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TiO_2/hydrophobic Cellulose Aerogel Nanocomposite as a New Photocatalyst for Oxidation of Alcohols and Ethylbenzene

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Abstract

Synthesis of new natural polymers-based nanocomposites is the center of attentions for the catalyst researchers on account of their sustainability. In this regard, cellulose aerogel was hydrophobized by polysilicon to give a hydrophobic bio-support which underwent deposition of TiO_2 nanoparticles afforded a catalyst with high lipophilicity, superior porosity as well as high catalytic activity. The prepared nanocomposite was structurally characterized, in which the deposition of polysilicon and TiO_2 nanoparticles on an aerogel compound was recognized. The aerogel exhibited good hydrophobicity, and high selectivity in oil/water absorption with 6.3 g oil absorbed by 1 g of the absorbent. Finally, the nanocomposite was employed as a heterogeneous photocatalyst in the transformation of alcohols to aldehydes/ketones, and ethylbenzene to acetophenone with the conversions laying in the range of 81-99%. Mild conditions, high yields, excellent selectivities, and recyclability and biocompatibility of the catalyst are advantages of the reactions.

Keywords: *Hydrophobic, Cellulose, Aerogel, Photocatalyst, Oxidation, Green chemistry.*

1. INRODUCTION

Use of biocompatible materials in chemical processes suppress the pollution concerns of the procedures for the environment [1]. For this purpose, natural polymers are exceptional material and among them cellulose has a special place due to the abundance, availability, and easy modification susceptibility [2]. Cellulose aerogel (CA) as the highly porous form of cellulose is interesting due to specific properties, including high surface area, excellent liquid absorption capacity, flexibility, and low density. These properties lead to the special applications for CA derivatives such as a high surface area support for catalysts [3, 4], and removal of pollutants [5]. Modified CAs are important category of organic pollutions absorbents due to their high absorption capacities (more than 40 times by weight), environmental friendliness, biodegrade-ability, and sustainability [6-8]. In the meantime, CA is reusable because of superior compression strength, and flexibility [9-11]. Despite the ability of CA for organic substrates absorption, the inherent hydrophilicity of the CA leads to the low selectivity of the polymer in oil/water absorption. Modification of CA with hydrophobic materials gives a hydrophobic polymer which enjoyed from the high porosity. Hydrophobizations of cellulose were reported via modifications by chlorosilanes [12], triethoxyl (octyl) silane [13], methyltrimethoxysilane [14], and methyltriethoxysilane [5].

Advanced oxidation processes (AOP) refer to the processes generated hydroxyl radical for the oxidation of organic substrates via a free radical mechanism [15]. A class of AOP consists of photoactivated processes such as photocatalytic oxidation of alcohols [16-18] and alkyl arenes [19, 20]. Development of oxidation reactions which avoids use of pollutant chemical oxidants such as

$KMnO_4$, ClO, Cl_2, Cr^{VI}, peroxy acids, and unrecoverable transition-metal catalysts is preferred beyond of the catalyst researchers. TiO_2 photocatalysis could easily initiate oxidation of most of the organic substrates [21-23]. A few successful cases of neat TiO_2 photocatalysed of selective oxidation of organic compounds in water and organic solvents have been reported [24-31]. Two main problems for the use of TiO_2 nanoparticles (NPs) as a catalyst are: 1) difficulty in removing of small TiO_2 NPs from the reaction mixture due to the slurry suspension nature of these NPs; 2) agglomeration of TiO_2 particles. Respect to the significance of aerogels and new heterogeneous oxidation reactions [32-37], herein we synthesized new hydrophobic CA supported TiO_2 NPs as a photocatalyst. High surface area, oleophilicity, easy recovery, and biocompatibility of the catalyst are important features of the new catalyst. We silanized CA using methyltrimethoxysilane (MTMS) for increasing the hydrophobicity (or oleophilicity) of the polymer. The hydrophobic CA (or oleophilic) as the catalyst support can help to the oxidation process because of its tendency in the absorption of organic compounds. Also, the polymer has high aspect ratio provided abundant sites for the reaction. Simultaneously, TiO_2 NPs as the photocatalyst was deposited on hydrophobic CA. The CA modified with polysiloxane/TiO_2 NPs (ST@CA) was recognized as an oleophilic biocompatible heterogeneous photocatalyst for the oxidation reactions.

