompatible implant materials. Zirconium is one of the major materials that present a suitable alternative. Due to its tooth-like colors (aesthetic advantage), superior mechanical properties, and biocompatibility, zirconium has been proposed to be used as a dental implant material [31] (Fig. 1b). Thus, in the present study, we evaluated titanium and zirconium as the most commonly used implant materials.

TiO_2 (bulk) and anatase TiO_2 (111) surfaces are shown in Fig. 2. Similarly, Fig. 3 shows ZrO_2 (111) and ZrO_2 (bulk). In Fig. 2, the red color represents the oxygen atom and the grey color shows the titanium atom. In Fig. 3, the red color represents the zirconium atom while the light blue color shows the oxygen atom.

The physical, chemical and surface properties of a biomaterial play fundamental roles in osseointegration. The surface characteristics of the implant material are one of the main factors that promote wound healing and enhance osseointegration of the implant within the tissue [32]. Particularly, surface energy has been shown to promote migration of bone cells to the implant surface during osteogenesis, thus boostingosseointegration. The hydrophilicity or hydrophobicity of the surfaces arecorrelated to the surface energy of the materials (Fig. 4a-b).The positive value of surface energy indicates that the surface is hydrophilic[18, 19]. In this study, both titanium dioxide and zirconium dioxide surfaces were found to have positive surface energy values and the surface energy of titanium was found to be higher.In vitro and in vivo studies that analyzed these two surfaces exhibited the biocompatibility of these two implant materials, and their clinical success [12].Hydrophilic surfaces enable the biomacromolecules in the blood to attach to the implant surface and fill the space between the implant and the bone tissue, thus causing osteoblasts to migrate to the region and ultimately resulting in complete osseointegration[13]. Our results suggest that the calculated positive surface energies of both of these materials may be related to their hydrophilic characteristics.

Lattice total energies together with surface area are presentedin Table 1 for both TiO_2 and ZrO_2. Surface energies of TiO_2 and ZrO_2 are shown in Table 2. The results in Table 2 clearly show that the surface energy of TiO_2 is higher than that of

ZrO_2, which is in agreement with the literature [33-35].

Several studies have previously evaluated the clinical usage of titanium and zirconium implants, which showed that the clinical success rates of titanium and zirconium implants are comparable [33-37]. The results of the current work suggest that the surface energy of the titanium dioxide surface is higher. In parallel with these results, several studies have shown that the bone-implant contact of titanium implants is higher compared to zirconium implants[33-35].

IV. CONCLUSION

To the best of our knowledge, this is the first study to compare the surface energies of two different implant surfaces that are frequently used in dental implants. Our results show that the surface energy of the titanium dioxide surface is higher than that of the zirconium dioxide surfaces. These results are consistent with the previous studies showing the clinical and experimental success of implants with titanium and zirconium surfaces. Results obtained in this study will shed light onto new theoretical studies about titanium and zirconium implants.

REFERENCES

[1]. P. Li, M. Zhou, L. Zhang, Y. Guo, andF.Liu,Formation of a quantumspinHallstate on a Ge(111) surface,Nanotechnology, 27(9), 2016, 095703.

[2]. G.Peng,andM.Mavrikakis,AdsorbateDiffusionTransitionMetalNanoparticles,NanoLetters, 15(1),2015, 629-634.

[3]. X.Yin, M.J. Stott,andA. Rubio, α- and β-tricalciumphosphate:Adensityfunctionalstudy, PhysicalReview B, 68, 2003, 205205.

[4]. F.Ren,X. Lu,andY. Leng,Ab initiosimulation on thecrystalstructureandelasticproperties of carbonatedapatite,JournaloftheMechanicalBehavior of BiomedicalMaterials, 26, 2013, 59-67.

[5]. Y. Lin,H. Ma, C.W. Matthews,B. Kolb, S. Sinogeikin, T. Thonhauser, andW.L. Mao,ExperimentalandTheoreticalStudies on aHighPressureMonoclinicPhaseofAmmonia Borane,TheJournal of PhysicalChemistry C, 116(3), 2012, 2172-2178.

[6]. H. Aeran,V. Kumar,S. Uniyal,andP. Tanwer, Nanodentistry: Is just a fiction orfuture, JournalofOralBiologyandCraniofacialResearch, 5(3),2015, 207–211.

