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Synthesis of the first magnetic nano particles with thiourea dioxide-based sulfonic acid tag: Application at the one-pot synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkanes under mild and green conditions

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A novel and recyclable thiourea dioxide-based magnetic nano particles with sulfonic acid tag {Fe₃O₄@SiO₂-(CH₂)₃-thiourea dioxide-SO₃H/HCl} was described. The described catalyst was fully characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), thermo gravimetric analysis (TGA), atomic force microscopy (AFM) and ultraviolet–visible spectroscopy (UV/Vis). The reported novel nano magnetic catalyst represents excellent activities and catalytic performance in the synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane derivatives through one-pot three-component mixed Mannich-type and Friedel–Crafts reactions under solvent-free conditions at 60 °C.

Introduction

In recent decades, one of the most significant issues and concerns is the usage of nanoscience in the development of environmental science, medicine and importantly, catalysis. Unique compatibility and consistency between the nanoscience and green chemistry is due to applications efficiently of nanotechnology in the process and produce products greener so that nanoscience acts as a savior in the environmental and energy challenges.^{1,2} The use of catalysts in order to achieve the goal of reducing or eliminating emissions and create a cleaner environment is one of the principles of green chemistry.³ An important class of nanoparticles are nano catalysts. Possess wide surface to volume ratio and thus increase the reaction rate due to the increase contact between the catalyst and the reactants, puts nano catalysts in the category of catalysts with high potency and activity.^{4,5} Better separation and reuse were the focus of attention, pursuing the expansion of usage of nano catalysts so these particles supported on a solid surface.

One of the important and significant groups of nanoparticles is magnetic nanoparticles (MNPs) because that as a catalyst supported have very particular properties such as high surface areas and ease separation of the catalyst on reaction completion to having magnetic properties.⁶⁻⁸ Ideal characteristics included chemically stable, low toxicity, affordable, and most importantly,

quickly, facility and convenience in separation using an external magnet without any filtration, making them a serious and considerable substitute than other heterogeneous catalytic systems. Magnetic nanoparticles can be functionalized with a wide range of diverse groups such as organic compounds, metals and polymers, so can be used as a catalyst with diverse and various applications.^{7d,9-11}

There are tend to aggregation between of the pure Fe₃O₄ nano magnetic due to the intense dipole–dipole attraction. Therefore, magnetic nanoparticles stuck together to form large clusters and they have limited functional groups and lose the specific properties.¹² One of the common methods used to modify and improve the performance surface, is a coating of magnetic nanoparticles (MNPs) with a layer of silica.¹³ Manipulate their surface could improve the chemical stability of magnetite nanoparticles *via* prevents magnetic nanoparticles from aggregation. Silica coating creates an inert surface so can be used in biological systems. Moreover, silica-coated nanoparticles can be easily functionalized by silanol group which can conjugation of with a range of different chemical entities. Subsequent enabling their use in a large number of application.¹⁴

Functioned based sulfonic acid is a significant branch of magnetic nano particles. Various solid acid catalysts with variety of acid sites were considered in many different processes. Frequently solid acids are mild, non-toxic, very selective and reusable therefore they can be regarded as environmentally friendly.^{15,16} Lately a group of catalysts known as ionic liquid is developed in the synthesis of compounds chemistry with having unique attributes. An important and useful category of ionic liquids (ILs) is Brønsted acidic ionic liquid functionalized with sulfonic acid that can be acted as a good acidic catalyst to advance different reactions.¹⁷

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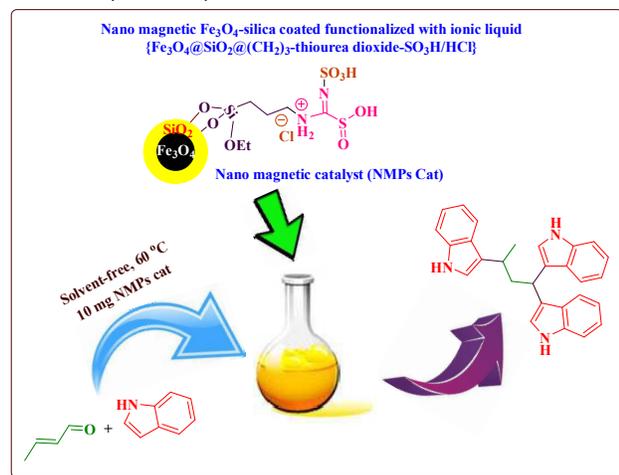
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Thiourea dioxide (TUD) has been prepared *via* the oxidation reaction of thiourea by hydrogen peroxide. TUD has several important advantages both in industry and in academia.¹⁸ It can have a variety of applications such as reagent with multiple roles,¹⁹ catalyst²⁰ and reductant.²¹

