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Visible light induced Efficient Selective Oxidation of Non-Activated Alcohols over {001} Faceted TiO_2 with Molecular Oxygen

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Abstract: In the presence of molecular oxygen, a {001} faceted nanocrystalline anatase TiO_2 catalyst enables the selective oxidation of non-activated aliphatic alcohols to the corresponding aldehydes or ketones in presence of oxygen under visible light. The reaction shows excellent conversion and selectivity towards the formation of the carbonyl products without over-oxidation to the corresponding carboxylic acids. The exceptional reactivity of the catalyst is possibly due to the absorption of visible light originating from stronger interaction of alcohol with (001) facet, which facilitates the modification of band structure of TiO_2, thus facilitating the photo-generated hole transfer and subsequent oxidation processes. The experimental results have also been corroborated by first principal quantum chemical DFT calculations.

Introduction

The selective oxidation of non-activated alcohols to corresponding aldehydes or ketones is a fundamental synthetic transformation given the abundance of the resulting carbonyl compounds in numerous fine chemicals, pharmaceuticals, flavour and fragrances, and biologically active compounds.[1-2] In general, stoichiometric strong oxidants are used to accomplish the reaction in-turn producing hazardous wastes.[3] With ever growing environmental concern, development of simple room temperature (RT) protocols using O_2 as a stoichiometric oxidant is highly in demand as an attractive alternative to the traditional approach because, it generates mainly water as a by-product.[4] Thus, numerous transition metal based homogeneous and heterogeneous catalysts have been developed for the purpose.[4b,5-6] However, homogeneous catalysts require additives and/or bases and are not reusable.[5] Whereas, most of the heterogeneous catalysts are based on costly metals. Catalytic efficiencies of non-noble metal based catalysts are low.[6] Both the catalytic system required temperature and selective oxidation of non-activated alcohols are rarely reported. Thus, it is essential to develop a simple, energy efficient catalytic procedure for selective oxidation of non-activated alcohols.

In recent years, harvesting of solar energy to obtain chemical energy, i.e., visible light driven chemical conversion (photocatalysis) has been triggered worldwide, as it is the only sustainable energy resource on earth and is produced through clean and economical path.[7] In the direction of sustainable development, heterogeneous room temperature based photocatalytic routes for selective oxidation of alcohols to the corresponding carbonyls in combination with O_2 as oxidant, without over oxidation to carboxylic acids, have been introduced and a number of photocatalysts have been developed, including CdS, carbon nitride, TiO_2, Ta_2O_5.[8-13] Although, all the catalysts showed moderate to good results for different activated alcohols (benzylic or allylic), however to the best of our knowledge, there has been no report on selective oxidation of non-activated aliphatic/cyclic alcohols.

Among the developed photocatalysts, TiO_2 has been studied extensively, as it is cheap, abundant and chemically stable.[8-11] It is well documented that activity of TiO_2 is highly controlled by its polymorph, exposed facet, size, shape and surface area.[14] Specifically, nanocrystalline anatase TiO_2 with exposed high energy {001} facet is catalytically more active than other.[15] However, Lu et.al.,[10] reported that there are no distinct facet selective effect of TiO_2 nanocrystals for selective oxidation of alcohol under VU light. Here, it is noteworthy to mention that for alcohol oxidation TiO_2 is active in both UV and visible light, but their energy ($h\nu$) absorption mechanism is different. Under UV light, it absorbs energy directly through band excitation, whereas under visible light, through modified band structure originate from alcohol adsorbed on the TiO_2.[9] Thus, it is expected to have a distinct facet selective catalytic activity under visible light, as it is supposed to vary the extent of adsorption of alcohol on TiO_2 surface with specific surface energy, in turn catalytic activity. Thus, there remains a definite possibility to develop efficient visible light driven photocatalytic process for selective oxidation of non-activated aliphatic/cyclic alcohols to the corresponding carbonyl compounds using a specific phase and facet selective nanocrystalline TiO_2.