[7]. A.P. Tomsia,J.S. Lee,U.G. Wegst,and E. Saiz,Nanotechnologyfordentalimplants,The International Journal ofOral&MaxillofacialImplants, 28(6), 2013, 535-546.

[8]. D.V.Kilpadi,andJ.E.Lemons,Surfaceenergycharacterizationofunalloyedtitaniumimplants, JournalofBiomedicalMaterialsResearch, 28(12), 1994,1419–1425.

[9]. Z.Schwartz,andB.D.Boyan,UnderlyingMechanismsattheBoneBiomaterialInterface, Journal of Cellular Biochemitry, 56(3), 1994,340–347.

[10]. K.Kieswetter,Z.Schwartz,D.D.Dean,andB.D. Boyan,Theroleofimplantsurfacecharacteristicsin thehealingofbone, CriticalReviews in Oral BiologyandMedicine, 7(4),1996, 329–345.

[11]. R.K. Sinha,F. Morris,S.A. Shah,andR.S. Tuan,Surfacecompositionoforthopaedicimplantmetalsregulatescellattachment, spreading, andcytoskeletalorganizationof primaryhumanosteoblastsinvitro,ClinicalOrthopaedicsandRelatedResearch, 305, 1994, 258–272.

[12]. V. Sollazzo,F. Pezzetti, A. Scarano,A. Piattelli, C.A. Bignozzi,L.Massari, G. Brunelli, and F. Carinci,Zirconiumoxidecoatingimprovesimplantosseointegrationin vivo,DentalMaterials, 24(3), 2008, 357–361.

[13]. S. Sista,C. Wen,P.D. Hodgson,andG. Pande,Theinfluence of surfaceenergy of titanium-zirconiumalloy on osteoblastcellfunctions in vitro, Journal of BiomedicalMaterialsResearchPartA, 97(1), 2011,27-36.

[14]. J.M. Sautier, J.R. Nefussi, and N.Forest,Surface-reactivebiomaterials in osteoblastcultures: an ultrastructuralstudy,Biomaterials, 13(6), 1992, 400-402.

[15]. F. Rupp,L. Scheideler,M. Eichler,andJ.Geis-Gerstorfer,WettingBehavior of DentalImplants, TheInternationalJournal of Oral&MaxillofacialImplants, 26(6), 2011,1256–1266.

[16]. S.K. Roehling, B.Meng,andD.L. Cochran,SandblastedandAcid-EtchedImplantSurfacesWithorWithout High SurfaceFreeEnergy: ExperimentalandClinical Background. In: Wennerberg, A.,Albrektsson, T., Jimbo, R. (eds) ImplantSurfacesandtheirBiologicalandClinicalImpact,(Berlin: Springer,Heidelberg, 2015) 93-136.

[17]. F. Rupp, R.A. Gittens, L. Scheideler, A. Marmur,B.D. Boyan,Z. Schwartz,andJ. Geis-Gerstorfer, A Review on theWettability ofDentalImplantSurfaces:TheoreticalandExp

erimentalAspects,ActaBiomaterialia,10(7), 2014,2894–2906.

[18]. T. Sawase,R. Jimbo,K. Baba,Y. Shibata,T.Ikeda,andM. Atsuta, Photo-inducedhydrophilicityenhancesinitialcellbehaviorandearly bone apposition,Clinical Oral ImplantsResearch, 19(5),2008, 491-496.

[19]. R. Jimbo, M.Ivarsson,A. Koskela,Y.T. Sul,andC.B.Johansson,Proteinadsorptiontosurfacechemistryandcrystalstructuremodificationoftitaniumsurfaces,JournalofOral&MaxilofacialResearch, 1(3), 2010, e3.

[20]. O.E. Pohler,Unalloyedtitaniumforimplants in bone surgery,Injury, 31(4), 2000, 7–13.

[21]. H.F.Hildebrand,andJ.C.Hornez,Biologicalresponseandbiocompatibility.In:J.A.Helsen,H.J. Breme(eds.)Metalsas Biomaterials, (UK, Wiley, Chichester, 1998) 265–290.

[22]. Y. Yang,J.L. Ong,and J.Tian,Deposition of highlyadhesiveZrO_2coatingonTiandCoCrMo implantmaterialusingplasmaspraying, Biomaterials, 24(4), 2003,619–627.

[23]. A.Christensen,andE.A.Carter,Firstprinciples study of thesurfaces of zirconia, PhysicalReview B, 58(12), 1998,8050-8064.