To the best of our knowledge, heterocyclic ring systems with widespread natural compounds have key role in the life.²² The Michael addition reaction that name as a conjugate addition is a versatile synthetic methodology that also used to as another efficient method for the formation of new C–C bonds.²³ The Friedel-Crafts reaction is a typical electrophilic substitution reaction for carbon-carbon bond forming process.²⁴ Michael/Friedel–Crafts cascade of indolyl moieties as electron-rich component of electron-deficient enals or enones is the most efficient strategy that can give a wide range of important biological activate molecules which have more applications in molecular medicine.^{25,26}

In our continued interest in the designing, synthesis, application and knowledge-based development of solid acids,²⁷ nano²⁸ and nano magnetic catalysts,²⁹ task- specific ionic liquids (TSILs)³⁰ and inorganic acidic salts,³¹ so due to the specific characteristics of magnetic nanoparticles, solid acids and ionic liquids, herein, we decided to join all of the above mentioned research proposal within the novel described catalyst. Thus, to achieve this goal, we have designed, prepared and used thiourea dioxide-based ionic liquid-stabilized on silica coated Fe₃O₄ magnetic nano particles {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl} in the synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane derivatives under solvent-free conditions (Scheme 1).



Scheme 1. The synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane derivatives using novel thiourea dioxide-based ionic liquid-stabilized on silica coated Fe₃O₄ magnetic nano particles {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl} as an efficient catalyst.

Results and discussion

Characterization of novel thiourea dioxide-based ionic liquid-immobilized on silica coated Fe₃O₄ magnetic nano particles {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide -SO₃H/HCl} with sulfonic acid tag as a catalyst

Studies to vouch the determination of the structure thiourea dioxide-based ionic liquid-immobilized on silica coated Fe₃O₄ magnetic nano particles {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl} as a green, mild, safe and potent novel magnetic catalyst was investigated and fully characterized by using FTIR, EDX, TG, XRD, SEM, TEM, AFM and UV/Vis analysis.

The infrared spectra (FT-IR) of bare Fe₃O₄ magnetic nano particles, Fe₃O₄@SiO₂ core-shell MNPs and the other core-shell surface altered samples are shown in Fig. 1. In the curve a, the spectrum of naked Fe₃O₄ nano particles illustrates an absorption band relevant to the bending vibration of Fe–O at about 580 cm⁻¹. The absorption peaks appearance in 1100, with small shoulder approximately 1200 and 798 cm⁻¹ likely come from Si–O–Si asymmetric and symmetric stretching vibration, respectively and all of them correspond to a layer of silica coated Fe₃O₄. In the curve c, the tendency of propyl group is confirmed by the band in circa 2930 cm⁻¹ related to the stretching vibration of the C–H bonds. Two observation bands at 3369 and 3212 cm⁻¹ can be connected to N–H stretching group on thiourea dioxide. The other peaks at 1698 and 1636 cm⁻¹ are due to stretching vibration of C=N group on imine moiety. In addition, the broad band of stretching vibration related to O–H in the SO₃H and SO₂H functional groups located at about 2700 to 3600 cm⁻¹ and a sharper peak at 3394 cm⁻¹. Also a peak at around 1208 cm⁻¹ linked to the vibrational modes of O–SO₂ more confirmed the presenting of sulfonyl moiety within the described catalyst.

FTIR spectra used to display alterations in the synthesis of {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl} as a MNPs catalyst. These changes step by step, with the addition of substances in each section, in this spectra approved that the materials are added in each section and represents a MNPs catalyst is formed. For more clarification, in Fig. 1 the spectral lines for each sample is assigned. (Now, all changes are obviously present in Fig. 1).

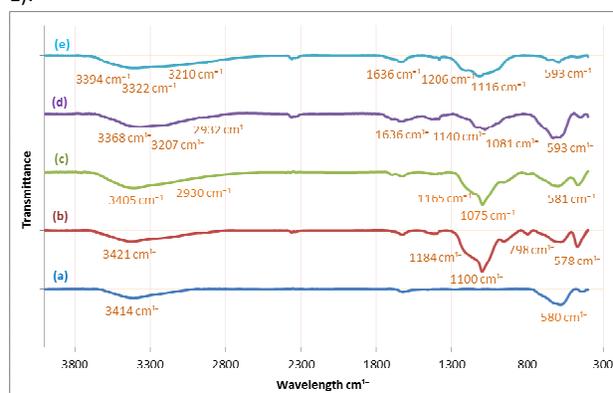


Fig. 1. The IR spectrum of (a) Fe₃O₄; (b) Fe₃O₄@SiO₂; (c) Fe₃O₄@SiO₂@(CH₂)₃Cl; (d) Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide; (e) {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl}.

Energy dispersive X-ray analysis (EDX) used for structure identification {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl} as an ionic liquid nano magnetic catalyst and shown elemental composition of the core-shell structures, including N, Fe, O, Si, S and

Cl which the obtained results were of acceptable concordance with expectations (Fig. 2).

