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# New method for preparation of MWCNT-SO₃H as an efficient and reusable catalyst for the solvent-free synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones

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ABSTRACT

Multiwall carbon nanotubes (MWCNTs) have been functionalized with -SO₃H groups using new three steps chemical routes. Firstly, OH groups have been attached to CNT surfaces through a radical reaction. The second step involves converting the hydroxyl groups into the oxide one and last step included the attachment of –SO₃H groups on the MWCNTs surfaces in the presenceof1-butyl-3-methyl imidazolium tetrafluoroborate[bmim]BF₄ionic liquid as catalyst. Functionalized MWCNTs were characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. Obtained product have be used as acidic nano catalyst in the Biginelli reaction for the synthesis of 3,4-dihydropyrimidin-2(*1H*)-one derivatives. The reaction was performed under solvent-free conditions with excellent yields and short reaction times in the presence of a reusable efficient catalyst.

*Keywords: Multiwalled carbon nanotubes, Functionalization, Sulfonation, [bmim]BF₄ Ionic liquid, MWCNTs-SO₃H, Biginelli reaction, Dihydropyrimidinones.*

## 1. Introduction

MWCNTs are important groups of nanomaterials, which have special properties such as the rich electronic properties, excellent chemical and thermal stability, high surface area and high mechanical strength but ultra-light weight [1,2]. Unique electrical and chemical properties of CNTs, have made them exciting to global researches [3-5] indifferent fields such as enhance the properties of polymeric compounds [6], energy storage [7], catalyst supports in heterogeneous catalysis [8-9], sensors [10], field emitters [11] and so on. Joining functional groups or other nano structures on the surfaces of CNTs is necessary because the chemical and physical properties of carbon nanotubes can be affected by organic and inorganic species through surface modification. The use of carbon nanotubes has been greatly regarded as a catalyst support that can offer the unique catalytic properties [12]. Chemical modification is a usual method for the deposition of various groups on the surfaces of carbon nanotubes for nano catalytic and various applications [13,14]. Broadly, methods of functionalization of CNTs can be divided into the endohedral and exohedral modification. Chemical groups are adjoined to the outer wall of the CNTs in the exohedral method. This procedure divided into, non-covalent and covalent approaches. Chemical groups are attached on nanotubes in the non-covalent approach by the sheeting of biomolecules, polymers, etc. Whilst, the functional groups are adjoined on the end caps, sidewalls, or defect sites of nanotubes through a covalent bond in the covalent approach [15,16]. Attachment of -SO₃H groups on the surfaces of CNTs for specially catalytic applications can performed through various reactions for example, Single-walled carbon nanotubes involve phenyl groups (SWCNTS-phenyl), can be sulfonated in oleum (H₂SO₄,20% free SO₃) to give materials that exhibit high solubility in water [17].

In recent years, ionic liquids have emerged as a set of green solvents with unique properties such as high thermal stability, tunable polarity and immiscibility

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with a number of organic solvents, recyclability and negligible vapor pressure [18,19]. Their high polarity and the ability to solubilize in both organic and inorganic compounds can result in enhanced the rate of chemical processes and can provide higher selectivity compared to conventional solvents. Because of ionic liquids are emerging as novel replacements for volatile organic solvents in organic synthesis, they are particularly promising as solvents or catalyst for various reactions [20,21].

One of the most famous Multicomponent reactions (MCRs) that recently have a lot of attentions is the Biginelli reaction. This reaction involve a one-pot cyclocondensation of an aldehyde, β-ketoester and urea (or thiourea) [22] to achieved 3,4-dihydropyrimidin-2(*1H*)-ones as products. Generally, the dihydro-pyrimidones and their derivatives are used for their diverse important pharmacological properties and biological activities [23] including antitumor, antiviral, anti-inflammatory, antibacterial, analgesic, cardio-vascular activity, blood palette aggregation inhibitor, and potent calcium channel blockers [24].
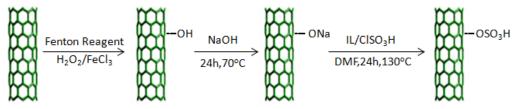
To raise the efficiency of the Biginelli reaction, different reaction conditions and various catalysts have been employed. Recently, several studies including classical conditions were applied with ionic liquids [25], ultrasound [26], microwave irradiation [27], solid-support [28], polymer-supported catalysts [29], zeolite [30], silica sulfuric acid [31], protic acids such as $H_2SO_4$, HOAc, conc. HCl [32], Lewis acid catalysts such as LiBr [33], $NH_4Cl$ [34], $MgBr_2$ [35], etc.