Herein, we have developed nanocrystalline (001) faceted anatase TiO_2 as an efficient visible light active photocatalyst for selective oxidation of non-activated aliphatic/cyclic alcohol to corresponding aldehyde/ketone. The origin of superior activity of (001) faceted anatase TiO_2 over other TiO_2 nanoparticles have also been corroborated by first principal quantum chemical DFT calculations. Based on our knowledge, this is the first report on photocatalytic selective oxidation of non-activated alcohol to aldehyde/ketone. Here it is essential to mention that simple house hold 40W CFL lamp is used to make the procedure easier.

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The use of CFL helped to avoid the required precautions to manage the heat generated from the generally used Xe-lamp for good activity. Synthesized {001} faceted anatase TiO_2 is too active to give excellent results under the used CFL lamp.

Results and Discussion

From the above mentioned alcohol oxidation reactions, varying phase and specific facet exposed TiO_2 nanoparticles were synthesized using previously reported methods. {001} faceted highly truncated octahedral TiO_2 nanoparticles and layered titanate were synthesized following our recently developed fluorine free protocol under hydrothermal conditions, using aqueous soluble peroxo-ammonium carbonate complex solution as precursor.[15] {100} and {101} faceted anatase, rutile and brookite TiO_2 nano particles were synthesized using the method as reported by Liu *et al.*[10] The detailed synthetic methods and corresponding characterization results are presented in Supporting Information (Supporting experimental procedures and Figure S1-S3, Supporting Information).

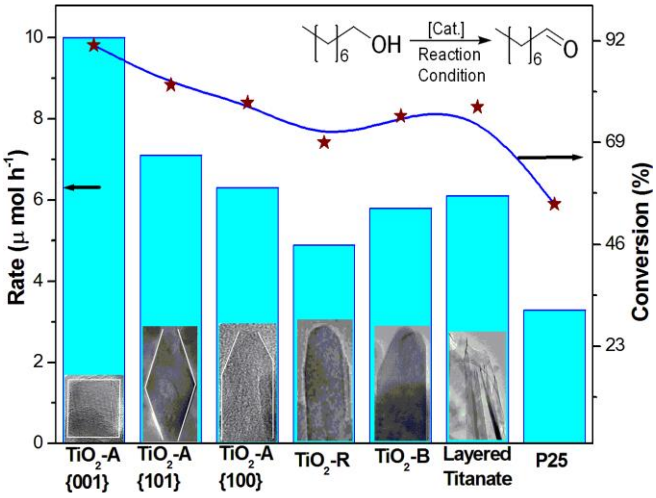


Figure 1. Visible light driven photocatalytic activity of different nanostructured facet selective anatase TiO_2 (TiO_2-A) and other polymorphs of TiO_2 (Rutile: TiO_2-R, Brookite: TiO_2-B) for selective oxidation of octanol to octanal.

All the synthesized TiO_2 nano particles were used for visible light driven photocatalytic selective oxidation of non-activated alcohols to corresponding carbonyl compounds under 40W simple house hold CFL lamp. To find out an active catalyst capable of oxidizing non-activated alcohols efficiently and selectively in the presence of molecular oxygen as oxidant, octanol ($C_8H_{17}OH$, simple C8 long chain alcohol) was initially chosen as a model substrate and BTF (benzotrofluoride) as solvent. It was observed that the concentration of photo-formed octanal, corresponding aldehyde, was increased gradually with the time of exposure to visible light for the whole reaction system. However, the reactivity varied with the phase and corresponding exposed facet. All the catalysts ended with 100% selectivity of octanal (Figure 1, Figure S4 and Table S1 Supporting Information). From the Figure 1, it is evident that the {001} facetted anatase TiO_2 nanocrystals showed superior catalytic activity, with respect to conversion and rate of reaction, compared to other tested facet and phase selective TiO_2 nanoparticles while commercial P25 showed lowest activity. The {001} faceted TiO_2 nanoparticles ended with >90% conversion (GC) of 1-octanol with 100% selectivity of 1-octanal after 24h of reaction. No over oxidation product was detected in GC/GC-MS, which indicates the 100% selectivity of octanal. Furthermore, ~ 85% isolated yield confirmed the extremely high selectivity of the performed reaction. The photocatalytic activity of facet selective TiO_2 follows the following order (001)>>(101)>(100) of reactivity. The calculated reaction rate (10 μmol h^{-1}), turn-over frequency (8.9 h^{-1}) and turnover number of 215 for (001) faceted TiO_2 are reasonably higher compared to that of other tested TiO_2 (Table S1, Supporting Information). Further, systematic solvent screening experiments evidenced the BTF to be ideal solvent for the performed alcohol oxidation (Figure 2). This is most probably due to the superior oxygen storage capacity of BTF. The catalyst is reusable at least 6 times for consecutive cycles (Figure S5, Supporting Information). The obtained yield is quite superior to that of literature reported results for selective octanol oxidation to octanal using transition/noble metal based homogeneous/heterogeneous catalysts at elevated temperatures (Table S2, Supporting Information).