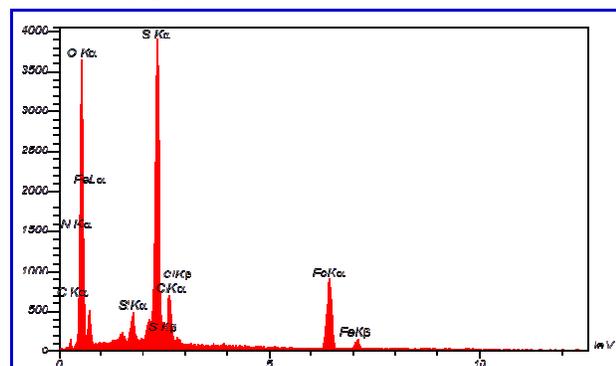


Fig. 2. The energy-dispersive X-ray spectroscopy (EDX) of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst.

The thermogram analysis (TG) and differential thermal gravimetric (DTG) of the catalyst $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ are considerable at a range of 10–550 °C in nitrogen atmosphere along with increasing temperature velocity of 10 °C min^{-1} (Fig. 3). In patterns of TG and its derivatives demonstrate multistage decomposition. The first mass loss nearby 100 °C is due to the elimination of physisorbed water and organic solvents. The second and most original weight loss around 410 °C which is a feature of the surface functionalities and the ionic liquid decomposition. Accordingly, this catalyst decomposed after 520 °C.

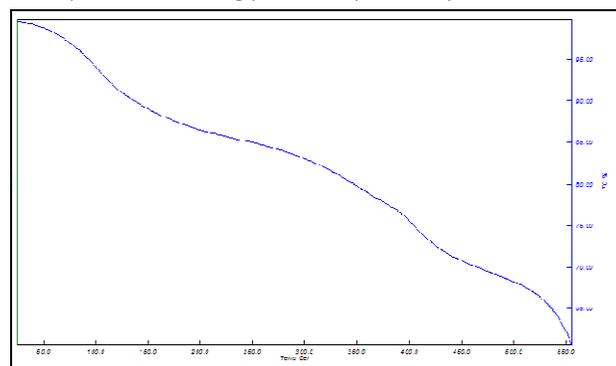


Fig. 3. The thermo gravimetric analysis (TGA) of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst.

X-ray diffraction is a tool for reconnaissance the structure of crystals which can be utilized for measuring the size and diameter as well as determining the crystal plates of nanoparticles. The X-ray diffraction (XRD) patterns of (a) Fe_3O_4 and (b) $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ were investigated (Fig 4). As can be seen uncoated Fe_3O_4 core-shell MNPs indicate sharp peaks in the areas $2\theta \approx 14.80, 30.10, 35.50, 43.10, 53.00, 57.00, 62.80, 70.50, 73.90$ which correspond to with Miller index values $\{h\ k\ l\}$ of (1 1 0), (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (5 1 1), (4 4 0) and (5 3 1), respectively. This information fully complies with the patterns of the crystalline spinel ferrites of nano particles of Fe_3O_4 MNPs characterized in the literature data (JCPDS card No. 85-1436) and

the obtained results acknowledge that the nanoparticles of Fe_3O_4 are pure with a spinel structure crystalline.³² As is observed, XRD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ indicated a broad peak in the region of $2\theta \approx 18^\circ\text{--}25^\circ$ That relates to amorphous nature of silica. Except for this difference, the XRD pattern of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres sample presented similar patterns of Fe_3O_4 nanoparticles that these results indicate that the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ complex has been synthesized and SiO_2 was amorphous thus the crystal structure of Fe_3O_4 does not change after being coated with SiO_2 . There are similar peaks in the XRD pattern of the $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ with XRD pattern of the structure of naked magnetite nanoparticles Fe_3O_4 that represents layered and spherical of catalyst preserved spherical and layered structure of catalyst maintain and sustain during the manufacturing process from prepare of Fe_3O_4 nano magnetic to final stage of synthesis of the nano magnetic ionic liquid catalyst $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$. In addition to the peaks in the pattern a, appeared another peak in the final XRD pattern of catalyst which would confirm manufacture of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$. XRD pattern of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ displayed diffraction lines of high crystalline nature at $2\theta \approx 14.40^\circ$ broad peak at 18.30° to 36.40° with sharp peaks on it at $23.70^\circ, 24.50^\circ, 28.10^\circ, 29.40^\circ, 32.00^\circ, 32.40^\circ, 37.50^\circ, 41.80^\circ, 43.60^\circ, 45.80^\circ, 52.90^\circ$ and 76.30° . The Debye-Scherrer's equation $[D = K\lambda/(\beta\cos\theta)]$ can be used to calculate the size of crystalline particles in the form of powder. In this equation D is the crystalline mean size, K is the dimensionless shape factor with typical values of about 0.9, λ is the x-ray wavelength, β is the bandwidth at half the maximum intensity of peak (FWHM) and θ is the Bragg angle in degree. Inter planer distance attains *via* the Bragg equation: $d_{hkl} = \lambda/(2\sin\theta)$. Size, the distance between the crystal plates and peak breadth (FWHM) at a distance of 9.55° to 52.44° in the XRD paradigm were evaluated and the gained results were brought in Table 1. The average crystallite size particles gained from this equation in the nanometer range (9.55–52.44 nm) that is a good match with observations made in the scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) (Fig. 5).