2. EXPERIMENTAL

2.1. Preparation of ST@CA

For preparation of CA [38], cellulose (2 g) was dispersed into a sodium hydroxide (2 g)/urea (10 g) solution (100 ml) by sonicating during 10 min. The procedure led to the solving of cellulose and the obtained solution was placed in a refrigerator during 24 h to give a frozen gel. The frozen gel was heated at ambient temperature for 4h, and then added into ethanol (99 vol %) for coagulation. Finally, the obtained gel was poured in water for performing solvent exchange process for 2 days, and then freeze-dried at −98 °C during 2 days to give CA.

For the modification of CA with polysiloxane and titania NPs (ST@CA), CA (2.00 g), TiO_2 nanoparticles (0.3 g), and MTMS (5 ml) was heated to 60 ºC, aged for 2 h, and washed with acetone (3 × 5 ml).

2.2. Determination of Ti on ST@CA using Flame Atomic Absorption Spectroscopy (FAAS)

A mixture of ST@CA (0.05 g) and HCl HNO_3 (3:1) (10 mL) were sonicated. After 3 h, the residue was filtered off and the volume of filtrate was increased to 20 mL using distilled water. The solution was analyzed with FAAS using the CA blank and calibration curve prepared with Ti solution standards.

2.3. Wettability and Liquid Absorption Capacity of ST@CA

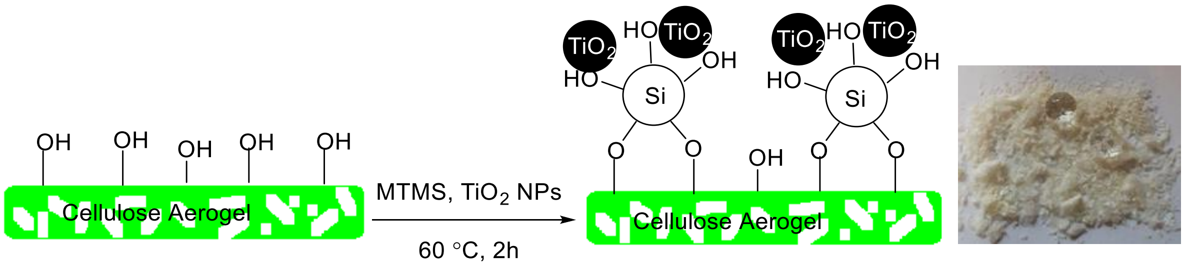
The surface wettability of ST@CA was evaluated by water contact angle (WCA) measurement (OCA20) equipped with a high-speed camera. Water droplet (1 μl) was placed on the surface of ST@CA and the WCA measured immediately. The liquid absorption test was carried out with addition of ST@CA (0.1 g) into 40 ml oil. After 30 min, ST@CA was removed from the mixture and the ST@CA filled with liquids was weighed after that the aerogel was wiped with a filter paper to remove excess liquids. The liquid absorption capacity obtained from eq (1):

$$C=(W_1-W_0)/W_0 \qquad (1)$$

where W_0 and W_1 are the weights of ST@CA before and after absorption, respectively.

2.4. Typical Procedure for the Oxidation of Benzyl Alcohol

H_2O_2 (1.1 mmol) was added to a stirring mixture containing alcohol (1 mmol), ST@CA (0.2 g), and $CHCl_3$ (5 ml) in UV box equipped to a 40 W Hg lamp at 25 ºC. Thin layer chromatography (TLC) was used for determining the reaction end. At the end, ST@CA was separated via filtration, and the mixture was analyzed by GC.



Scheme 1. *Synthesis of the ST@CA.*

3. RESULTS AND DISCUSSION

3.1. Synthesis of ST@CA

Cellulose was transformed to CA through freeze-drying in three steps (Experimental section). The hydrophobicity of CA was improved with the modification of the polymer with MTMS/TiO_2 through the chemical binding of produced polysilicon containing TiO_2 particles to the surface of CA. This process created roughness on the polymer as the obstacle for the penetration of water drops (Scheme 1).

3.1.1. Catalyst Characterization

FT-IR spectra were prepared to confirm the transformation on CA to produce ST@CA (Fig. 1). As can be seen from the spectrum of ST@CA, new absorption bands were appeared at 1147 cm^{-1} for C-O-Si stretch vibration mode of polysilicon [39] and 748 cm^{-1} for Ti-O stretch vibration mode of TiO_2 [40]. In addition, band shifts and change in peak shapes were observed at above 3300 cm^{-1} due to new hydroxyl groups of polysilicon and TiO_2.

