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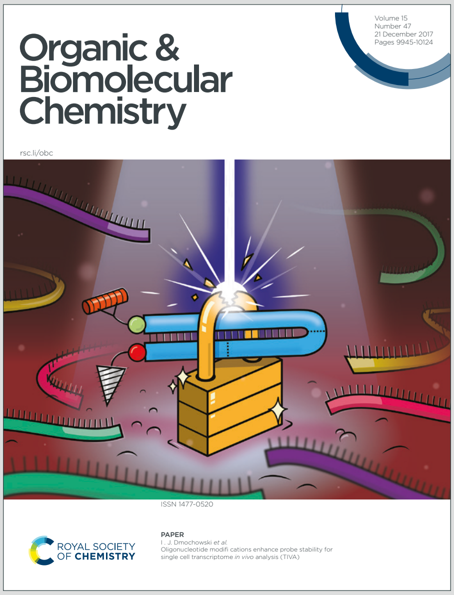

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Chemoselective photocatalytic oxidation of alcohols to aldehydes and ketones by nitromethane on titanium dioxide under violet 400 nm LED light irradiation

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In this study, for the first time, nitroalkanes especially nitromethane, have been used as an electron acceptor for the highly chemoselective oxidation of alcohol**s** in the presence of TiO_2 photocatalyst under 400 nm LED irradiation. The reactions showed excellent selectivity for the production of aldehydes. Interestingly aldehydes such as benzaldehyde and p-methoxybenzaldehyde are stable in the reaction condition. In the case of the use of 2-nitropropane and 2-methyl-2- nitropropane, the product of imine, which is the result of the reaction of aldehyde with aliphatic amine, is also produced.

The nitroalkanes are used widely as raw materials for synthesis. Nitromethane, the simplest member of the nitroalkanes family, is often used as a solvent in organic chemistry and it is also served as a very important building block to access a wide range of useful compounds such as β-nitroalcohols, nitroalkane, nitroalkenes, amines, carbonyl compounds, heterocycles[1-3]. Nitroalkanes are also used as building blocks for pharmaceutical synthesis, for example, nitromethane is used in the synthesis of the ranitidine [4].

Nitromethane has many industrial applications, for example it can be used to stabilize halogenated hydrocarbons, to clean electronic circuit boards, the use of it as fuel by professional drag racers**,** hobbyists and utilization of it in a binary explosive formulation in explosives industry and also its usage as a polar solvent in the industry [5, 6].

Photochemistry is a powerful method for chemical transformation. Since the beginning of scientific chemistry, chemists have been interested in using light in chemical reactions [7]. Photocatalyst technology has been taken into consideration since 1972 when Fujishima and Honda showed that the TiO_2 electrode could decompose water into hydrogen and oxygen [8]. Now photocatalysts are used for degradation of air and water pollutants, hydrogen production, organic transformations [9-12].

Among the semiconductors, TiO_2 is much used because of low cost, high environmental resistance, non-toxicity, and commercial availability [13, 14] and it has three allotrope types, which are anatase, rutile and brookite [15]. TiO_2-P25 as a standard heterogeneous photocatalyst, which is used frequently, is formed 80% anatase and 20% rutile phase. The connection between two-phase increases charge separation and its rutile phase also drives the photoactivity to the visible wavelengths [16, 17]. TiO_2 has a big band gap that its application limits in the visible region. Thus some modifications of TiO_2 are necessary to extend its response to the visible region. So far, TiO_2 has been used as a catalyst for various organic reactions in different conditions [18-24].

The oxidation of alcohols to aldehydes and ketones is one of the most important transformations in organic chemistry both in the laboratory and industrial scale**,** because the corresponding carbonyl compounds are valuable compounds such as pharmaceuticals, agricultural chemicals and fine chemicals [25, 26]. TiO_2 with metals such as Au, Pd has converted to an excellent photocatalyst and can oxidize aromatic alcohols [27, 28]. Zhao et al. reported that the system of dye-sensitized TiO_2 and tempo could catalyse selective oxidation of alcohols under visible light irradiation. These modifications photocatalytic activity of the TiO_2 expand to the visible region [29]. Also, the unmodified TiO_2 can catalyse benzyl alcohol and its derivatives under visible light in the presence of O_2 [30, 31].