In this study, MWCNTs have been covalently functionalized with $SO_3H$ groups using a three step procedure and the sulfonated MWCNTs were used as catalyst in the Biginelli reaction. To synthesis of this catalyst, initially hydroxyl groups were covalently attached to the MWCNTs surfaces by Fenton reagents (ferrous salt and hydrogen peroxide mixture) [36]. In this reaction, the hydrogen peroxide is broken down by ferrous iones to form hydroxyl radicals. Hydroxyl radicals react with unsaturated bonds on MWCNTs surfaces to produce hydroxylated CNTs. The second step involves converting the hydroxyl group in to the oxide one (using NaOH) and last step included sulfonation of carbon nanotubes by chlorosulfonic acid in the presence of [bmim] $BF_4$ ionic liquid as catalyst (Scheme 1). The sulfonated MWCNTs were characterized by FTIR, XRD, SEM and Raman spectroscopy and used for the synthesis of 3,4-dihydropyrimidin-2(*1H*)-ones **4** under solvent free conditions (Scheme 2).
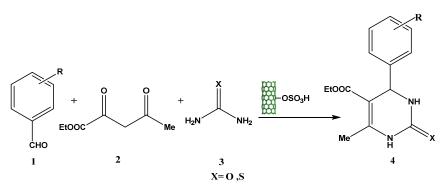
## 2. Experimental

### 2.1. Material and methods

MWCNTs were purchased from Shenzhen Nanotechnologies China with length of 20–40 nm. The Purity of the CNTs was about 90–95% and the diameters and lengths ranging are between 20–40 nm and 5–15 µm respectively. Hydrogen peroxide, ionic liquid, chlorosulphonic acid, benzaldehydes derivatives, ethylacetoacetate, urea, thiourea and all solvents, purchased from Merck and Aldrich Companies.



**Scheme 1.** The procedure of sulfonation of MWCNTs.



**Scheme 2.** Synthesis of 3,4-dihydropyrimidin-2(*1H*)-ones/ thiones in the presence of MWCNTs-OSO₃H.

## 2.2. Apparatuses

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna 551 spectrometer with a disc of KBr (pellet; 4000–400 cm⁻¹).^{1}HNMR and $^{13}$CNMR spectra were recorded in DMSO-d$_6$ solutions and TMS as an internal reference on a Bruker Avance 400NMR spectrometer operating at 400 ($^1$H) and 100 ($^{13}$C) MHz. All sonication processes were carried out with an ultrasonic bath (UA03MFD, Fungi Ultrasonic) with a frequency of 40 kHz and power of 80 W. The X-ray diffraction (XRD) patterns were obtained with a diffractometer of D$_8$ Avance using a Cu anode at 40 kV and wavelength of 0.154 nm. Scanning electron microscopy (SEM) was conducted at 26 kV using a KYKY-EM 3200 field emission scanning microscope with energy dispersive Xray spectroscopy (EDX) analysis for characterization of functionalized MWCNTs. Raman spectroscopy were carried out using an Almega Thermo Nicolet Dispersive Raman Spectrometer, with a second harmonic @532 nm of a Nd:YLF laser and a 4 cm⁻¹ resolution.