Afterward, the scope and limitations of the presently developed and optimized protocol were evaluated by using a large variety of non-activated aliphatic / cyclic primary,

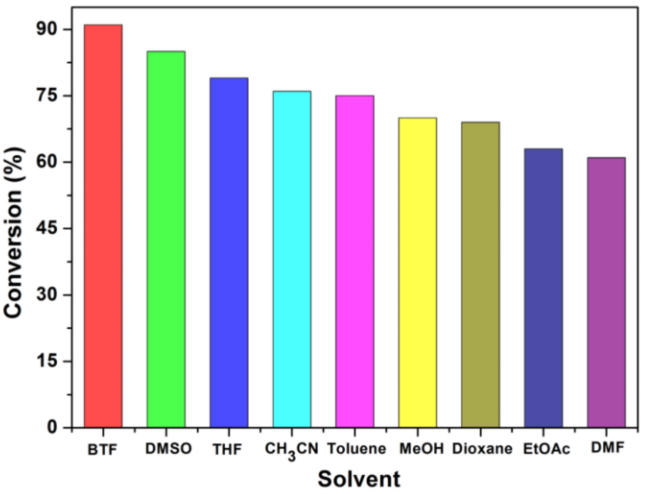
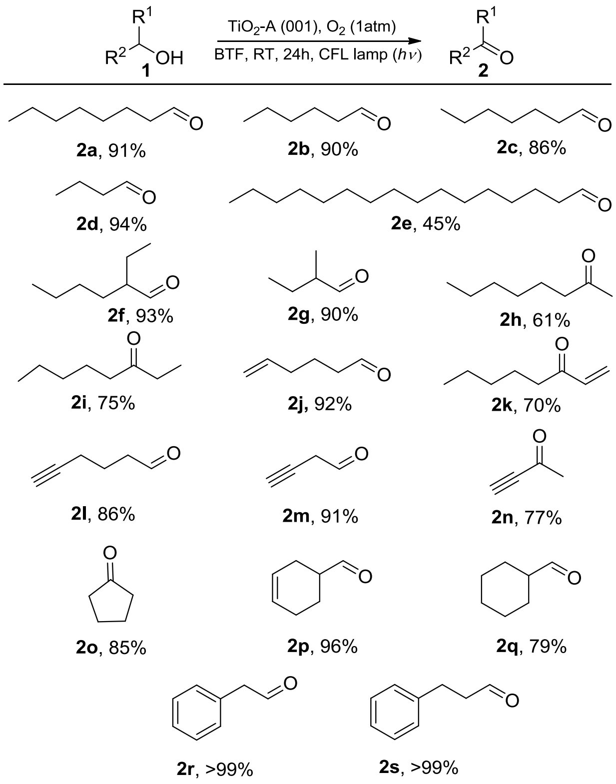


Figure 2. Visible light induced photocatalytic performance of (001) faceted TiO_2 in oxidation for selective conversion of 1-Octanol to 1-Octanal in different solvents.