Alcohol oxidation reactions usually occur in the presence of oxygen as consuming oxidant [10, 32, 33]. However, recently Chen et al. used nitrobenzene as an electron acceptor in aromatic alcohols oxidation using catalyst CdS/g-C_3N_4. In this report, selective oxidation of aromatic alcohols to aromatic aldehydes and reduction of nitrobenzene into aniline was realized using CdS/g-C_3N_4 composite as a photocatalyst under visible light

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illumination [34]. Also Higashimato et al. by CdS-TiO_2 catalyst under visible light irradiation, simultaneously oxidized benzyl alcohol to benzaldehyde and reduced nitrobenzene to aniline and they reported the one-pot synthesis of imine from benzyl alcohol and nitrobenzene on CdS-TiO_2 photocatalysts [35].

Compared to traditional light sources, LEDs convert electrical energy into light energy, more efficient and instead of producing all the unnecessary wavelengths, they produce a narrower range of wavelengths. Other advantages of LEDs include high photon efficiency, low voltage of electricity, and power stability [36, 37]. Due to the advantages of LEDs, our group is interested in using them in various photocatalytic reactions [38-40].

Here we report for the first time, selective photocatalytic oxidation of alcohols by nitromethane on titanium dioxide under under violet 400 nm LED light irradiation. Nitromethane has acted as an oxidizing and electron acceptor in an argon atmosphere.

For the investigation of nitromethane oxidative activity in photocatalytic reactions, as a model reaction, the benzyl alcohol oxidation in nitromethane solvent in the presence of TiO_2-P25 photocatalyst was carried out under argon and violet LED light irradiation (400 nm). Benzaldehyde was produced as the sole product in 52% yield and the only trace over oxidized benzoic product was observed after 12 hours. The result of the reaction in the absence of oxygen (argon atmosphere) indicated the oxidizing role of nitromethane (Table1, entry 1).

In the next step, to reduce the nitromethane amount, the reaction solvent was changed to acetonitrile and nitromethane (4:1) and fortunately, product yield enhanced to 72% (Table 1, entry 2). The reaction in the presence of oxygen produced 88% aldehyde with selectivity of 91% with 9% overoxidation to benzoic acid (Table 1, entry 3). In order to consider the light effect, the oxidation of benzyl alcohol was investigated in dark and LED (20 W) irradiation (365, 400, 460 nm) in the presence TiO_2, that the benzaldehyde was produced in 2%, 59%, 72% and 11% yield respectively (Table 1, entries 2, 4-6). Then, 400 nm LED was selected as a suitable light source. Using two 400 nm LED (20 W) did not increase the yield of reaction (Table 1, entry 7).

Table 1 Optimization of the selective photocatalytic oxidation reaction of benzyl alcohol to benzaldehyde in presence of TiO_2 by nitromethane

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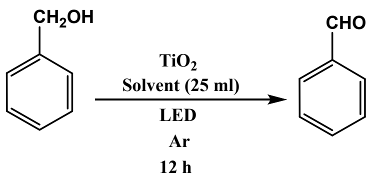

entry	Solvent (ratio)	TiO_2(mg)	LED (electrical power)	Yield [a,b] (%)
1	CH_3NO_2	40	400 nm (20 W)	52
2	CH_3NO_2:CH_3CN (1:4)	40	400 nm (20 W)	72
3[c]	CH_3NO_2:CH_3CN (1:4)	40	400 nm (20 W)	88
4	CH_3NO_2:CH_3CN (1:4)	40	-	2
5	CH_3NO_2:CH_3CN (1:4)	40	365 nm (20 W)	59
6	CH_3NO_2:CH_3CN (1:4)	40	460 nm (20 W)	11
7	CH_3NO_2:CH_3CN (1:4)	40	400 nm (2×20 W)	72
8	CH_3NO_2:EtOAc (1:4)	40	400 nm (20 W)	72
9	CH_3NO_2: EtOAc (1:2.33)	40	400 nm (20 W)	59
10	CH_3NO_2: EtOAc (1:9)	40	400 nm (20 W)	79
11	CH_3NO_2: EtOAc (1:24)	40	400 nm (20 W)	72
12 [d]	CH_3NO_2: EtOAc (1:9)	0	400 nm (20 W)	6
13	CH_3NO_2: EtOAc (1:9)	60	400 nm (20 W)	81
14	CH_3NO_2: EtOAc (1:9)	80	400 nm (20 W)	91
15	CH_3NO_2: EtOAc (1:9)	100	400 nm (20 W)	97
16 [e]	CH_3NO_2: EtOAc (1:9)	150	400 nm (20 W)	99