## 2.3. Preparation of MWCNT-OSO3H

0.1 g of MWCNTs and 5 g of FeSO$_4$.7H$_2$O were put into a flask and placed in an ultrasonic bath and kept for 20 mines. Afterward, 10 ml aqueous H$_2$O$_2$30% was added to the above solution stepwise (drop by drop). The reaction mixture was continuously stirred for 40 mines (sulfuric acid was used to adjust pH value of about 3±0.5). At the end, the solution was filtered and washed with distilled water and dilute hydrochloric acid for removal the untreated FeSO$_4$. The Product was dried in an oven at 80°C for 10 hours. 0.1 g of CNT-OH obtained from previous section, was placed into a100 ml round bottomed flask and then, 70 ml NaOH 0.1 N was added. After that, the flask was placed in an ultrasonic bath and kept for 15 mines in order to debundling the CNT ropes then the mixture was refluxed for 24 h at 80°C. After that, the solution was filtered and obtained Product (MWCNT-ONa) dried in an oven at 80°C. In Third step, 0.1 g of MWCNT-ONa was placed into a50 mL round bottomed flask and then 10 ml DMF, 0.1 g of [bmim] BF$_4$ ionic liquid and 0.5 g of chlorosulfonic acid were added to the flask. The mixture was refluxed for 24h at 130°C. Finally, the solution was filtered and washed with warm EtOH. Finally, functionalized sample dried in oven at 80°C.

## 2.4. Determination of concentration of sulfonic acid groups on MWCNTs

MWCNT-OSO$_3$H (0.01 g) was added to Sodium hydroxide 0.1 N (10 mL) and was stirred for 24 hours at room temperature. After that, the reaction mixture filtered and the filtrated solution were titrated with hydrochloric acid of 0.1 N in order to additional primary base was determined and the concentration of sulfonic acid groups (formed on the CNT surfaces) was specified.

## 2.5. General procedure for the synthesis of 3,4-dihydropyrimidinones

A mixture of aldehyde (1mmol), ethyl acetoacetate (1mmol), urea or thiourea (1mmol) and catalytic amount of MWCNTs-SO$_3$H (0.005 g) was taken in solvent free conditions. The progress of the reaction was monitored by TLC. The mixture of reaction was cooled to room temperature and hot ethanol was added. The catalyst was insoluble in hot ethanol and it could therefore be separated by a simple filtration. After the evaporation of Ethanol, crude product was obtained. The solid product was collected by filtration, dried and recrystallized from hot alcohol to obtain the pure materials. Products were characterized by melting point, FT-IR, $^1$HNMR and $^{13}$CNMR methods.

## 3. Results and Discussion

FTIR is one of the strongest techniques of studying the surface attributes of carbon nanotubes. Therefore, we used this technique for characterization of the structure of functionalized MWCNTs. Fig. 1 shows FT-IR spectra of (a) raw MWCNTs, (b) MWCNT-OHs and (c) MWCNT-OSO$_3$H. Since the raw nanotubes are totally symmetric, vibrations had the least change in the dipolar moment of C-C bands and sharp peaks didn't observed in their FTIR spectra (compare with organic compounds) so, the absorption bands of the stretching vibrations of C=C in the structure of raw carbon nanotubes (at 1575 cm⁻¹), are not observed. Broad peak at about 3500 cm⁻¹ is related to the absorption of water by KBr (a in Fig. 1). In FT-IR spectrum of MWCNT-OH, The sharp peaks at 3400 cm⁻¹ is from the stretching vibration band of O-H. 2924 cm⁻¹ is related to the stretching vibration band of C-H. Peak in 1628 cm⁻¹ is from the stretch mode of the aromatic C=C bonds in MWCNT-OH. Finally, the stretching vibration band of C-O occurs at 1117 cm⁻¹. This result much more indicates that MWCNTs are modified with hydroxyl groups. The FT-IR spectrum of MWCNT- OSO$_3$H (c in Fig. 1) shows a broad band at 3300-3500 cm⁻¹, which is attributed to OH groups. The broad band at 1089 cm⁻¹ assigned to the stretching vibration modes of sulfate groups (S=O) and the band at 501 cm⁻¹ is due to the stretching vibration band of S-O [37].
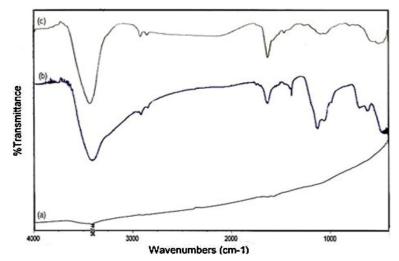
**Fig. 1.** FT-IR spectra of (a) raw MWCNTs, (b) MWCNT-OHs and (c) MWCNT-OSO₃H.

