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Original Research Article

Solar light photocatalytic activity of Zr-doped TiO_2 for degradation of common food colorant: Investigation through combined approach

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ABSTRACT
Doped TiO_2 is an important well analysed molecular semiconductor widely used is in semiconductor photocatalysis. Photo degradation using doped TiO_2 is a promising method to abate pollution of water bodies as well as other contaminate. In this work initially growth behaviour and stability of small stoichiometric $(TiO_2)_n$ clusters have been analysed by using density functional theory which reveals that clusters prefers three-dimensional structures. Improved by this Zr-doped TiO_2 is synthesized by simple sol-gel method and the obtained nano Zr-doped TiO_2 is analysed with UV-Vis, IR, SEM, EDX and PXRD. The methods Zr-doped TiO_2 shows good photo degradation efficiency towards brilliant green a common food colorant used in everyday life.

1. Introduction

Titanium dioxide (TiO_2) has many promising applications because of its low cost, long-standing stability, catalytically active surfaces and environmental compatibility, production of hydrogen from water and solar energy, solar cells [1-8], sensors [9], cleaning of water and air from organic contaminants [10, 11] and photocatalysis [12-15]. The physical and chemical properties of TiO_2 nanomaterials, namely nanowires, nanoparticles and clusters, might be different from those of bulk titania [16]. The ratio of surface to volume increases as the cluster size decreases; smaller TiO_2 nanoparticles have more active sites and so the catalytic activity of the TiO_2 materials is enhanced [17]. Due to their scientific and technological importance, there are several experimental [18-27] and theoretical studies on small neutral, negatively and positively charged TiO_2 clusters [28-48] and nanoparticles [49-52]. Structure, stability, electron affinities, harmonic vibrational frequencies of stoichiometric and non-stoichiometric neutral and charged clusters have been studied by employing density functional theory (DFT) based methods [36-44].

An accessibility to safe drinking water has arisen as among the most critical matters that has arisen as a result of increased urbanization and industrialization. The presence of pure and clean water is a necessary requirement for aquatic and living things to survive. In recent years, while revolutionary industrial progress has substantially enhanced living standards, it has also become a menace human health and the environment [45]. Food colorants perform an important component in meal selection since they improve the appearance of the food, making it more appealing to consumers. Mostly colorants might be harmful to health if used for a long time. A few studies have found a link between various azo colors and unfavorably susceptible reactions, such as asthma and contact hypersensitivity [46]. Furthermore, certain colorants promote food prejudice, hypersensitivity, and hyperactivity in children. Among several synthetic food colorants available, because of the wide potential use of TiO_2 clusters it is essential to know their physical and chemical properties. TiO_2 clusters has been analysed in terms of their size, binding energy, geometry, binding site, bond length and HOMO–LUMO energies. In this work Zr- doped TiO_2 is used for the photodegradation of brilliant green (BG), which is azo derivatives dye, an edible food color. It has been found that the photocatalytic degradation mechanism over the surface of Zr-doped TiO_2 can be well explained by considering the charge flow from TiO_2 to Zirconium. Such type of structure offered higher redox capability as well as improved separation of photogenerated charge carriers, thus providing phenomenal photocatalytic performance. Considering the low-cost preparation process and high photocatalytic performance, the resultant Zr- doped TiO_2 can further be used as an efficient photocatalyst for organic pollutant removal from aqueous and industrial wastewater.

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2. Experimental

2.1 Materials and measurements

TEM analysis was carried out using JEOL JEM 2100 high resolution transmission electron microscope (HR-TEM) with an accelerating voltage of 200 KV. X-ray diffraction (XRD) patterns were recorded for the centrifuged and dried samples using X–ray Rigaku diffractometer with CuK_α source (30 kV, 100 mA), at a scan speed of 3.0000 deg/min, step width of 0.1000 deg, in a 2θ range of 20-80̊. The energy dispersive X-ray spectra (EDX) of the nanosemiconductors were recorded with a JEOL JSM-5610 scanning electron microscope (SEM) equipped with back electron (BE) detector and EDX. Theoretical calculations were performed using Gaussian-03 program [56].