[a] Reaction conditions: benzyl alcohol (0.25 mmol), solvent (25 mL), reaction time(12 h), Ar atmosphere, room temperature [b] GC yield [c] Reaction conditions: O_2 balloon, Selectivity % 91 (Production of 9% benzoic acid) [d] Without TiO_2 [e]Reaction time: 10 h

In order to apply the safer solvent, ethyl acetate was used instead of acetonitrile and the same yield was obtained**,** fortunately (Table 1, entry 8). Different volume ratios of nitromethane in 25 ml mixed solvents were used in the reaction. By decreasing nitromethane to 7, 5 and 2.5 ml, the yield of reaction reached 59, 72 and 79%, respectively (Table 1, entries 8-10). If 1 ml nitromethane is used, the yield dropped to 72 % (Table 1, entry 11). Therefore, 2.5 ml of nitromethane was selected in the optimized mixed solvents (CH_3NO_2: EtOAc (1:9)). The result also showed the reaction without catalyst afforded only 6% benzaldehyde in an argon atmosphere (Table 1, entry 12). The optimization amount of TiO_2 was essential in the development of the reaction. The different amounts of the photocatalyst: 60, 80 and 100 mg showed 81, 91 and 97% yield of the product respectively (Table 1, entries 13-15) at 12 hours. Finally, 150 mg TiO_2 produced 99% of benzaldehyde at 10 hours (Table 1, entry 16). Therefore, 100 mg TiO_2 was chosen as the optimum amount of the catalyst.

After optimizing the reaction conditions, to expand the application of this new method, the oxidation of various alcohol compounds such as benzyl alcohol and its derivatives containing different functional groups and aliphatic alcohols was performed (Table 2).

Table 2 Photocatalytic excellent selective oxidation of alcohols in the presence of TiO_2 at nitromethane/ ethyl acetate solvent

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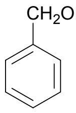
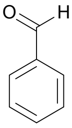
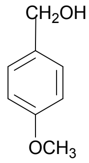
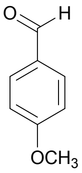
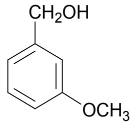
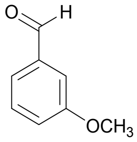
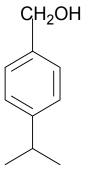
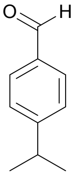
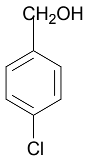
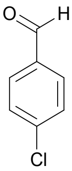
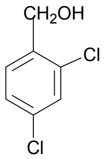
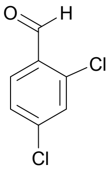
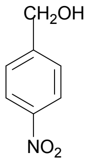
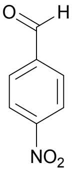
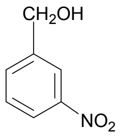
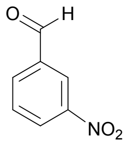
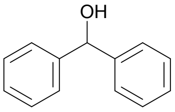
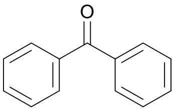
Entry	Substrate	Products	Time (h)	% Yield ^{a,b} (% Isolated yields)
1			12 12^{c} 12^{d}	97 (94) 93 91
2			6 9 9 9 9	93 97 87^{e} (85) 61^{f} 95^{g}
3			12	83 (80)
4			12 18	88 92 (88)
5			10	95 (90)
6			12 24	72 90 (87)
7			12 48	66 90 (86)
8			12 48	62 82 (80)
9			12 22	74 92 (90)