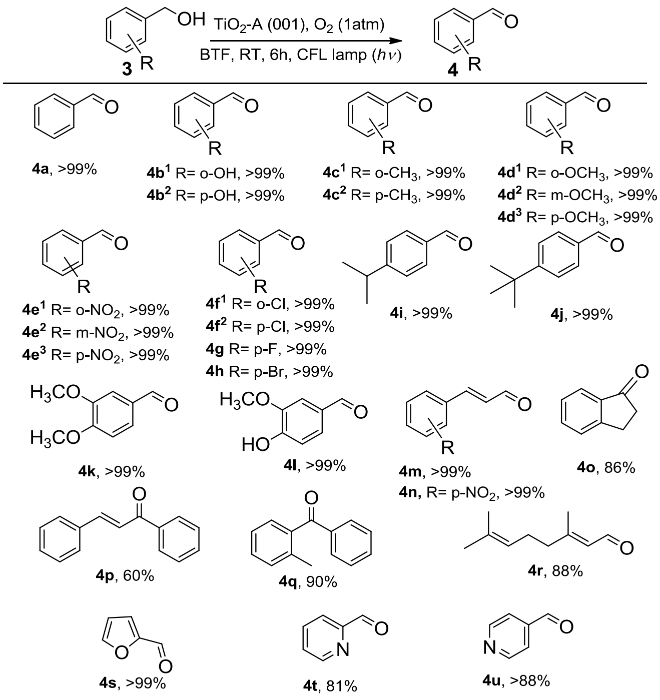
Scheme 1. Visible light driven aerobic oxidation of non-activated aliphatic/cyclic alcohol using over (001) faceted TiO_2 in presence of O_2; Substrate: 0.5mmol, BTF (solvent): 1.5ml; Atmosphere: oxygen; Catalyst TiO_2: 15mg.

secondary, branched alcohols under the optimized reaction conditions (optimized for octanol) and the results are summarized in Scheme 1. Most of the simple long chain and branched primary aliphatic alcohols were converted into the corresponding aldehydes with high to excellent yields (>85%, **2a-d, 2f-g**), except hexadecane-1-ol. Hexadecane-1-ol converted to palmitaldehyde (**2e**) with 45% conversion and the yield is lower due to the solubility of the hexadecane-1-ol in the reaction medium. Secondary aliphatic alcohols were also converted to corresponding ketones with moderate yield (>60%, **2h-i**). Alcohols with unsaturated group (alkene and alkyne) were converted to the corresponding aldehyde/ketone giving an excellent yield without affecting alkene and alkyne groups (**2j-m**). Cyclic aliphatic alcohols were also converted to the corresponding aldehyde/ ketone compounds in excellent yields (**2j-m**).

Although the obtained results for visible light driven photocatalytic selective oxidation of non-activated alcohols to the corresponding carbonyl compound are excellent, but it is not possible to compare the activity with literature reported results, as there are no such reports available. All the reports are on selective oxidation of activated benzylic/allylic alcohol.[17] With the promising results for aliphatic/cyclic aldehyde/ketone synthesis, further exploration was done to check the possibility to extend the alcohol oxidation reaction towards selective oxidation of activated benzylic/allylic alcohols to the corresponding aldehydes/ketones, which are more prone to over-oxidation to corresponding carboxylic acid. All the tested TiO_2 for the oxidation of benzyl alcohol had been well utilized. All the TiO_2 showed similar trend of photocatalytic activity for benzyl alcohol oxidation as obtained for octanol oxidation and {001} faceted TiO_2 showed superior activity (Figure S6, Supporting Information). However, the rate of photocatalytic oxidation of benzyl alcohol is much faster than that of octanol and completed (100% conversion) within 6 h with 100% selectivity of benzaldehyde. The calculated rate of reaction is 71.1 μmolh^{-1}, almost 7 times higher than octanol oxidation. Difference in photocatalytic activity of (001) faceted TiO_2 for benzyl alcohol oxidation is more prominent and the reaction rate more than double than that of other TiO_2. The obtained photocatalytic activity of (001) faceted TiO_2 in terms of overall rate and yield is much superior to that of other literature reported photo-catalysts, including TiO_2, as well as other homogeneous/heterogeneous thermo-catalyst (Table S3, Supporting Information). {001} faceted TiO_2 nano particles were also applied for visible light driven selective oxidation of other activated benzylic/allylic alcohols to evaluate the scope and limitations of the developed protocol and the results are summarized in Scheme 2. It is important to mention that both electron-donating and electron-withdrawing substituents at ortho-, meta- and para- position work excellently and almost quantitative yield of corresponding aldehydes were obtained (Scheme 2, **4b-h**). Oxidation of cinnamyl alcohols also worked smoothly (**4m-n**). Benzylic secondary alcohols, were also converted to the corresponding keto compounds (**4o-q)** with good to excellent yields. Methanol's bearing hererometic substituents also underwent the desired oxidation (**4s-u**).