2.2 Chemicals

Commercial titanium isopropoxide, zirconium chloride, extra pure water were supplied from Loba chemie. Avra provided BG. SD Fine Chemicals supplied the solvents methanol and dichloromethane. The aforementioned chemicals were analytically pure and were used as such with no further purification. The entire experiment was conducted with distilled water.

2.3 Synthesis of Zr-doped TiO_2 by sol-gel method

To the reaction mixture of titanium isopropoxide (0.1g) in PVP K-30 (0.01 M, 10 ml) zirconium chloride (0.1g) and aq. NH_3 (1:1) was added (30 min : pH 7) and the filtered gel was purified with diluted ethanol, dried at 100 °C (12 h) and calcinated (500°C: 2 h:heating rate 10°C/ min) to form solid.

2.4 Photocatalytic degradation of food colorant Brilliant Green (BG)

In this study, the effectiveness of the obtained Zr-doped TiO_2 as photocatalytic active material for the degradation of BG by solar light has been investigated The experiment was carried out by adding 5 mg amount of photocatalyst in 10 ml of 10 ppm aqueous solution of the food colorant BG. Degradation efficiency (%) = $(C_o\text{-}C_t)/ C_o \times 100$, where, C_o is the initial concentration of BG and C_t is concentration after time 't'.

3. Results and discussion

3.1 Characterization of TiO_2

XRD pattern of TiO_2 nanoparticles are shown in Figure 1. The diffraction patterns of TiO_2 matches with the standard JCPDS pattern of anatase (89-4921), body centered tetragonal with crystal constants $a = b = 3.7774$A° and $c = 9.501$ Å and (89-4920) with crystal constants a and b as 4.584 Å and c as 2.953 Å, respectively. The average crystallite sizes (D) of the TiO_2 (A) and TiO_2 (R) have been obtained as 11.4 and 27.2 nm, respectively, by using the Scherer equation.

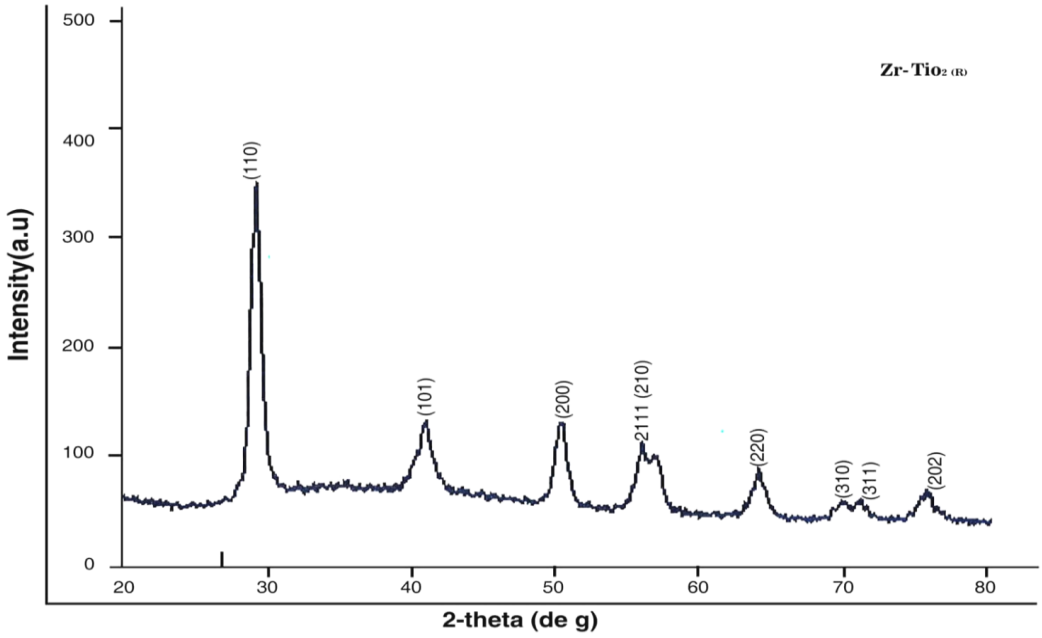

Figure 1: X-ray diffraction pattern of TiO_2.