One of the most powerful techniques for probing the changes of structure and surface of the carbon nanotubes is Raman scattering. This technique provides very useful information about the structural changes of the nanotubes. Raman spectra of the pristine and sulfonated CNTs are shown in Fig. 2. In Raman spectra of raw MWCNTs, the band observed at around 1345 $cm^{-1}$ is related to the breathing mode of defects, $sp^3$ hybridized carbons or other impurities. This band is called the D-band. The other band that called as G-band, observed at around 1583 $cm^{-1}$. This band corresponds to the $sp^2$ hybridized carbons in graphene layers. The $I_D/I_G$ ratio (the intensity ratio of D-band ($I_D$) to G-band ($I_G$)) can be calculated in the chemical reactions. Significantly, as shown in Fig. 2, the patterns of raw and modified CNTs are similar but the $I_D/I_G$ ratio is different. As a result, this indicates the changes in the surface and structure of the nanotubes. The $I_D/I_G$ ratio for pristine MWCNTs was 0.85. In contrast, the $I_D/I_G$ of MWCNT-OSO₃H was increased to 1.43. In fact, the creation of a covalent bond between a carbon on the carbon nanotube surfaces and functional groups, converts the hybridization of this carbons from $sp^2$ towards greater

$sp^3$ character. So the number of surface defects is thus increased and hence contributes to increase the intensity of the D-band. As shown in Fig. 2b, a shoulder at around 1184 $cm^{-1}$, assigned to the band of S=O, Which is not seen in the raw nanotubes [38,39].

Fig. 3 show the XRD patterns of (a) raw MWCNTs, (b) MWCNT-OHs and (c) MWCNT-OSO₃H. The broad C (002) diffraction peak (2θ = 25.95º) can be ascribed to the amorphous carbon structures. The weak and broad C (101) diffraction peak (2θ = 43.38º) is due to the axis of the graphite structure. There is no significant diversity in the XRD patterns between three samples. As can be seen, the XRD patterns were similar to pristine MWCNTs. As a result, shaft wall structure and inter-planner spacing of modified MWCNTs remained stable during the reactions.

SEM images were obtained from (a) pristine MWCNTs and (b) MWCNT-OSO₃H. Fig. 4a presents SEM image of the Pristine MWCNTs. It can be shown spaghetti-like network with clean and flat surfaces. Also, the length and diameter of the pristine nanotubes are about 20-40 nm. Fig. 3b presents SEM image of the MWCNTs after functionalized with the -SO₃H groups.
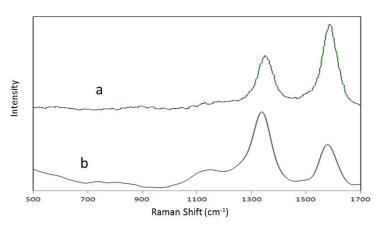


**Fig. 2.** Raman spectra from: (a) pristine MWCNTs (b) MWCNT-OSO₃H.

It can be seen that diameter dimensions of MWCNT-OSO$_3$H are increased, while the length of the nanotubes remained stable. This shows that functionalization of CNTs occurred successfully and many -SO$_3$H groups are attached.

The presence of -SO$_3$H groups on the MWCNTs surfaces have also been studied by EDX (Fig. 5). The plot shows the existence of C, O and S in the functionalized CNTs. These results were confirmed by other characterization data and show that the –SO$_3$H groups were successfully attached on the CNT surfaces.

According to back titration method, the concentration of the sulfonic acid groups attached on CNT surfaces was 19.2 mmol/g. This result indicates that acidic site produced on the CNT surfaces have high concentration.

We wish to use the MWCNT-OSO$_3$ has an efficient heterogeneous catalyst of the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones (**4**) under solvent free conditions (Scheme 2). Therefore, we developed the catalyst by impregnation of SO$_3$H on MWCNTs which enhances the yield of products and subsequently decreases the reaction time.