EDX analysis showed all the elements used in the synthesis of ST@CA such as Si and Ti (Fig. 2). Since EDX is a surface analysis, the high intensity of the Si, and Ti peaks compared to C, and O peaks show that the surface of the CA was covered with a silicon/titania coating. Therefore, CA is a porous template for silicon/titania and cannot be affected the catalytic activity of silicon/titania. The Ti loading on the catalyst was determined to be 0.093 g (1.98 mmol) per 1g of the catalyst according to FAAS analysis.

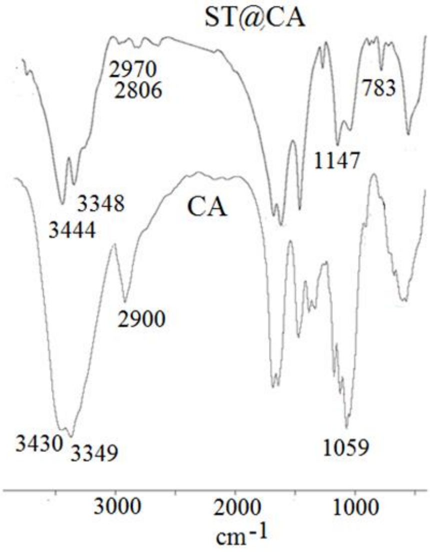


Figure 1. *FT-IR spectra of CA, and ST@CA.*

SEM micrographs of ST@CA were prepared to show the formation of a cover of ST on cellulose (Fig. 3). The elemental mapping also demonstrated homogeneous distribution of Si and Ti elements on the composite surface. Moreover, the micrographs demonstrated formation of particles with the size of about 60 nm, in which these particles were in charge of making roughness on the surface of support. This roughness surface led to the obtaining a hydrophobic compound.

3.1.2. Wettability

The wettability of ST@CA was determined by the water contact angles (WCA) of the aerogel surface. Unlike CA, ST@CA exhibited hydrophobic properties with WCA above 152.0º. Reinforcement of the energy in nanocomposite surface as well as increasing the surface roughness led to improving WCA. Silanization reaction increases the surface energy of the CA as well as the formation of the polysilicon particles and deposition of TiO_2 nanoparticles endowed the ST@CA with high surface roughness. The oleophilicity of ST@CA was tested by dripping oil drops on the surface of the ST@CA which showed lipophilicity.

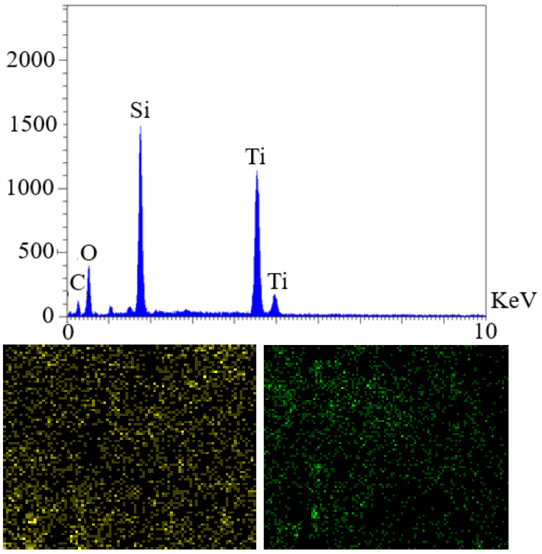


Figure 2. *EDX and elemental mapping of ST@CA (Yellow for Si and green for Ti elements).*