3.2 Optical properties

Figure 2 shows the diffuse reflectance spectra (DRS) of sol-gel synthesized rutile TiO_2. They are presented in terms of $F(R)$, deduced from the recorded reflectance (R) by application of the Kubelka-Munk algorithm [$F(R) = (1 - R)^2/2R$]. The absorption edges of rutile and anataseTiO_2 are 379 and 343 nm respectively. The deduced absorption edges provide the band gap of 3.61 eV.

3.3 Electronic properties of TiO_2 clusters

The bent TiO_2 is energetically more stable by about 1.9 eV than its linear isomer. The Ti–O bond length and O–Ti–O bond angle are 1.65 Å and 108°, respectively. The bent TiO_2 formation is explained by the interaction of Ti atom with O_2 molecule which results in a metastable structure in which the O–Ti–O bond angle and Ti–O and O–O inter-atomic distances are 46.80, 1.82 and 1.47 Å, respectively. The energy of the bent structure is lower by 4.12 eV than the metastable isomer and the energy barrier between these two structures is 0.26 eV. On interaction of Ti atom with metastable TiO_2 cluster, the O–O bond is broken and planar Ti_2O_2 is formed. Ti–Ti and Ti–O bond lengths are 2.23 and 1.89 Å, respectively. The interaction of Ti_2O_2 cluster with O_2 molecule results Cis and Trans Ti_2O_4 clusters. Trans Ti_2O_2 is 0.28 eV lower energy than its cis-

isomer. The ring isomer of Ti_3O_6 is less stable than its cage isomer by 1.47 eV. Similar results are obtained for Ti_4O_8 and Ti_5O_{10} clusters (Figure 3).

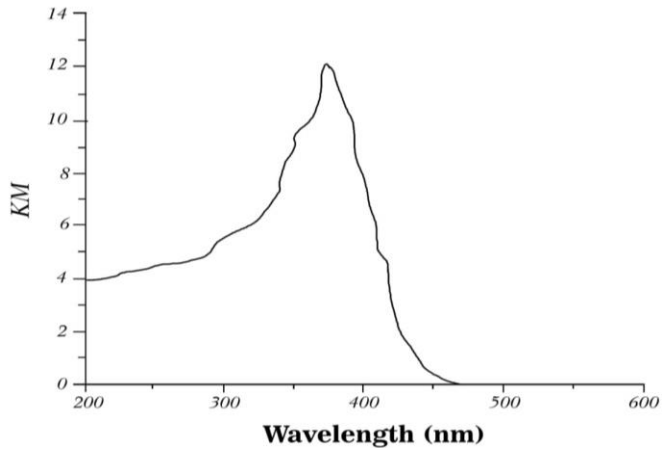

Figure 2: Diffused reflectance spectra of TiO_2.

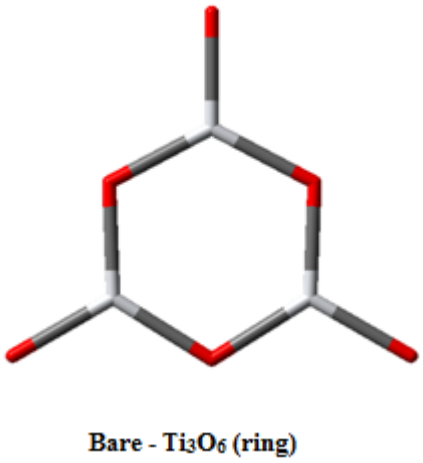

Figure 3: Optimized structure of $(TiO_2)_n$ model nano cluster.

3.4 Photodegradation of BG by Zr-TiO₂

3.4.1 Evaluation of photocatalytic degradation of food colorant (BG) by solar photocatalysts

The photo-active materials Zr-TiO_2 has been designed. The comparison between the photocatalytic performances of the catalyst has been given. The photo-degradation reaction was carried on 10 ml of 10 ppm BG solution (pH = 7.1), by placing it under direct solar radiation for 60 min in the presence of 5 mg of photocatalyst. The relative concentration of the BG molecules at a particular time interval't' is depicted in Figure 4. The relative percentage degradation afforded by these photocatalysts is shown in Figure 4. The photodegradation reaction performed in the absence of catalyst (blank) clearly depicted that in the presence of solar light irradiation, the colorants were quite stable and exhibited no notable change in the concentration. It can be concluded that the self-degradation of the taken colorants is almost negligible under sunlight illumination. As shown, the prepared exhibited a very little degradation rate, having % degradation of 7.0 % for BG. The existence of small band gap resulted in recombination of e^-/h^+ pairs at faster rate. The Zr- TiO_2 resulted in significant enhancement in % degradation because of being synergistic effect between the zirconium and TiO_2 [60]. It has been found that, since the band gap of the prepared Zr-doped TiO_2 is quite narrow, thus is well suited for the visible light absorption which is primarily a U.V active photocatalytic material.