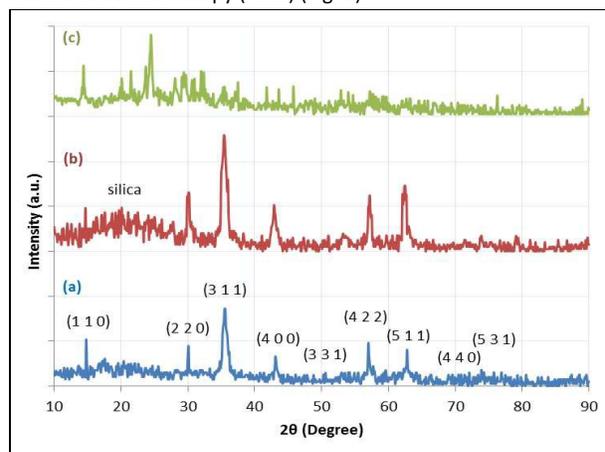
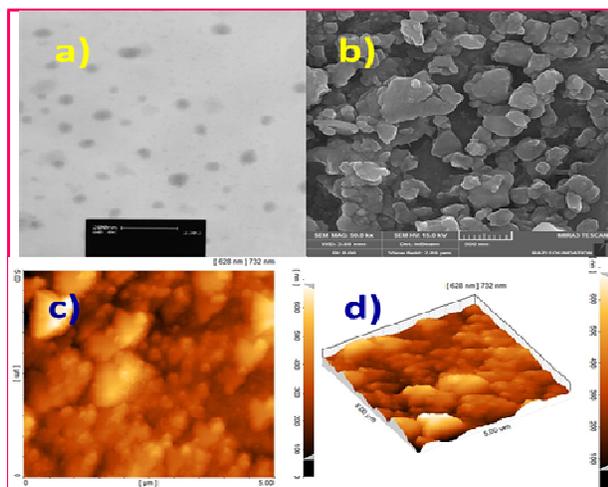
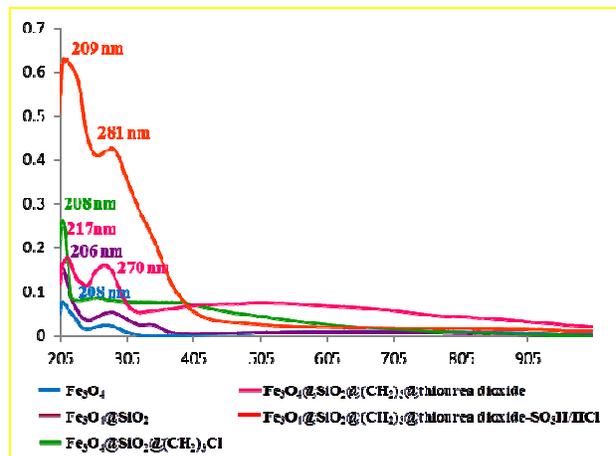


Fig. 4. The x-ray diffraction (XRD) pattern of the Fe_3O_4 MNPs (a); $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b); $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ (c) as a MNPs catalyst.

Table 1. X-ray diffraction (XRD) data for the $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst.

Entry	2θ	Peak width [FWHM] (degree)	Size [nm]	Inter planer distance [nm]
1	14.40	0.25	32.03	0.614378
2	23.70	0.45	18.04	0.374969
3	24.50	0.5	16.26	0.632304
4	28.10	0.5	16.38	0.317175
5	29.40	0.86	9.55	0.303438
6	32.00	0.35	23.61	0.279352
7	32.40	0.2	39.56	0.275994
8	37.50	0.16	52.44	0.239547
9	41.80	0.2	42.52	0.215845
10	43.60	0.19	45.03	0.207341
11	45.80	0.17	50.73	0.197880
12	52.90	0.24	36.97	0.172871
13	76.30	0.22	45.92	0.124651

UV/Vis spectrum was another tool which was used for confirming the structure of the $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst. This analysis was applied to compare changes in different stages of catalyst synthesis. Thereby, it was found that there are differences in absorption maximum between catalyst structure $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ with other structures, and this is an affirmation of the synthesis of this compound. λ_{max} related to MNPs catalysts has appeared in about 209 nm (Fig. 6). As a result, changes in steps, which are associated with changes in the value of λ_{max} , as well as changes in the curves represents the MNPs catalyst is constructed. For more clarity, λ_{max} value of each step on the curve specified.

**Fig. 5.** Scanning electron microscopy (SEM) (a); transmission electron microscopy (TEM) (b); atomic force microscopy (AFM) (c and d) of the $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst.**Fig. 6.** The UV Absorption curves of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst.

Application of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs-TUD-SO₃H catalyst in the synthesis of 1,1,3-tri(1H-indol-3-yl) alkane derivatives.