In order to optimization the reaction conditions affecting the yields (the amounts of catalyst, temperature and time), we chose the reaction of benzaldehyde, ethyl acetoacetate and urea as model reaction. The results for optimization of the temperature of the model reaction using 1:1:1 mmol ratios of aldehyde, 1,3-dicarbonyl and urea, were summarized in Table 1 (the reaction was monitored by TLC). As shown in this Table, 120$^o$C was the best temperature in solvent free conditions.

After determining the reaction temperature, the amount of the catalyst must be evaluate in model reaction. The results in Table 2 show that 0.005 g of catalyst was the best amount for completion of reaction in solvent free conditions.

Best reaction time was obtained after four reactions depicted in Table 3. Results show the optimum time of reaction is 25 minutes.
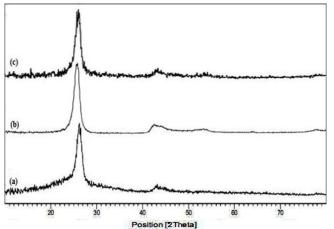


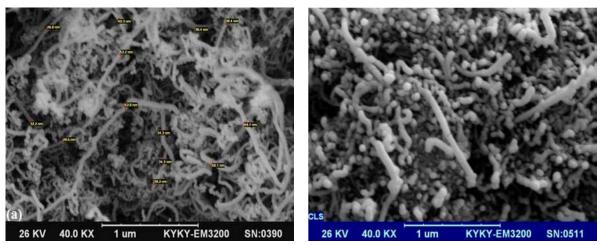**Fig. 3.** XRD pattern for (a) raw MWCNTs, (b) MWCNT-OHs and (c) MWCNT-OSO$_3$H.



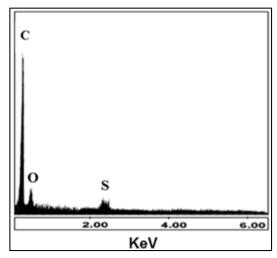**Fig. 4.** SEM images of (a) pristine MWCNTs and (b) MWCNT- OSO$_3$H.

**Fig. 5.** EDX of MWCNT-SO$_3$H.

**Table 1.** The optimization of reaction temperature.[a]

| Entry | Temp. (°C) | Yield[b] (%) |
|-------|-----------|-------------|
| 1 | 80 | 70 |
| 2 | 100 | 80 |
| 3 | 120 | 90 |
| 4 | 130 | 87 |

[a]1:1:1 mmol ratios of aldehyde, 1, 3-dicarbonyl and urea in the presence of 0.005 g of MWCNTs-SO$_3$H after 25 min.
[b]Isolated Yield.

To investigate the scope and limitation of catalyst, we try to study on the solvent free synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones in thermal conditions. In this way, we use a variety of benzaldehyde derivatives, ethylacetoactate and urea (or thiourea) in the presence of MWCNTs-SO$_3$H as reusable efficient catalyst after 25 min.

**Table 2.** The optimization of reaction catalysts.[a]

| Entry | Catalyst(gr) | Yield[c](%) |
|-------|-------------|-------------|
| 1 | 0[b] | 90 |
| 2 | 0.001 | 80 |
| 3 | 0.003 | 85 |
| 4 | 0.005 | 90 |
| 5 | 0.006 | 90 |

[a]1:1:1. mmol ratios of aldehyde, 1, 3-dicarbonyl after 25 min.
[b]Time of reaction: 2h.
[c]Isolated yield.

**Table 3.** The optimization of reaction time.[a]

| Entry | Time (min) | Yield[b] (%) |
|-------|-----------|-------------|
| 1 | 10 | 20 |
| 2 | 15 | 75 |
| 3 | 25 | 90 |
| 4 | 35 | 90 |

[a]1:1:1. mmol ratios of aldehyde, 1, 3-dicarbonyl and urea in the presence of 0.005 g of MWCNTs-SO$_3$H.
[b]Isolated yield.

Table 4 shows the time and yield of the reaction products in thermal conditions. All reactions performed efficiently, and the products were obtained in high yields in short reaction times and also no by-product was formed during the reaction.

The Biginelli reactions in the presence of MWCNT-OSO$_3$H as catalyst were performed expeditiously and achieved good yields with various aromatic aldehydes containing electron withdrawing and electron donating groups.