[24]. A.A. Levchenko, G.Li,J. Boerio-Goates, B.F. Woodfield,andA. Navrotsky, TiO_2StabilityLandscape: Polymorphism, SurfaceEnergy, andBoundWaterEnergetics,Chemistry of Materials,18(26), 2006, 6324–6332.

[25]. A.L.Silva,D.Hotza,andR.H.R.Castro,Surface energyeffectsonthestabilityofanataseandrutilenanocrystals:Apredictivediagramfor Nb_2O_5-doped-TiO_2, AppliedSurfaceScience, 393, 2017, 103-109.

[26]. F. Yuan,S.X. Lu,W.G. Xu, H.F. Zhang, andT.Ning,FirstprinciplesStudyontheSurface Energies of Rutile TiO_2(110) vs (011)-2×1Surfaces,Advanced MaterialsResearch, 937,2014, 113-117.

[27]. J.D. Gale, GULP: Acomputer program forthesymmetry-adaptedsimulation of solids, JournaloftheChemicalSocietyFaradayTransactions,93, 1997,629.

[28]. J.D.Gale,andA.L.Rohl,TheGeneralUtilityLatticeProgram(GULP),MolecularSimululation, 29, 2003, 291-341.

[29]. S.L.Mayo,B.D.Olafson,andW.A.Goddard,DREIDING:agenericforcefieldformolecularsimulations,TheJournal of PhysicalChemistry, 94(26), 1990,8897-8909.

[30]. M. Gahlert,T. Gudehus,S. Eichhorn,E. Steinhauser,H.Kniha,andW.Erhardt,Biomechanicalandhistomorphometriccomparisonbetweenzirconiaimplantswithvaryingsurfacetexturesand a titaniumimplant in themaxilla of miniaturepigs,ClinicalOralImplantsResearch , 18(5), 2007, 662–668.

[31]. R. Depprich, H. Zipprich, M.Ommerborn, C. Naujoks,H.P.Wiesmann, S. Kiattavorncharoen,H.C. Lauer, U. Meyer, N.R. Kübler,andJ.Handschel,Osseointegrationofzirconiaimplantscomparedwithtitanium: an in vivostudy, Head&FaceMedicine, 4, 2008, 30.

[32]. T.Albrektsson,P.I.Branemark,H.A.Hansson, andJ.Lindström,Osseointegratedtitaniumimplants. Requirementsforensuring a long-lasting, direct bone-to-implantanchorage in man,ActaOrthopaedicaScandinavica, 52(2), 1981, 155–170.

[33]. R.J. Kohal, D.Weng, M. Bächle,and J.R.Strub,Loadedcustommadezirconiaandtitaniumimplants Show similarosseointegration: ananimalexperiment,JournalofPeriodontology, 75(9), 2004, 1262–1268.

[34]. O.Hoffmann,N. Angelov,F. Gallez,R.E. Jung,andF.E.Weber,Thezirconiaimplant-boneinterface:apreliminaryhistologicevaluationinrabbits,TheInternationalJournalofOral& MaxillofacialImplants, 23(4), 2008, 691–695.

[35]. B. Bacchelli,G. Giavaresi,M. Franchi, D.Martini, V. De Pasquale, A. Trirè, M. Fini, R. Giardino,and A. Ruggeri,Influence of a zirconiasandblastingtreatedsurface on periimplantbonehealing:anexperimentalstudy in sheep,ActaBiomaterialia, 5(6), 2009, 2246–2257.

[36]. J.H.Dubruille,E.Viguier,G.LeNaour,M.T.Dubruille,M.Auriol,andY. Le Charpentier, Evaluation of combinations of titanium, zirconia, and alümina implantswith 2 bone fillers in thedog,TheInternationalJournalof Oral&MaxillofacialImplants,14(2),1999, 271–277.

[37]. M.Franchi,B.Bacchelli,D.Martini,V.D.Pasquale,E.Orsini,V.Ottani,M.Fini,G. Giavaresi,R. Giardino,and A. Ruggeri,Earlydetachment of titaniumparticlesfromvariousdifferentsurfaces of endosseousdentalimplants,Biomaterials, 25(12),2004, 2239–2246.

Figure captions

Fig.1. a) Titaniumimplant, **b)**Zirconiumimplant

Fig.2: Graphicaldisplay of (a) TiO_2 (111) surfaceand (b) TiO_2 (bulk). Redcoloredatoms in (a) and(b) areoxygenandgreycoloredonesaretitaniumatoms.