After full characterization of MNPs-TUD-SO₃H and serve as the first application of this new nanostructure catalyst, we peruse the catalytic activity of nano particles in the synthesis of 1,1,3-tri(1H-indol-3-yl) alkanes. Herein, we wish to find the appropriate reaction conditions to the synthesis of 1,1,3-tri(1H-indol-3-yl) alkanes, *via* condensation reaction between of crotonaldehyde and indole as a model reaction and tested impact changes of the amounts of MNPs-TUD-SO₃H catalyst and temperature at range of 25-60 °C under solvent-free conditions (Table 2).

Table 2. Optimization results of the amounts of the catalyst and temperature in the synthesis of 1,1,3-tri(1H-indol-3-yl) alkanes under solvent-free conditions.

Entry	Catalyst loading (mg)	Reaction temperature (°C)	Reaction time (min)	Yield ^b (%)
1	Catalyst-free	60	180	N.R
2	1	60	180	40
3	3	60	180	40
4	5	60	120	75
5	7	60	60	85
6	10	r.t.	60	90
7	10	40	40	93
8	10	60	25	96
9	15	60	20	97
10	20	60	20	96

Reaction conditions: ^a crotonaldehyde (1 mmol), indole (3.2 mmol); ^b isolate yield.

According to the results shown in Table 2, the best conditions for carrying out this reaction is the use of 10 mg of MNPs-TUD-SO₃H catalyst at temperature 60 °C (Table 2, entry 8). As pointed out in Table 2, in the absence of catalyst (Table 2, entry 1) the reaction was not proceeded, thus, product was not formed. Clearly demonstrated that with respect to the quantity of the catalyst,

significant improvements in reaction performance by increasing the amount of catalyst is not observed (Table 2, entries 9 and 10). Eventually, after obtaining the best conditions of temperature and catalyst, to investigate the effect of solvent the MNPs-TUD-SO₃H catalyst (10 mg) and temperature (60 °C) was kept constant and compared the reaction in solvent-free conditions and in various solvent conditions such as ethanol, acetonitrile, dichloromethane, ethyl acetate and toluene. We realized solvent-free condition is more effectual than solvent conditions for described reaction. With the optimized conditions at hand, we then assess the efficiency and the scope of the MNPs-TUD-SO₃H catalyst in the reaction. Various α,β -unsaturated compounds reacted with 3.2 equivalents of indole to give the corresponding 1,1,3-tri(1*H*-indol-3-yl) alkanes with excellent yields in proper time of reaction under optimized conditions. The influence of different functional groups such as electron-withdrawing and electron-donating were studied and pleased to see that both groups of substituents produced corresponding products in high yield. As specified in Table 3,

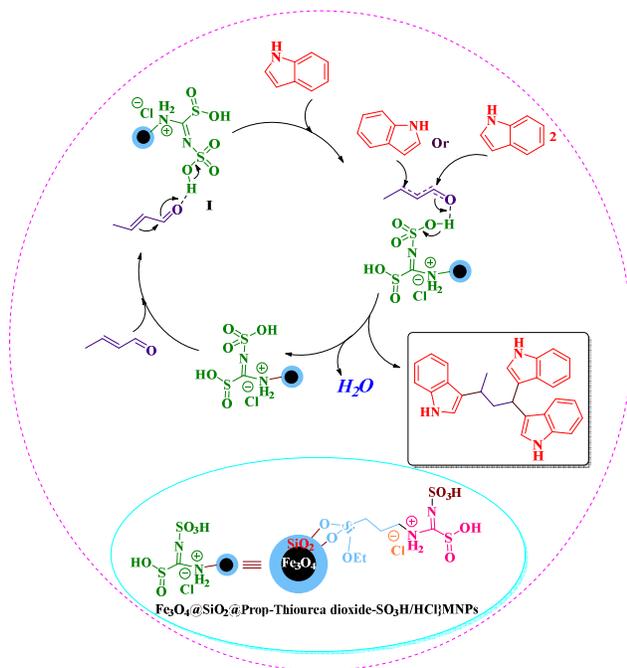
electron donating groups add electron density to the system, therefore increase the rate and decrease the reaction's time, in contrast, electron withdrawing groups with less nucleophilic decrease the rate and hence increase the time of reaction.

Proposed a simple and acceptable mechanism for the synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkanes catalyzed with MNPs-TUD-SO₃H depicted in Scheme 2. According to the reaction pathway in the beginning, the carbonyl group of α,β -unsaturated compound will be activated in the presence of MNPs-TUD-SO₃H catalyst and formed the active intermediate I. Indole easily attacked to this unstable intermediate and the product corresponding provides due to the 1,4- and 1,2-additions. Next step followed by activation of existing intermediate *via* nano magnetic particles MNPs-TUD-SO₃H and a nucleophilic reaction of a third molecule of indole with this intermediate that eventually this catalytic cycle completed by removing a water molecule and the desired product 1,1,3-tri(1*H*-indol-3-yl) alkane was produced at present of the novel nanostructured catalyst.