Photodegradation mechanism

The e^-/h^+ pair separation provided an enhancement in photodegradation efficiency by suppressing the recombination of desired charged species. Because of the optimum band potential; the electron residing in the conduction band of TiO_2 gets transferred towards zirconium, resulting into the freely availability of h^+ and e^-, requisite for the photodegradation reaction (Figure 4).

$$Zr/TiO_2 + hv \longrightarrow Zr/TiO_2\ (e^+ + h^+)$$

$$h^+ + H_2O \longrightarrow {}^\bullet OH + H^+$$

$$e^- + O_2 \longrightarrow {}^\bullet O_2^-$$

$${}^\bullet O_2^- + H^+ \longrightarrow {}^\bullet OOH$$

$$e^- + 2\,{}^\bullet OOH \longrightarrow {}^\bullet OH + OH^- + O_2$$

$$AM/BB + {}^\bullet O_2^- \longrightarrow \text{Degraded products}$$

$$AM/BB + h^+ \longrightarrow \text{Degraded products}$$

$$AM/BB + {}^\bullet OH \longrightarrow \text{Degraded products}$$

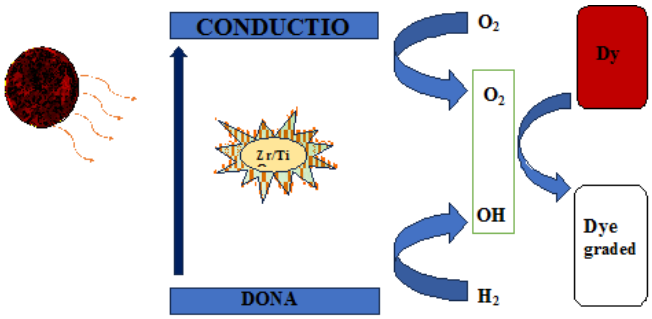

Figure 4: Schematic illustration of proposed photocatalytic mechanism for the photodegradation of BG by Zr-TiO_2.

4. Conclusions

In summary, the present report delivers the designing and construction of Zr-TiO_2 for the effective degradation of the food colorant (BG), under the abundant and freely available solar irradiation. We were studied the stability, structural and electronic properties of the bare $(TiO_2)_n$ clusters of different sizes. The calculated HOMO–LUMO orbital energies and their differences, exhibit geometry and size dependence cohichare not follow a regular pattern. The electronic properties of the TiO_2 clusters and the HOMO-LUMO analysis confirms the occurrence of charge transfer. The prepared Zr-TiO_2 photocatalyst demonstrated the enhanced photocatalytic performance. The improvement in the degradation efficiency can be attributed to the efficient charge separation and transportation afforded by the constructed mechanism. Moreover, the existence of synergistic effect between the zirconium and TiO_2 also significantly improved the visible light absorption capacity. Under optimized conditions, the

maximum degradation efficiency achieved by the prepared Zr-TiO_2 was noted to be 99.68 % for BG within just 40 min of light irradiation. Additionally, the in-situ radical trapping experiment was also conducted which indicated that $.O_2^-$ and .OH played a major role in the photo-degradation process. Besides this, such nano metal doped metal oxide photocatalyst makes them a potential catalyst for treating common food colorant based pollutants.

Authors' contributions

The author read and approved the final manuscript.

Conflicts of interest

The author declares no conflict of interest.

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Data availability

No new data were created.