Mechanistic Study.

To understand the mechanism of the performed reaction and origin of superior activity of {001} faceted TiO_2, we did some additional control experiments, as well as theoretical studies (DFT calculations). In control reactions, under dark condition and without catalyst, no product was formed in both the cases, confirming that the reaction took place only when exposed to light (Table S1). During alcohol oxidation, TiO_2 adsorbed visible light through energy level modification by alcohol adsorption. Thus, it is observed that the extent of adsorption is prime controlling factor for its activity.[9] The light absorption characteristic of octanol absorbed TiO_2 dispersed in BTF was investigated. All the pure TiO_2 showed similar absorption characteristics and was adsorbed only in UV region. Whereas, a threshold absorption in visible region was observed for octanol adsorbed TiO_2 (Figure 3). However, the extent of visible light absorption was observed to vary with TiO_2. Both the {001} and {101} faceted TiO_2 absorbed visible light strongly than that of other TiO_2. These absorption characteristics imply that the extent of binding of octanol in {001} and {101} facets of TiO_2 is more and should give high catalytic activity. Practically, similar trend of catalytic activity is found. In another set of controlled experiments for octanal oxidation reactions with as-synthesized, dried (200°C), calcined (500°C) {001} faceted and HF treated TiO_2 showed that the as-synthesized TiO_2 ended with maximum



Scheme 2. Visible light driven aerobic oxidation of activated benzylic- / allylic-alcohol using over (001) faceted TiO_2 in presence of O_2; Substrate: 0.5mmol, BTF (solvent): 1.5ml; Atmosphere: oxygen; Catalyst TiO_2: 15mg.

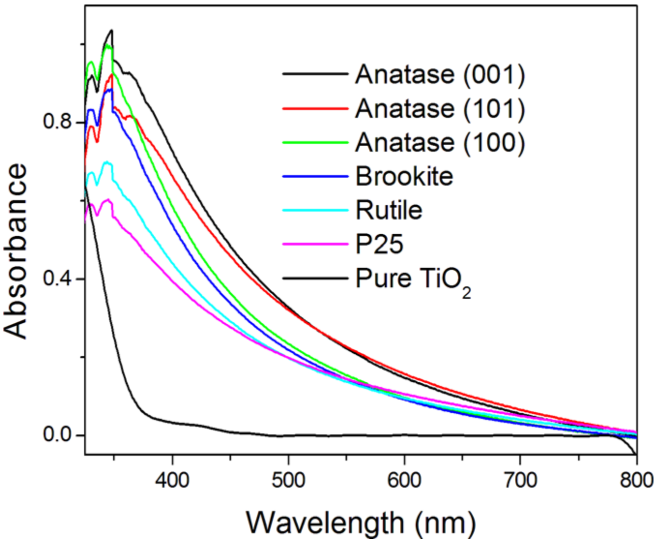


Figure 3. UV-vis absorption spectra of octanol absorbed different facet selective anatase TiO_2 and TiO_2 with different phase dispersed in BTF.