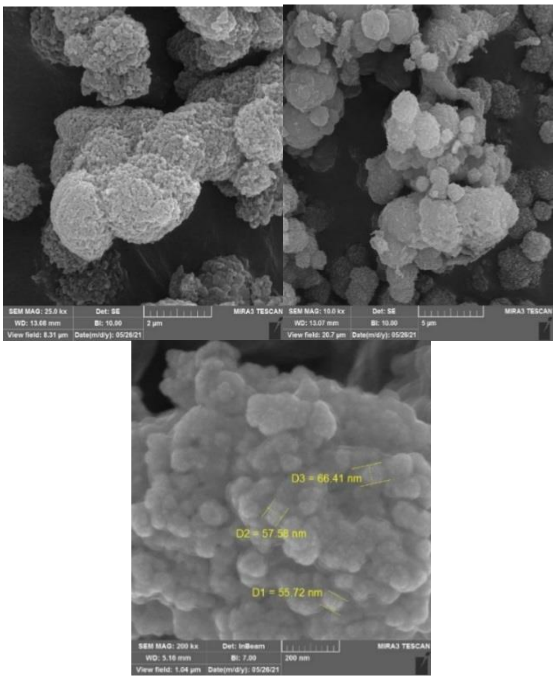


Figure 3. *SEM micrographs of ST@CA.*

Owing to its hydrophobicity and lipophilicity, the ST@CA was a potential candidate for the separation of oils and organic pollutants from water. When the ST@CA was placed in gasoline/water mixture solution it selectively absorbed the gasoline, leaving the clean water. The ST@CA was floated on the water surface after absorbing the gasoline due to its low density. Also, the capacity of ST@CA was investigated for the gasoline which 6.3 g/g with 14.1 g/g selectivity of gasoline per water was obtained. Furthermore, the absorbent performance was examined for the second cycle through washing the recovered ST@CA with acetone (3 × 10 ml), drying in oven at 50 °C, and reusing. The recovered ST@CA demonstrated 4.9 g/g gasoline absorbing with the selectivity of 14.0 g/g.

Table 1. *Optimization of the reaction conditions for the oxidation of 1-pentanol*

Entry	A (g)	Solvent	B (%)
1	0.3	$CHCl_3$	96
2	0.4	$CHCl_3$	> 99
3	0.5	$CHCl_3$	> 99
4	0.4	H_2O	37
5[b]	0.4	EtOH	43
6	0.4	MeOH	59
7	0.4	CH_3CN	95
8	0.4	Ph-CH_3	84

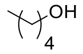
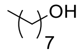
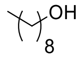
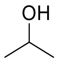
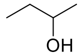
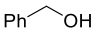
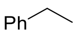
[a] Reaction conditions: 1-pentanol (1.0 mmol), H_2O_2 (1.1 mmol), catalyst (0.4 mmol), solvent (5 ml), r.t., 2 h. A: catalyst amounts. B: GC yield.

3.1.3. Oxidation of Alcohols, and Ethylbenzene

The photocatalytic activity of ST@CA was investigated in the oxidation reactions of alcohols, and ethylbenzene. At first, the oxidation of 1-pentanol was studied with H_2O_2 as the oxidant under UV irradiation (Hg lamp). The catalyst amount and solvent were optimized. The reaction gave >99% conversion and 99.4% selectivity using 0.4 mmol catalyst in $CHCl_3$ as the solvent. The reaction was studied with excess amounts

ST@CA which improvement in the conversion and reaction time did not achieve. (Table 1).

Table 2. *Oxidation of various substrates with ST@CA*[a]

Entry	Substrate	A (%)	B (%)
1		> 99	99.4
2		93	99.2
3		91	99.2
4		> 99	100
5		> 99	100
6[b]		> 99	100
7[c]		81	100

[a]Reaction conditions: substrate (1 mmol), H_2O_2 (1.1 mmol), catalyst (0.4 mmol), $CHCl_3$ (5 ml), r.t., UV, 2 h. [b]1h. [c]3h. A: GC yield. B: conversion

The photocatalyst activity was also examined for various aliphatic alcohols such as 1-octanol, 1-decanol, 2-propanol, and 2-butanol which the corresponding aldehydes or ketones were obtained (Table 2). High conversions and excellent selectivities were obtained for the oxidation reactions. 1-Decanol was oxidized with 91% yield, showing the difficult oxidation reaction of the large molecules. 2-Butanol and 2-propanol were examined in the reaction, which butanone and acetone were obtained with high selectivity, respectively. Benzyl alcohol was also investigated in the oxidation reaction in short reaction time. Oxidation of ethylbenzene was performed to yield acetophenone as the sole product with 81% yield and 100% selectivity during 3h (Table 2, entry 6). The low yield of this reaction is related to the difficult oxidation of alkyl arenes compared to alcohols.

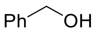
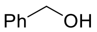
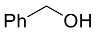
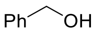
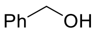
Due to importance of aerobic oxidation, the oxidation reaction of 1-pentanol was studied with O_2 as the oxidant in the presence of ST@CA in $CHCl_3$. The oxidation reaction gave 31% yield at reflux conditions during 24 h and the yield did not elevate at high temperatures, and even long reaction duration.