References

[1] U. Diebold, The surface science of titanium dioxide, *Surf. Sci. Rep.* 48 (2003) 53-229.
[2] T.L. Thompson, J.T. Yates, Surface science studies of the photoactivation of TiO_2-new photochemical processes, *Chem. Rev.* 106 (2006) 4428-4453.
[3] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, *Chem. Rev.* **107** (2007) 2891-2959.
[4] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, *Nature* **353** (1991) 737-740.
[5] M. Grätzel, Photoelectrochemical cells, *Nature* **414** (2001) 338-344.
[6] M. Grätzel, Dye-sensitized solar cells, *J. Photochem. Photobiol. C.* **4** (2003) 145-153.
[7] A. Hagfeldt, M. Grätzel, Light-induced redox reactions in nanocrystalline systems, *Chem. Rev.* **95** (1995) 49-68.
[8] D. Cakir, O. Gulseren, E. Mete, S. Ellialtioglu, Dye adsorbates BrPDI, BrGly, and BrAsp on anatase TiO_2 (001) for dye-sensitized solar cell applications, *Phys. Rev. B.* **80** (2009) 035431.
[9] N.L. Wu, S.Y. Wang, I.A. Rusakova, Inhibition of crystallite growth in the sol-gel synthesis of nanocrystalline metal oxide, *Science* **285** (1999) 1375-1377.
[10] A.G. Agrios, P. Pichat, State of the art and perspectives on materials and applications of photocatalysis over TiO_2, *Appl. Electrochem.* **35** (2005) 655-663.
[11] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* **95** (1995) 69-96.
[12] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature* **238** (1972) 37–38.
[13] A. Fujishima, K. Hashimoto, H. Watanabe, TiO_2 Photocatalysis: Fundamentals and Applications, BKC, Tokyo (1997).
[14] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Light-induced amphiphilic surfaces, *Nature* **388** (1997) 431-432.
[15] K. Sunada, Y. Kikuchi, K. Hashimoto, A. Fujishima, Bactericidal and detoxification effects of TiO_2 thin film photocatalysts, *Environ. Sci. Technol.* **32** (1998) 726-728.
[16] D. Cakir, O. Gulseren, First-principles study of thin TiO_x and bulklike rutile nanowires, *Phys. Rev. B* **80** (2009) 125424.
[17] M. Anpo, T. Shima, S. Kodama, Y. Kubokawa, Photocatalytic hydrogenation of CH@3^CCH with H@2^O on small-particle TiO@2^: Size quantization effects and reaction intermediates, *J. Phys. Chem.* **91** (1987) 4305-4310.
[18] N.S. McIntyre, K.R. Thompson, W. Weltner, Spectroscopy of titanium oxide and titanium dioxide molecules in inert matrices at 4.deg.K, *J. Phys. Chem.* **75** (1971) 3243-3249.
[19] G. Balducci, G. Gigli, M. Guido, Mass spectrometric study of the thermo chemistry of gaseous $EuTiO_3$ and TiO_2, *J. Chem. Phys.* **83** (1985) 1909-1912.
[20] G. Balducci, G. Gigli, M. Guido, Identification and stability determination of the gaseous Titanium Oxides molecules Ti_2O_3 and Ti_2O_4, *J. Chem. Phys.* **83** (1985) 1913-1916.
[21] W. Yu, R.B. Freas, Formation and fragmentation of gas-phase titanium/oxygen cluster positive ions, *J. Am. Chem. Soc.* **112** (1990) 7126-7133.
[22] B.C. Guo, K.P. Kerns, A.W. Castleman, Formation and stability of metallocarbohedrenes: $Ti_xM_yC_{12}$(x + y = 8, M = Nb, Ta, Y, and Si), *J. Mass Spectrom. Ion Processes* **117** (1992) 129-144.
[23] G.V. Chertihin, L. Andrews, Reactions of laser ablated titanium, zirconium, and hafnium atoms with oxygen molecules in condensing argon, *Phys. Chem.* **99** (1995) 6356 - 6366.
[24] H. Wu, L.S. Wang, Electronic structure of titanium oxide clusters: TiO_y (y = 1−3) and $(TiO_2)_n$ (n = 1−4), *J. Chem. Phys.* **107** (1997) 8221 - 8228.
[25] M. Foltin, G.J. Stueber, E.R. Bernstein, On the growth dynamics of neutral vanadium oxide and titanium oxide clusters, *J. Chem. Phys.* **111** (1999) 9577 - 9586.
[26] Y. Matsuda, E.R. Bernstein, On the titanium oxide neutral cluster distribution in the gas phase: Detection through 118 nm single - photon and 193 nm multiphoton ionization, *J. Phys. Chem. A.* **109** (2005) 314 - 319.
[27] H.J. Zhai, L.S. Wang, Probing the electronic structure and band gap evolution of titanium oxide clusters $(TiO_2)_n^-$ (n = 1-10) using photoelectron spectroscopy, *J. Am. Chem. Soc.* **129** (2007) 3022 - 3026.
[28] A. Hagfeldt, R. Bergstrom, H.O.G. Siegbahn, S. Lunell, Structure and stability of small titanium/oxygen clusters studied by ab initio quantum chemical calculations, *J. Phys. Chem.* **97** (1993) 12725-12730.
[29] R. Bergstrom, S. Lunell, L.A. Eriksson, Comparative study of DFT methods applied to small titanium/oxygen compounds, *Int. J. Quantum Chem.* **59** (1996) 427-443.
[30] M.B. Walsh, R.A. King, H.F. Schaefer, The structure, electron affinities and energetic stabilities of TiO_n and TiO_n – (n = 1,3), *J. Chem. Phys.* **110** (1999) 5224-5230.
[31] T. Albaret, F. Finocchi, C. Noguera, First principles simulations of titanium oxide clusters and surfaces, *Faraday Discuss.* **114** (1999) 285-304.
[32] T. Albaret, F. Finocchi, C. Noguera, Ab initio simulation of titanium dioxide clusters, *Appl. Surf. Sci.* **144/145** (1999) 672–676.
[33] T. Albaret, F. Finocchi, C. Noguera, Density functional study of stoichiometric and O-rich titanium oxygen clusters, *J. Chem. Phys.* **113** (2000) 2238-2249.
[34] K.S. Jeong, C. Chang, E. Sedlmayr, D. Sulze, Electronic structure investigation of neutral titanium oxide molecules Ti_xO_y, *J. Phys. B: At. Opt. Phys.* **33** (2000) 3417-3430.
[35] S. Hamad, C.R.A. Catlow, S.M. Woodley, S. Lago, J.A.