Table 3. The synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane derivatives using 10 mg of {Fe₃O₄@SiO₂-(CH₂)₃-thiourea dioxide-SO₃H/HCl} as a MNPs-TUD-SO₃H catalyst.^a

Entry	Heteroaryl	α,β -Enal or Enone	Time (min)	Yield ^b (%)	M.p (°C) [Lit] ^{Ref.}
1	Indole	Crotonaldehyde	25	96	115-117[114-116] ^{23a}
2	1-Methylindole	Crotonaldehyde	15	97	109-110[108-112] ^{23a}
3	2-Methylindole	Crotonaldehyde	20	94	186-189[186-189] ^{23a}
4	7-Nitroindole	Crotonaldehyde	60	85	140-141
5	5-Bromoindole	Crotonaldehyde	90	95	143[158-160] ^{23a}
6	2-Methylfuran	Crotonaldehyde	120	89	-
7	Indole	Acrolein	30	97	182-184[180-185] ^{23a}
8	1-Methylindole	Acrolein	20	95	89-91[88-93] ^{23a}
9	2-Methylindole	Acrolein	30	97	159-161[158-159] ^{23a}
10	5-Bromoindole	Acrolein	150	92	170-171[170-174] ^{23a}
11	2-Methylfuran	Acrolein	180	86	-
12	Indole	Trans-2-heptenal	30	91	134-135[136-141] ^{23a}
13	1-Methylindole	Trans-2-heptenal	20	93	127-129[129] ^{23a}
14	Indole	Trans-2-hexenal	30	90	127-128[129-133] ^{23a}
15	1-Methylindole	Trans-2-hexenal	20	92	129-131[129-131] ^{23a}
16	7-Nitroindole	Trans-2-hexenal	75	88	129

Reaction conditions: ^a α,β -unsaturated (1 mmol), indole (3.2 mmol), ^bisolate yield.



Scheme 2. The probable mechanism for the synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane derivatives catalyzed by $\text{Fe}_3\text{O}_4@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}$ as a MNPs-TUD- SO_3H catalyst.

The goal of this protocol that was pointing out the effects of combined of solid Brønsted acid catalyst supported on nanostructure materials with inherent magnetic property for the expansion of new eco-friendly and care about the environment. The combined had synergistic effects the noteworthy point that we noticed.

As previously mentioned, magnetic nanoparticles (MNPs) have many benefits such as small size, good chemical stability and above all else, ease in separation and purification using an external magnet. Coating the surface of the magnetic nanoparticles with an inert silica layer the magnetic dipole attraction will be decreased. Then, the suitable deposition of (3-chloropropyl) triethoxysilane seated onto Fe_3O_4 silica coated surface that can react with a variety of diverse compounds. Thiourea dioxide serves as a linker. Meaning that, on the one side, thiourea dioxide attack to propyl chloride pending group leads to eliminate of chloride (in the third stage of the synthesis of catalyst), that causes anchored TUD on the silica surface. On the other hand, attack to chlorosulfonic acid leads to addition of sulfonic acid tags to the pending thiourea dioxide moieties of catalyst (in the fourth stage of the synthesis of catalyst). According to the reaction mechanism, The reaction proceeds due to

acidic hydrogen react with reactive sites in the components and thiourea dioxide acts only as linker between propyl group and sulfonic acid tag.

To examine this matter, the reaction between crotonaldehyde and indole was considered under the same reaction condition in the presence of 10 mol% thiourea dioxide as a catalyst. The corresponding 1,1,3-tri(1*H*-indol-3-yl) alkane was synthesized in 40% yield at 4h (Scheme 3). The obtained results confirmed that the acidic protons play the major role of catalyst in the reaction and the progress of the reaction.



Scheme 3. Synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane in the presence of Thiourea dioxide (TUD) as a catalyst.

To prove the recycle and reusability of MNPs-TUD- SO_3H as a catalyst after collecting and separating from the reaction mixture by using of external magnet was examined *via* reaction of crotonaldehyde with indole under optimized conditions for several runs. It was found that the recycled catalyst could be reused five times without any appreciable loss in the catalytic activity. The results are presented in Fig. 7.

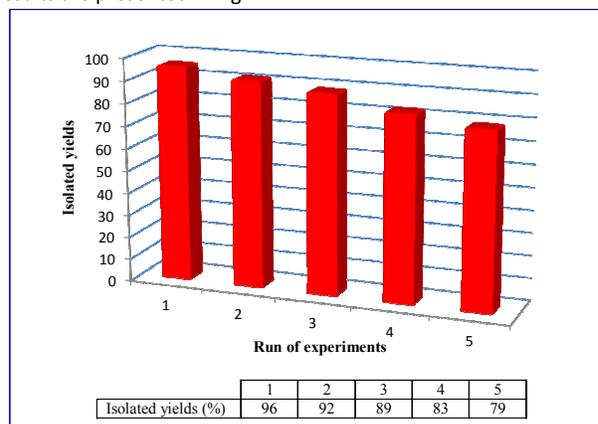


Fig. 7. Recycle and reusability of the $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ in the synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane in 25 minutes.