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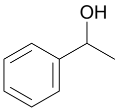
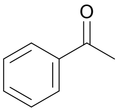
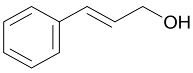
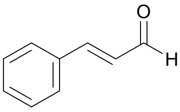
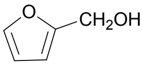
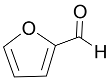
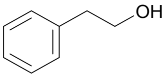
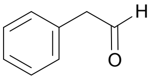
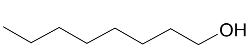
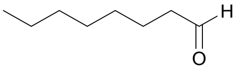
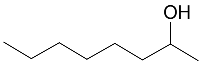
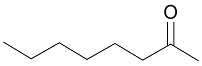
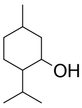
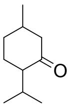
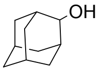
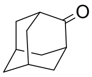
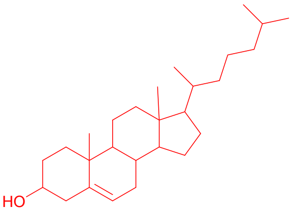
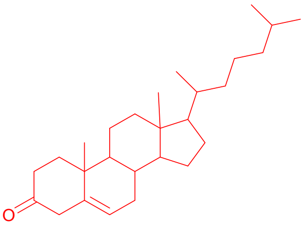
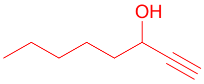
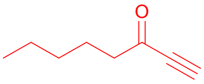
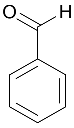
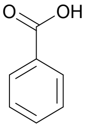
10			12 27	63 73 (69)
11			12 16	88 100 (98)
12			12	71 (68)
13			12	48 (45)
14			12 24	33 63 (61)
15			12 48	16 48 (45)
16			27	0
17			12	0
18			27	0
19			21 48	22 65
20[h]			27	2

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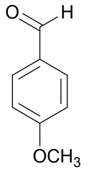
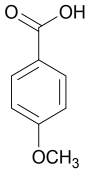
21[i]			9	0

[a] Reaction conditions: alcohol (0.25 mmol), TiO_2-P25 (0.1 g), CH_3NO_2: EtOAc (1:9, 25 ml), irradiation with LED (400 nm, 20 W) [b] GC yield [c] Reaction conditions: in the presence of BHT (0.25 mmol) [d] Reaction conditions: in the presence of Tempo (0.25 mmol) [e] 0.5 mmol 4-methoxybenzyl alcohol was used [f] 0.75 mmol 4-methoxybenzyl alcohol was used [g] Reaction conditions: in the presence of Tempo (0.25 mmol) [h] Reaction conditions: Benzaldehyde (0.5 mmol), TiO_2-P25 (0.04 g), CH_3NO_2: CH_3CN (1:9, 10 ml), irradiation with LED (400 nm, 20 W) [i] Reaction conditions: 4-Methoxybenzaldehyde (0.1 mmol), TiO_2-P25 (0.04 g), CH_3NO_2: CH_3CN (1:9, 10 ml), irradiation with LED (400 nm, 20 W)

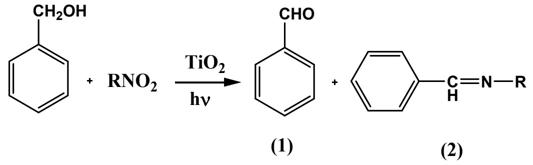
As shown in Table 2, different alcohols including benzyl alcohol and its derivatives substituted by $–OCH_3$, $–CH(CH_3)_2$, –Cl and – NO_2 groups were oxidized to corresponding aldehydes with a high selectivity on TiO_2 in the presence of nitromethane (Table 2, entries 1-10). Among benzylic alcohols, electron-rich alcohols are more reactive than electron-poor ones. Also, relative position of the substituents on the phenyl ring was important. 4-Methoxybenzyl alcohol was efficiently converted into the corresponding aldehydes in excellent yields 93 and 97% at 6 hours and 9 hours respectively. Interestingly, an increasing amount of this alcohol to 0.5 and 0.75 mmol gave a good result after 9 h of irradiation (Table 2, entry 2). 3-Methoxybenzyl alcohol was reacted with a lower yield (Table 2, entry 3). 4-Chlorobenzyl alcohol also reacted well with 95% yield under 10 hours irradiation (Table 2, entry 5). 2,4-Dichlorobenzyl alcohol reacted slower than 4-chlorobenzyl alcohol, probably due to its steric hindrance (Table 2, entry 6).