**Table 4.** MWCNTs-OSO$_3$H catalyzed synthesis of dihydropyrimidones.

| Entry | Product | R | X | Time (min) | Yield[a] (%) | m.p. (°C) Found | m.p. (°C) Reported | Ref. |
|-------|---------|---|---|-----------|-------------|-------|----------|------|
| 1 | 4a | C$_6$H$_5$ | O | 25 | 90 | 197-199 | 198-200 | [40] |
| 2 | 4b | 4-O$_2$NC$_6$H$_4$ | O | 20 | 94 | 202-204 | 205-207 | [41] |
| 3 | 4c | 4-MeOC$_6$H$_4$ | O | 32 | 90 | 198-200 | 199-201 | [42] |
| 4 | 4d | 4-OHC$_6$H$_4$ | O | 30 | 88 | 227-228 | 227-229 | [43] |
| 5 | 4e | 4-ClC$_6$H$_4$ | O | 22 | 90 | 212-214 | 213-215 | [44] |
| 6 | 4f | 4-CH$_3$C$_6$H$_4$ | O | 35 | 88 | 212-214 | 214-215 | [45] |
| 7 | 4g | 2,4-(Cl)$_2$C$_6$H$_3$ | O | 15 | 92 | 245-247 | 246-248 | [40] |
| 8 | 4h | C$_6$H$_5$ | S | 40 | 85 | 202-204 | 202-204 | [40] |
| 9 | 4i | 4-ClC$_6$H$_4$ | S | 20 | 90 | 181-183 | 184-186 | [40] |
| 10 | 4j | 4-MeOC$_6$H$_4$ | S | 20 | 90 | 136-138 | 137-139 | [40] |

[a]Isolated yield.

We also obtained the reusability of the catalyst. Similarly, the same model reaction was used under optimized conditions. At the end of reaction, the reaction mixture was heated up to boiling with hot ethanol and immediately catalyst was separated by simple filtration. The catalyst was dried in an oven at 80°C and reused to repeat the reaction for three times. Fig. 6 shows that the catalyst has high efficiency even after reused for three times.

Comparison of sulfonated carbon nanotubes efficiency with previously reported catalysts in the synthesis of 3,4-dihydropyrimidin-2(*1H*)-one derivatives were shown in Table 5. The results indicate that MWCNT-SO$_3$H is a high efficient solid acid catalyst with superior in reaction times, yields and reusability.
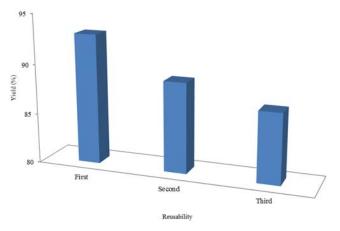


**Fig. 6**. Reusability of MWCNTs-OSO$_3$H in Biginelli reaction.

**Table 5.** Comparison of catalytic activity of MWCNTs-SO$_3$H with other reported catalysts.[a]

| Entry | Catalyst | Time | Yield (%)[b] | Ref. |
|-------|----------|------|----------|------|
| 1 | MWCNT-SO$_3$H | 25 min | 90 | This work |
| 2 | Molybdophosphoric acid | 5 h | 80 | [46] |
| 3 | Tungestophosphoric acid | 6 h | 75 | [47] |
| 4 | Sr(NO$_3$)$_2$ | 6 h | 77.8 | [48] |
| 5 | Fecl$_3$/Si(OEt)$_4$ | 3 h | 88 | [49] |
| 6 | Natural HEU Zeolite | 5 h | 75 | [50] |
| 2 | NaBF$_4$ | 3 h | 85 | [51] |
| 3 | *p*-Sulfonic acid/calixarenes | 8 h | 69 | [52] |
| 4 | Amberlyst 15 DRY | 5.5 h | 88 | [53] |
| 5 | Al$_2$(SO$_4$)$_3$/ acetic acid | 3 h | 88 | [54] |

[a]1:1:1 mmol ratios of aldehyde, 1, 3-dicarbonyl and urea in the presence of catalyst.
[b]Isolated yield.