Fig.3: Graphicaldisplay of (a) ZrO_2 (111) surfaceand (b) ZrO_2 (bulk). Redcoloredatoms in (a) and(b)

arezirconiumandlightbluecoloredonesareoxygenatoms.

Fig.4.a) Hydrophobicsurface, **b)**Hydrophilicsurface. Acceleratedcoveringof theimplantsurfacewithblood [16].

TABLES

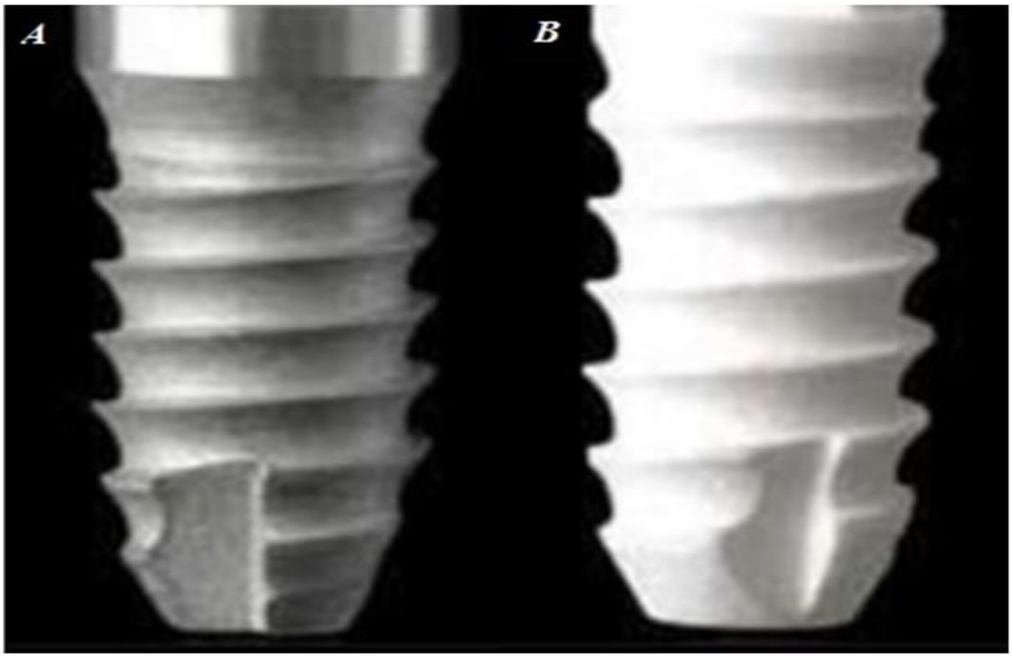
Table 1: Total latticeenergies of TiO_2 (Bulk), TiO_2 (111), ZrO_2 (Bulk) and ZrO_2(111) giventogetherwiththesurfacearea of TiO_2 (111) and ZrO_2 (111).

System	Total LatticeEnergy (kJ/mol)	SurfaceArea (Å^2)
TiO_2 (Bulk)	6550,0375	
TiO_2 (111)	34749,5781	52,624291
ZrO_2 (Bulk)	-10700,5076	
ZrO_2 (111)	-8199,2380	11,130353

Table 2: Surfaceenergy of TiO_2 (111) and ZrO_2 (111).