Actually, when the number of step recycling process of catalyst increased, the loss of some of the performances is observed. The occurrence has a result of washed off a percentage of the catalyst during the product separation and therefore reaction time was slightly increased and an isolated yield of obtained product was decreased. Really, decreasing in yields and increasing of the reaction times is due to the pouring and decreasing of molar ratio of catalyst in the course of reaction work-up in any recovery cycle. Also, the structure of reused $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ was confident *via* IR spectrum, XRD pattern and elemental analysis after its application in the reaction. The results of these spectra indicate a high congruence with the spectra of fresh catalyst, and is confirmed on the stability of the catalyst during the reaction. (Fig. 8, Fig. 9 and Table 4 respectively)

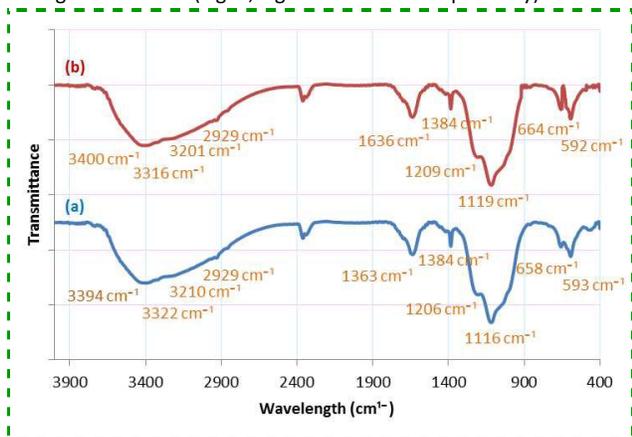


Fig. 8. The IR spectrum of recycled (a) and fresh (b) of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst.

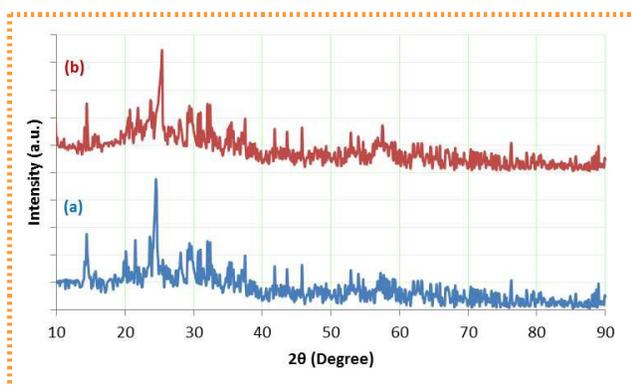


Fig. 9. The XRD pattern of recycled (a) and fresh (b) of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst.

Table 4. The elemental analysis (CHNS) to fresh and recycled of $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as a MNPs catalyst.

Weight %	Fresh MNPs	Recycled MNPs
Nitrogen	4.01	3.82
Carbon	18.98	19.15

Hydrogen	3.80	3.57
Sulfur	11.51	11.76

To compare the efficiency of the MNPs catalyst with some reported catalysts for the synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkanes derivatives, we have introduced the results of these catalysts to attain the condensation of crotonaldehyde and indole in Table 5. As can be seen, the MNPs catalyst has inordinately improved the synthesis of products in different terms (reaction time, yield and the amount of catalyst).

Table 5. Comparison of the results in the synthesis of model product in the presence of MNPs catalyst with other studied catalysts

Entr y	Reaction condition	Catalyst loading	Time (hours)	Yield (%)	Ref.
1	MNPs, Solvent-free, 60 °C	10 mg	0.41	96	This work
2	Yb(OTf) ₃ , CH ₃ CN, 13 kbr	32 mg	168	6	26c
3	Zr(OTf) ₄ , EtOH/H ₂ O, r.t.	5 mol%	72	87	26b
4	Cerium Ammonium Nitrate (CAN), DMSO/H ₂ O, r.t.	10 mol%	1	99	26e
5	I ₂ , Et ₂ O, r.t.	50 mol%	1	99	26e
6	AuCl ₃ , CH ₃ CN, Ar, r.t.	1 mol%	12	70	23f
7	SbCl ₅ , CH ₃ CN, r.t.	10 mol%	3	94	26g
8	AlCl ₃ , CH ₃ CN, r.t.	10 mol%	0.13	96	26a
9	Modified silica sulfuric acid (MSSA), CH ₃ CN, r.t./ reflux (R)-(-)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate, CH ₂ Cl ₂ , r.t.	200 mg	12/0.58	92/96	26h
10					

Conclusion

In conclusion, a novel, green and mild thiourea dioxide functioned by chlorosulfonic acid on the surface of silica-coated magnetic nanoparticles $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ was designed, synthesized and fully characterized by FT-IR, EDX, XRD, TG, SEM, TEM, AFM and UV/Vis analysis. Catalytic activity of MNPs-TUD-SO₃H as a recyclable and remarkable catalyst was studied in the synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane derivatives. Condensation of crotonaldehyde and indole at 60 °C and under solvent-free conditions lead to the formation of the corresponding product. Eco-friendly, general, easy purification of the catalyst, high yield, short reaction time and easy work-up are including the salient and attractive features of this research.