## 4. Conclusions

In this study, a new and impressive method of MWCNTs functionalization (through chemical modification) has been applied. MWCNTs were functionalized with -SO$_3$H groups using new three step reactions and obtained acidic product was confirmed using various techniques such as FTIR, XRD, SEM, EDX, back titration and Raman spectroscopy. Sulfonated MWCNT scan be used as an efficient reusable heterogeneous catalyst in various chemical fields. Here, we have developed a catalytic method for Biginelli reaction using MWCNTs-OSO$_3$H under solvent free conditions. This procedure is much simpler and faster than the protocols published to date.MWCNT-OSO$_3$H as a new heterogeneous catalyst can be easily regained by simple filtration and reused in same reaction without decrease of catalytic activity. The procedure also consistent with a green chemistry approach since no solvent is needed.

## References

[1] P.M. Ajayan, Chem. Rev. 99 (1999) 1787-1800.
[2] S. Iijima, Nature 354 (1999) 56-58.
[3] T.W. Ebbesen, H.J. Lezec, H. Hiura, J.W. Bennett, H.F. Ghaemi, T. Thio, Nature 382 (1996) 54-56.
[4] N.H. Thai, M.K. Yeh, J.H. Liu, Carbon 42 (2004) 2774-2777.
[5] Z.H. Gan, Q.Zhao, Zh. N. Gu, Q.K. Zhuang, Anal. Chim. Acta 511 (2004) 239-247.
[6] R.H. Baughman, A.A. Zakhidov, W.A. Heer, Science 297 (2002) 787-792.
[7] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377-379.
[8] E. Steen, F.F. Prinsloo, Catal. Today 71 (2002) 327-334.
[9] M. Salavati-Niasari, E. Esmaeili, H. Seyghalkar, M. Bazarganipour, Inorg. Chim. Acta 375 (2011) 11-19.
[10] M. Penza, F. Antolini, M.V. Antisari, Sens. Actuators B 100 (2004) 47-59.

[11] G.S. Choi, K.H. Son, D.J. Kim, Microelect. Eng. 66 (2003) 206-212.

[12] L.Q. Jiang, L. Gao, Carbon 41 (2003) 2923-2929.

[13] N. Karousis, N. Tagmatarchis, D. Tasis, Chem. Rev. 110 (2011) 5366-5397.

[14] Z. Li, Y.Q. Dong, M. Haussler, J.W.Y. Lam, Y.P. Dong, L.J. Wu, K.S. Wong, B.Z. Tang, J. Phys. Chem. B 110 (2006) 2302-2309.

[15] W.Z. Yuan, Y. Mao, H. Zhao, J.Z. Sun, H.P. Xu, J.K. Jin, Q. Zheng, B.Z. Tang, Macromolecules 41 (2008) 701-707.

[16] X. Peng, S.S. Wong, Adv. Mater. 21 (2009) 625-642.

[17] F. Liang, J.M. Beach, P.K. Rai, W. Guo, R.H. Hauge, M. Pasquali, R.E. Smalley, W.E. Billups, Chem. Mater. 18 (2006) 1520-1524.

[18] Z. Zarnegar, J. Safari, J. Nanopart. Res. 16 (2014) 2509-2523

[19] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772-3789.

[20] R. Sheldon, Chem. Comm. (2001) 2399-2407.

[21] C.M. Gordon, Appl. Catal. A 222 (2001) 101-117.

[22] C.O. Kappe, Acc. Chem. Res. 33 (2000) 879-888.

[23] C.O. Kappe, Eur. J. Med. Chem. 35 (2000) 1043-1052.

[24] U.M. Lindstrom, Chem. Rev. 102 (2000) 2751-2572.

[25] (a) J.C. Legeay, J.J.V. Eynde, J.P. Bazureau, Tetrahedron Lett. 48 (2007) 1063-1068. (b) B. Desai, D. Dallin-ger, C.O. Kappe, Tetrahedron. 62 (2006) 4651-4664.

[26] P.G. Mandhane, R.S. Joshi, D.R. Nagargoje. C.H. Gill, Tetrahedron Lett. 51 (2010) 3138-3140.