System	SurfaceEnergy (J/m^2)
TiO_2	88,91
ZrO_2	37,33

FIGURES



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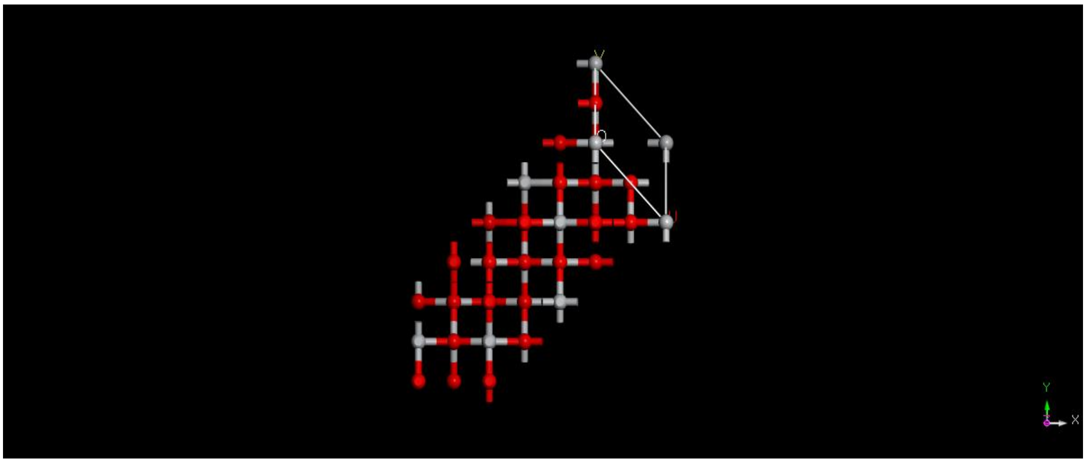
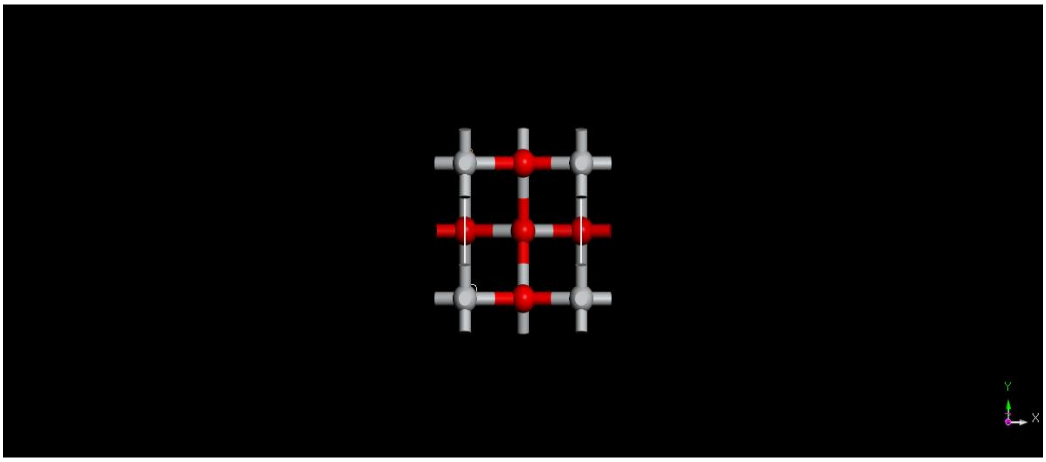
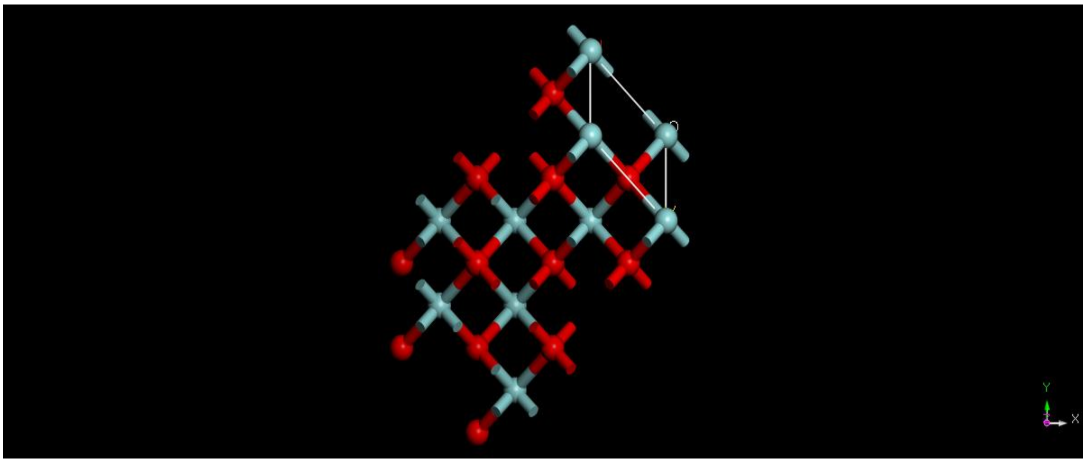


(a)