conversion with 100% selectivity of octanal (Table S4, Supporting Information). This is due to the variation of concentration of surface hydroxyl groups, as the adsorption of octanol on TiO_2 surface takes place through interaction with surface hydroxyl group and act as active sites. FTIR spectra of corresponding TiO_2 samples are also evident that as-synthesized and dried TiO_2 contains maximum surface hydroxyl group (Figure S7, Supporting Information). Surface hydroxyl group was reduced for de-hydroxylation during calcination or replacement of hydroxyl group by fluoride in the calcined and HF treated samples, respectively. As-synthesized TiO_2 having maximum hydroxyl groups showed higher activity due to higher concentration of surface hydroxyl groups facilitate to absorb reactant molecules. . 36% conversion of octanol after 24h for photocatalytic oxidation of octanol in nitrogen atmosphere(withoutoxygen) was obserev which confirmed that the reaction undergoes photocatalytic way (Table S1, Supporting Information). Photocatalytic activity of TiO_2 is mainly related to the formation of electrons and holes in conduction and valence bands, respectively, through the adsorption of photon energy. Subsequently, oxidation took place in valence band through the transformation of photo-generated holes to the surface adsorbed octanol and resulted in the oxidized product octanal. During photo-induced selective oxidation of octanol to octanal under nitrogen atmosphere, TiO_2 acts as acceptor for electrons and protons. Li *et.al.*,[8] showed the presence of enhanced Ti^{3+} and surface hydroxyl group of the used catalyst under N_2 environment due to the acceptance of electrons and protons. However, this process is slow and in-turn the reaction proceeds slowly. Whereas, in presence of oxygen, oxygen acts as acceptor and as a result the reaction rate is high. Selective photocatalytic oxidation of octanol to octanal is a two electron transfer process. However, enormous electron-hole pair is generated continuously on photo-irradiation. Thus, there is a definite probability of over oxidation of oxidized product, but here only first oxidation product was obtained, i.e., octanal selectively and the obtained carbon balance was >98%.

Thus, to understand the origin of high selectivity of carbonyl compound, without over oxidation, and superior reactivity of {001} faceted TiO_2, we performed the DFT calculations to evaluate the possible electronic interaction of benzyl alcohol and benzaldehyde on {001} and {101} facet of TiO_2. Both the alcohol and aldehyde groups can coordinate through the oxygen atom of the functional group with TiO_2 surface and corresponding adsorption energy (Figure 4) has been calculated. The calculated adsorption energies of benzaldehyde on {001} & {101} surface are -26.0 & -5.9 kcal/mol respectively and the adsorption energies of benzyl alcohol on {001} & {101} surface are -28.9 & -7.4 kcal/mol, respectively Energy calculations suggest that benzaldehyde is bounded weakly to the TiO_2 surface than the benzyl alcohol. These results suggested that the benzaldehyde can be released easily from the TiO_2 surface immediately after transformation of alcohol to aldehyde and restricts over oxidation.[18] Such process is termed as "*self-adjustable photo-oxidation system*".[8] Further, reasonably high absorption energy of benzyl alcohol on {001} surface (28.9 kcal/mol) compared the most stable {101} (-7.4 kcal/mol) implies that benzyl alcohol interacts with {001} surface. Such preference might facilitate the hole transfer process, i.e., oxidation and resulted in much higher visible light driven photocatalytic activity. Therefore, the DFT results suggest that the transformation of alcohol to aldehyde would be more preferred in {001} TiO_2 surface than {101} surface and hence the adsorption can affect the reactions and products. Thus the DFT calculated results corroborate the experimental findings.

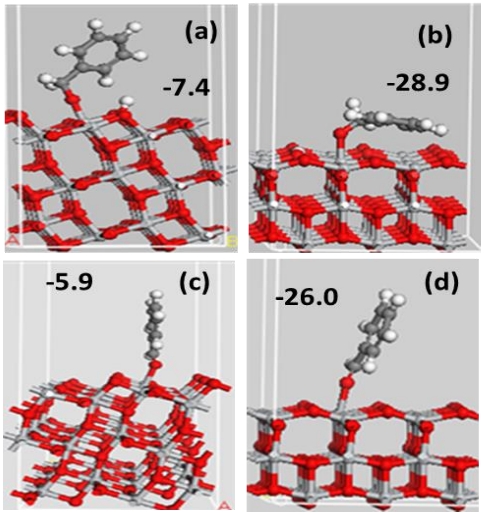
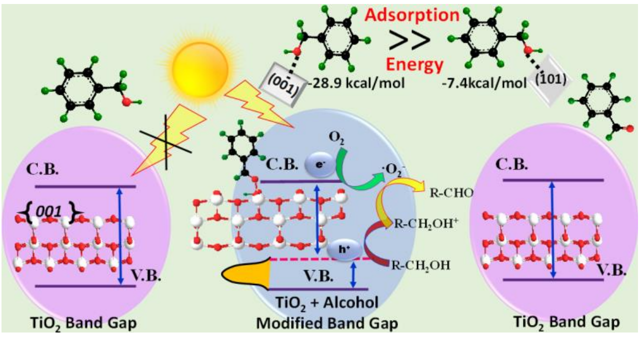