[27] M.S. Manhas, S.N. Ganguly, S. Mukherjee, A.K. Jain, A.K. Bose, Tetrahedron Lett. 47 (2006) 2423-2425.

[28] K.K. Kapoor, B.A. Ganai, S. Kumar, C.S. Andotra, Can. J. Chem. 84 (2006) 433-437.

[29] A. Dondoni, A. Massi, Tetrahedron Lett. 42 (2001) 7975-7978.

[30] V.R. Rani, N. Srinivas, M.R. Kishan, S.J. Kulkarni, K.V. Raghavan, Green. Chem. 3 (2001) 305-307.

[31] P. Salehi, M. Dabiri, M.A. Zolfigol, M.A. Fard, Tetrahedron Lett. 44 (2003) 2889-2892.

[32] J.C. Bussolari, P.A. McDonnell, J. Org. Chem. 65 (2000) 6777-6779.

[33] G. Maiti, P. Kundu, C. Guin, Tetrahedron Lett. 44 (2003) 2757-2758.

[34] A. Shaabani, A. Bazgir, F. Teimouri, Tetrahedron Lett. 44 (2003) 857-859.

[35] H. Salehi, Q.X. Guo, Synth. Commun. 34 (2004)171-179.

[36] W. Li, Y. Bai, Y.K .Zhang, M.L. Sun, R.M. Cheng, X.C. Xu, Y.Chen, Y. Mo, Synth. Met. 155 (2005) 509-515.

[37] R. Fareghi-Alamdari, M. Golestanzadeh, F. Agend, N. Zekri, J. Chem. Sci. 125 (2013) 1185–1195.

[38] E. Smith, G. Dent, Modern Raman spectroscopy: A practical approach. Wiley & Sons, 2005, 135-140.

[39] R.E. Barletta, B.N. Gros, M.P. Herring, J. Raman Spectrosc. 40 (2009) 972–981

[40] Y. Yu, D. Liu, C. Liu, G. Luo, Bioorg. Med. Chem. Lett. 17 (2007) 3508-3510.

[41] H. Khabazzadeh, K. Saidi, H. Sheibani, Bioorg. Med. Chem. Lett. 18 (2008) 278-280.

[42] A.K. Bose, M.S. Manhas, S. Pednekar, S.N. Ganguly, H. Dang, W. He, A. Mandadi, Tetrahedron Lett. 46 (2005) 1901-1903.

[43] C.O. Kappe, D. Kumar, R.S. Verma, Synthesis (1999) 1799-1803.

[44] B.C. Ranu, A. Hajra, U. Jana, J. Org. Chem. 65 (2000) 6270-6272.

[45] A. Debache, R. Boulcina, R. Tafer, A. Belfaitah, S. Rhouati, B. Carboni, Chin. J. Chem. 26 (2008) 2112-2116.

[46] S. Besoluk, M. Kucukislamoglu, M. Nebioglu, M. Zengin, M. Arslan, J. Iran. Chem. Soc. 5 (2008) 62-66.

[47] A.V. Narsaiah, B.K. Nagaiah, Synthesis (2004) 1253-1266.

[48] K.A. Kumar, M. Kasthuraiah, C.S. Reddy, D. Reddy, Tetrahedron Lett. 42 (2001) 7873-2875.

[49] G.L. Zhang, H.X. Cai, Synth. Commun. 35 (2005) 829-833.

[50] G. Maiti, P. Kundu, C. Guin, Tetrahedron Lett. 44 (2003) 2757-2768.

[51] B.P. Bandgar, V.T. Kamble, S.N. Bavikar, Abasaheb Dhavane, J. Chinese Chem. Soc. 54 (2007) 263-266.

[52] D.L. da Silva, S.A. Fernandes, A.A. Sabino, A. de Fatima, Tetrahedron Lett. 52 (2011) 6328-6330.

[53] S.R. Jetti, N. Babu, P. Paliwal, A. Bhatewra, T. Kadre, S. Jain, Der. Pharm. Chem. 4 (2012) 417-427

[54] B.J. Khairnar, R.J. Kapade, K.M. Borse, B.R. Chaudhari, Orient. J. Chem. 26 (2010) 655-660.