The electron-withdrawing substituent, such as $–NO_2$ in the para and meta positions, reacted slower than the electron-donation substituents. p-Nitro derivative required 48 hours of time to reach 90% yield, while meta-nitro produced 82% of corresponding aldehyde (Table 2, entries 7-8).

Oxidation of secondary benzyl alcohols such as diphenylmethanol and 1-phenylethanol was investigated at 22 and 27 hours that they produced 92 and 73% corresponding aldehyde respectively (Table 2, entries 9-10). Cinnamyl alcohol converted quantitatively to its corresponding aldehyde at 16 hours and the double bond was remained intact (Table 2, entriy11). Furfuryl alcohol as a heteroaromatic compound also reacted effectively (Table 2, entry 12). It is worth mentioning that oxidation of aliphatic primary and secondary alcohols take place very slowly with only 33 and 16% yields at 12 hours (Table 2, entries 14-15). Subsequently, menthol, 2-Adamantanol and cholesterol were not oxidized in the reaction conditions, (Table2, entries 16-18). 1-Octyn-3-ol in 48 hours, produced the corresponding ketone 65% (Table2, entry 19). All of the reaction of alcohols in Table 2, were carried out in excellent selectivity. The chemoselectivity of the photocatalytic oxidation of alcohols was also shown with the stability of benzaldehyde and p-methoxybenzaldehyde (Table2, entries 20-21).

In the following, other nitro-alkanes such as nitroethane, 2-nitropropane and 2-methyl-2-nitropropane were studied to expand the method. In all these cases, the corresponding aldehydes were produced (Table3). For the reaction of 2-nitropropane and 2-methyl-2-nitropropane, in addition to the corresponding aldehyde, their imines also were detected by GC-Mass analysis (Table 3, Fig. S1, see the ESI).

Table 3 Photooxidation of benzyl alcohol by nitroalkanes



Entry	Nitroalkane	Yield [a,b] (%)	
		(1)	(2)
1	Nitroethane	83	-
2	2-Nitropropane	81	20
3	2-Methyl-2-nitropropane	68	32

[a] Reaction conditions: alcohol compound (0.1 mmol), TiO_2-P25 (0.04 g), CH_3NO_2: EtOAc 10 ml (1:9) and irradiation with LED 400 nm (20 Watt) [b] GC yield

According to the result of imine formation, it can be concluded the nitroalkanes converted to the corresponding amines. The reaction of benzyl alcohol and p-methoxybenzyl alcohol in the presence of tempo and BHT without any decrease in reaction efficiency was carried out. It can be concluded that reaction pathway was not radical (Table2, entry 2,3; Scheme 1).

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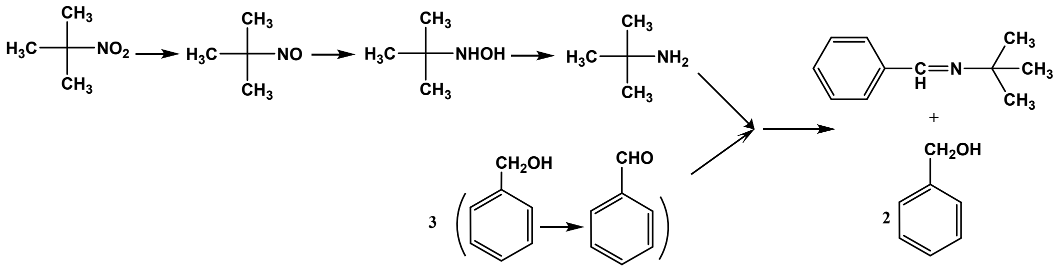

Scheme 1 Oxidation of benzyl alcohol in the presence of 2-methyl-2-nitropropane using TiO_2 catalyst under light irradiation

TEM images of TiO_2 before and after the model reaction, showed that there were no differences in its size (Fig. S2, see the ESI). Figure S3 (see the ESI) shows the thermogravimetric analysis (TGA) of TiO_2 after the reaction. From the TGA curve**,** it were observed that there was around 2.17 % organic residues on TiO_2. Also, the decreased surface area of recycled TiO_2 was observed with Brunauer–Emmett–Teller (BET) method and it can be attributed to the attachment of organic materials to the titania surface under light irradiation (Fig. S4, see the ESI).