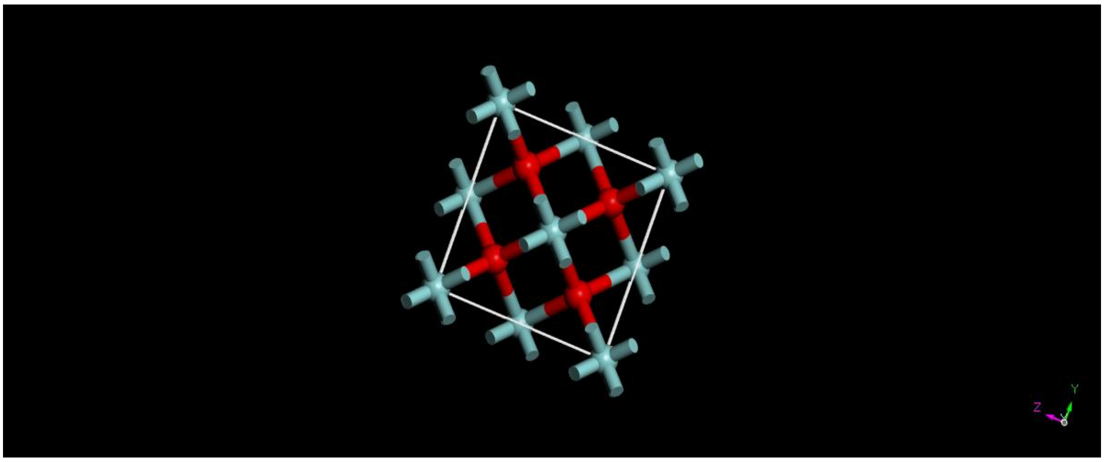


(b)

Fig. 2: Graphicaldisplay of (a) TiO_2 (111) surfaceand (b) TiO_2 (bulk). Redcoloredatoms in (a) and (b) areoxygenandgreycoloredonesaretitaniumatoms.

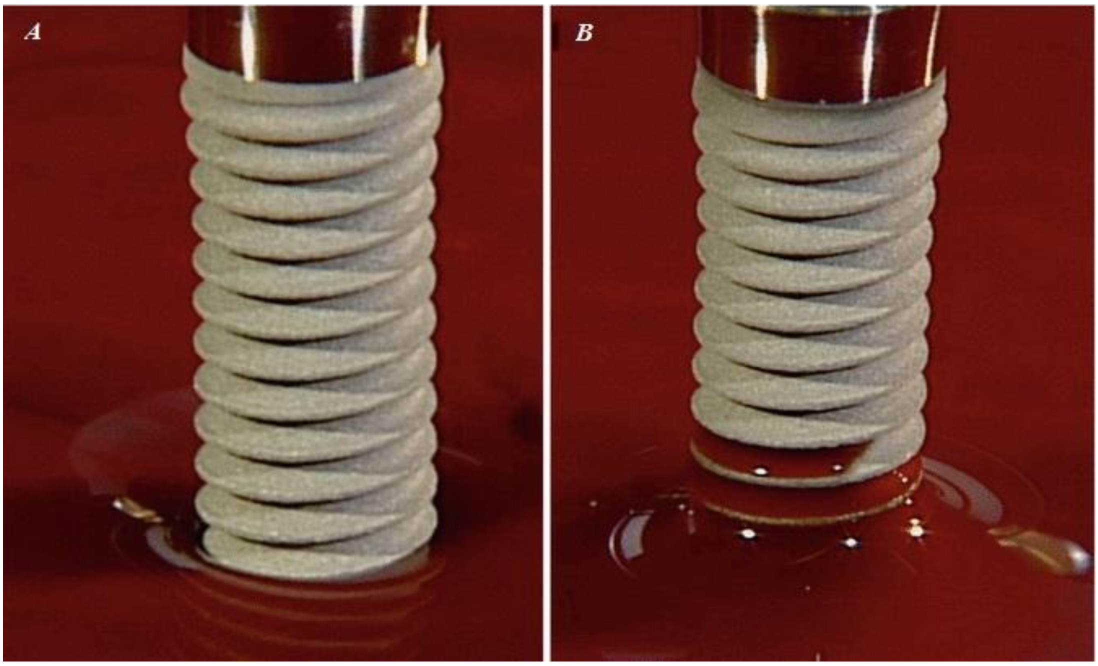


(a)



(b)

Fig. 3: Graphicaldisplay of (a) ZrO_2 (111) surfaceand (b) ZrO_2 (bulk). Redcoloredatoms in (a) and (b) arezirconiumandlightbluecoloredonesareoxygenatoms.



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