Figure 4. The optimized geometries of TiO_2-absorbed systems: (a) (101) TiO_2-benzyl alcohol, (b) (001) TiO_2-benzyl alcohol, (c) (101) TiO_2-benzaldehyde, (d) (001) TiO_2-benzaldehyde and corresponding absorption energies in kcal/mol.

From the above discussed experimental results and theoretical study, a probable path has been proposed for the performed selective oxidation of octanol to octanal using {001} faceted nanocrystalline TiO_2 under visible light (Scheme 5). In the first step, alcohol adsorbed on TiO_2, generate a new energy level through charge transfer which is capable of absorbing visible light (hγ) and hence generate photo-excited electron hole pairs in the new band structure. Then, adsorbed alcohol transformed into its oxidized state through transformation of photo-generated hole from VB. Successively, the oxidized state of alcohol was converted to corresponding carbonyl compound by releasing protons and electrons. Simultaneously, oxygen (O_2) acted as acceptor of electrons and formed superoxide radical anion oxygen radical (O_2^-), which eventually formed H_2O_2, the two electron reduction product of O_2, by combination with proton and electron generated from oxidized state of alcohol.



Scheme 3. Proposed reaction mechanism of visible light driven selective aerobic oxidation of alcohol to aldehyde/ketone..

Conclusions

In conclusion, we have developed a novel protocol for visible light induced photocatalytic oxidation of non-activated aliphatic/cyclic alcohol as well as activated benzylic/allylic alcohol to corresponding carbonyl compound over (001) faceted TiO_2 at room temperature using O_2 as oxidant and simple house hold 40W CFL lamp as visible light source. {001} faceted anatase TiO_2 nanocrystals showed 90% conversion of 1-octanol with 100% selectivity of 1-octanal which is superior than that of other phase and facet selective TiO_2. Experimental results evidenced that {001} faceted TiO_2 showed superior activity due to absorption of light in visible range through stronger adsorption of alcohol in {001} facet of TiO_2. This was further corroborated by computational DFT calculations and showed adsorption energy of alcohol on {001} facet to be quite higher than that of {101} facet. Further, due to lower adsorption energy of aldehyde (product), the photo-generated aldehyde went out from TiO_2 surface and restricted over oxidation. The obtained catalytic activity is much higher than that of other reported metal based homogeneous /heterogeneous catalyst as well as photocatalysts. Thus, it is expected that the synthesized {001} faceted TiO_2 should have a wide range of potential applications in photocatalytic organic transformation.

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Keywords: aliphatic alcohol • nanoparticles • Photooxidation • TiO_2 • visible light

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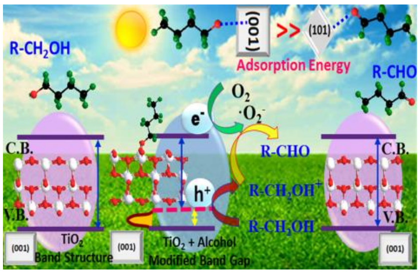
Entry for the Table of Contents

FULL PAPER

Visible light induced efficient photocatalytic selective oxidation of non-activated aliphatic/cyclic alcohols over {001} faceted TiO_2 nanoparticles in the presence of molecular oxygen is presented. The superior activity of {001} faceted TiO_2 has also been corroborated by first principal quantum chemical DFT calculations.



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Visible light induced Efficient Selective Oxidation of Non-Activated Alcohols over {001} Faceted TiO_2 with Molecular Oxygen