Mejias, Structure and stability of small TiO_2 nanoparticles, *J. Phys. Chem. B.* **109** (2005) 15741-15748.
[36] A.M. Woodley, S. Hamad, J.A. Mejias, C.R.A. Catlow, Properties of small TiO_2, ZrO_2 and HfO_2 nanoparticles, *J. Mater. Chem.* **16** (2006) 1927-1933.
[37] Z.W. Qu, G.J. Kroes, Theoretical study of the electronic structure and stability of titanium dioxide clusters $(TiO_2)_n$ with n = 1-9, *J. Phys. Chem. B.* **110** (2006) 8998-9007.
[38] Z.W. Qu, G.J. Kroes, Theoretical study of stable, defect-free (TiO_2)(n) nanoparticles with n = 10–16, *J. Phys. Chem. C.* **111** (2007) 16808-16817.
[39] P. Persson, J.C.M. Gebhardt, S. Lunell, The smallest possible nanocrystals of semiionic oxides, *J. Phys. Chem. B.* **107** (2003) 3336-3339.
[40] M.J. Lundqvist, M. Nilsing, P. Persson, S. Lunell, DFT study of bare and dye-sensitized TiO_2 clusters and nanocrystals, *Int. J. Quantum Chem.* **106** (2006) 3214-3234.
[41] A.S. Barnard, S. Erdin, Y. Lin, P. Zapol, J.W. Halley, Modeling the structure and electronic properties of TiO_2 nanoparticles, *Phys. Rev. B* **73** (2006) 205405.
[42] S. Li, D.A. Dixon, Molecular structures and energetics of the $(TiO_2)_n$ (n = 1-4) clusters and their anions, *J. Phys. Chem. A.* **112** (2008) 6646-6666.
[43] M. Calatayud, L. Maldonado, C. Minot, Reactivity of $(TiO_2)_N$ clusters (N=1-10): probing gas-phase acidity and basicity properties, *J. Phys. Chem. C.* **112** (2008) 16087-16095.
[44] M. Calatayud, C. Minot, Is there a nanosize for the activity of TiO_2 compounds, *J. Phys. Chem. C.* **113** (2009) 12186-12194.