For the discovery of the catalytic effects of CA and silicon, the oxidation reaction of benzyl alcohol was performed using CA, CA modified with MTMS (S@CA), cellulose modified with MTMS/TiO_2 (ST@C), unsupported TiO_2, and mechanically mixed CA/TiO_2, separately. The oxidation reactions did not perform in the presence of CA or S@CA. The result approves the photocatalytic activity of TiO_2 in the oxidation reaction (Table 3, entries 1 and 2). In addition, the low catalytic activity was observed for the mechanically mixed CA/TiO_2 which evinced the effect of polysilicon on the oxidation reaction (Table 3, entry 3). The high catalytic activity of ST@CA compared to the mechanically mixed CA/TiO_2 may be attributed to the lipophilicity of ST@CA due to the presence of polysilicon on the CA. The high aspect ratio of CA as a support had a positive effect on the reaction yield, since decrease in the reaction yield was observed in the presence of ST@C (Table 3, entry 5). Unsupported TiO_2 showed low catalytic activity compared to ST@CA (Table 3, entry 6). These results demonstrated that the uniform deposition of TiO_2 on a hydrophobic porous structure is essential for obtaining a high photocatalytic oxidation yield.

Leaching studies of Ti into the mixture of benzyl alcohol oxidation reaction with FAAS analysis could elucidate the ST@CA stability in the reaction mixture. Therefore, a sample was taken from the ST@CA catalyzed oxidation reaction of benzyl alcohol by a filter after 10 min. The sample was dissolved in HNO_3 and FAAS analysis was performed which showed the Ti concentration in the reaction mixture was undetectable.

This result indicated that virtually no Ti leached from ST@CA into the mixture. The leaching study was also evaluated for the 7th times recycled catalyst and again the Ti concentration was undetectable by FAAS in the reaction media.

Table 3. *Oxidation of benzyl alcohol with S@CA, T@CA and ST@CA*[a]

Entry	Substrate	Catalyst	A (%)
1		CA	0
2		S@CA	0
3		TiO_2/CA	70
4		ST@CA	> 99
5		ST@C	84

[a] Reaction conditions: substrate (1.0 mmol), H_2O_2 (1.1 mmol), catalyst (0.4 mmol), $CHCl_3$ (5 ml), r.t., 1 h. A: GC yield.

Table 4*. Successive trials by using recoverable ST@CA for the oxidation of benzyl alcohol*[a]

Trial	Conversion (%)
1	> 99
2	> 99
3	> 99
4	> 99
5	> 99
6	> 99
7	> 99
8	96

[a]Reaction conditions: benzyl alcohol (1 mmol), H_2O_2 (1.1 mmol), catalyst (0.2 g or 0.4 mmol), $CHCl_3$ (5 ml), r.t., 1 h.

3.1.4. Recyclability of ST@CA

The recyclability of ST@CA was investigated in the oxidation reaction of benzyl alcohol. For this test, ST@CA was separated in the end of the reaction, washed with acetone (2× 5 ml), dried in oven at 70 ºC, and reused. The GC analysis showed a little decrease in the reaction yields after 8 repetitive cycles for these reactions (Table 4).

3.1.5. Comparison of the Oxidation Results

The oxidation results of benzyl alcohol by ST@CA was compared with some of the recent valuable reports, including Pd/PdO supported on polymer like graphene quantum dots (Pd/PdO/GQD) [41], Ru(II) supported on dimercaprol modified cellulose aerogel [42], Ru supported on zirconia (Ru/zirconia) [43], and Au(III) supported on dimercaprol modified cellulose aerogel [4]. The most eminent characteristic of ST@CA compared to all of the mentioned catalysts is the cheap nature of its ingredients. In the meantime, the catalyst showed significant activity compared to most of this catalyst, in which excellent conversion were obtained in milder reaction conditions during short time.

4. CONCLUSION

A new porous hydrophobic aerogel containing TiO_2 photocatalyst was synthesized with the ability of organic substrates absorption in high efficiency and oxidation of alcohols, and ethylbenezene to the corresponding ketones or aldehydes. The aerogel was obtained via the transformation of cellulose to cellulose aerogel, and hydrophobization of cellulose aerogel with deposition of polysilicon and titania nanoparticles. High capacity in oil absorption with 6.1 g of gasoline/g of absorbent and good selectivity in the oil to water of 14.1 g/g for ST@CA were observed. Also, excellent catalyst activity was observed for ST@CA in the oxidation reactions of alcohols, and ethylbenzene with the conversions of 81-99% at room temperature during 1-2 h. The catalyst is recyclable, and chemically stable.

ACKNOWLEDGEMENT

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

Table 5. *Comparison of the benzyl alcohol oxidation results with some of the recent reports.*

Entry	Catalyst	Oxidant	Temp. °C	Time (h)	Conversion (%)
1	Pd/PdO/PG [41]	H_2O_2	r.t.	20	82
2	RuD@CA [42]	O_2	80	2	81
3	Ru/zirconia [43]	O_2	100	1	100
4	AuD@CA [4]	H_2O_2	r.t.	1	99
5	ST@CA	H_2O_2	r.t.	1	99

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