Next, we examined the UV–Vis spectrum of TiO_2–P25. The UV–Vis absorption spectra of TiO_2 -P25 and emission of 400 nm LEDs are shown in Figure 1. The emission spectrum overlaps with a part of the UV–Vis absorption spectrum of TiO_2 and this confirm**s** the photoactivity of the catalyst in 400 nm.

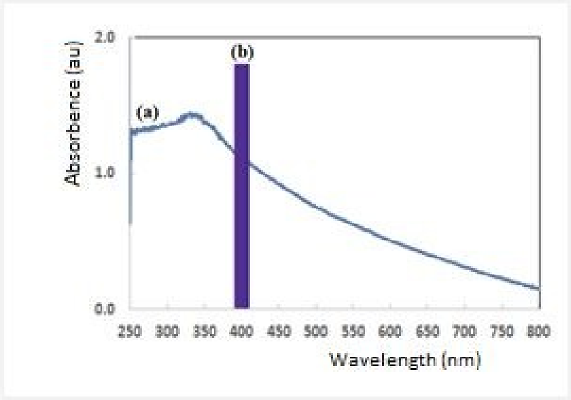

Figure 1 a) UV–Vis absorption spectrum of TiO_2–P25 in solvent CH_3NO_2: EtOAc b) the emission spectrum of the LED lamp (400 nm)

We also investigated reusability of TiO_2-P25 photocatalyst in optimum condition for 4-methoxybenzyl alcohol. The catalyst was separated and washed with solvent at the end of each run then it was reused in the next run. The catalyst was successfully reused in five consecutive runs and showed only a slight decrease in the catalytic activity after each recycling (Fig. S5, see the ESI).

Experimental

Chemicals

All solvents, alcohols compounds were purchased from Merck (Germany). TiO_2–P25 and Nitromethane were supplied by Degussa Co. and Roth respectively. All other chemicals were used as received without further purification. Silica gel 60 F254 plates (No. 5744) were purchased from Merck and used for the preparative TLC.

Photocatalytic reactions

Alcohols compounds (0.25 mmol) were dissolved in 2.5 ml of nitromethane and 22.5 ml of ethyl acetate and was added to the solution 100 mg commercial TiO_2-P25 in a round bottom Pyrex flask (50 ml). The reaction mixture sonicated using an ultrasonic bath for 10 min and was degassed by bubbling argon gas (15 min) and sealed with a septum. Afterward, the flask was irradiated by LED (400 nm, 20 W) under stirring. The LED was placed within 2 cm from the bottom center of the flask. The reaction progress was monitored by TLC and GC.

Conclusions

An efficient method for the selective oxidation of alcohols to the corresponding carbonyl compounds has been developed using the photoactive TiO_2-P25 catalyst in the presence of nitromethane in argon. A wide range of alcohols were selectively converted to the corresponding aldehydes and ketones. The reactions proceed at room temperature under violet 400 nm LED light and the recyclability of catalyst was very good over several reactions cycles. Also, the imine formation for some nitroalkanes was shown the conversion of nitroalkanes to the corresponding amines.

In our method, nitromethane is used instead of oxygen, as a valuable alternative that has high selectivity for the production of aldehydes. Due to the non-radical reaction mechanism, the oxidation of aldehydes does not occur in the reaction medium. In addition, chemistry of nitroalkanes is important and their transformations can be considered and synthesis of other products such as imine is valuable.

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Conflicts of interest

There are no conflicts to declare.

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In this study, for the first time, nitroalkanes especially nitromethane, have been used as an electron acceptor for the highly chemoselective oxidation of alcohols in the presence of TiO_2 photocatalyst under 400 nm LED irradiation.