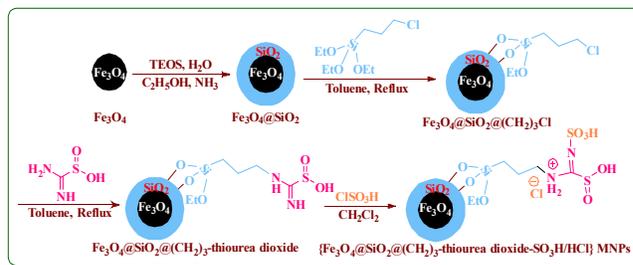
Experimental

General procedure for preparation of nano ionic liquid catalyst based thiourea dioxide functionalized by chlorosulfonic acid stabilized on the surface of silica-coated magnetic nano particles {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl}

In the beginning, Fe₃O₄ (magnetite phase) was prepared by the addition of 3 mL FeCl₃ (2 M dissolved in 2 M HCl) to 10.33 mL double distilled water continued to drop wise adding 2 mL Na₂SO₃ (1 M) for 3 min in conditions magnetic stirring. Subsequently the solution changes color from red to light yellow, 80 mL of an ammonia solution (0.85 M) were added under severe stirring. After lapse of 15 minutes, the black magnetite precipitate (Fe₃O₄) was washed to pH < 7.5 by distilled water and separated with a magnet.³³ To cover the surface of the iron oxide nanoparticles with a layer of silica, 1 g of Fe₃O₄, 20 mL double distilled water, 80 mL ethanol, 3 mL ammonia solution and 3 mL tetraethylorthosilicate (TEOS) were mixed under reflux to achieved Fe₃O₄-silica coated (Fe₃O₄@SiO₂).³⁴ In the following, 3 g of Fe₃O₄-silica coated (Fe₃O₄@SiO₂) and (3-chloropropyl) triethoxysilane (10 mmol) in 80 mL of dry toluene was refluxed under nitrogen atmosphere for 12 h. Nano particles synthesized (Fe₃O₄@SiO₂@(CH₂)₃Cl) was filtered, washed twice with dry toluene and anhydrous diethyl ether, and dried at 80 °C for 6 h in vacuum. Thereupon, thiourea (10 mmol) dissolved in 50 mL dry toluene added to contain 2 g of Fe₃O₄@SiO₂@(CH₂)₃Cl and the mixture was refluxed for 12 h. Magnetic nanoparticles obtained was filtered, washed and dried in a similar process to make the Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide. Finally, chlorosulfonic acid (10 mmol) was added drop wise to the vessel containing a mixture of 2 g of magnetic nanoparticles {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide} in dry dichloromethane and the mixture was stirred for 6 h. After performing the steps of filtering, washing and drying, the thiourea dioxide-based ionic liquid-stabilized on silica coated Fe₃O₄ magnetic nano particles {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl} as a MNPs-TUD-SO₃H catalyst was attained. Overarching theme preparing the MNPs-TUD-SO₃H catalyst illustrated in Scheme 3.

General procedure for the synthesis of 1,1,3-tri(1H-indol-3-yl)alkane derivatives.

A mixture of crotonaldehyde (1 mmol, 0.070 g), indole (3.2 mmol, 0.374 g) and MNPs-TUD-SO₃H (10 mg) was stirred magnetically under solvent-free conditions at 60 °C for the required period of time as showed in Table 3. Upon completion of the reaction, as indicated by TLC, the catalyst easily separated magnetically by using an external magnet to be reused in subsequent reactions. Purification of the corresponding product was carried out by column chromatography over silica gel (70-230 Mesh) that using *n*-hexane-ethyl acetate (8:2) as eluent. To ensure the formation of the desired products, physical data obtained was compared with those reported known compounds.



Scheme 3. The synthesis of thiourea dioxide functionalized by chlorosulfonic acid on the surface of silica-coated magnetic nano particles {Fe₃O₄@SiO₂@(CH₂)₃-thiourea dioxide-SO₃H/HCl}.

Spectral data analysis of compounds

3-(1,3-bis(7-nitro-1H-indol-3-yl)butyl)-7-nitro-1H-indole (Table 3, entry 4): Orange solid; M.p. 140-141 °C; Yield: 85%; IR(KBr, Cm⁻¹): 3438, 3089, 2925, 1630, 1556, 1513, 1481, 1320, 1222, 1089, 806, 733, 538; ¹H NMR (300 MHz, DMSO-d₆): δ (ppm) 1.37 (d, J = 6.2 Hz, 3H), 2.55 (m, 1H), 2.75 (m, 1H), 2.96 (m, 1H), 3.40 (s, 2H), 4.58 (t, J = 6.9 Hz, 1H), 7.01 (q, J = 8.3 Hz, 2H), 7.31 (s, 1H), 7.59 (m, 3H), 7.90 (d, J = 7.6 Hz, 2H), 8.00 (t, J = 8.0 Hz, 3H), 11.71 (d, J = 15.8 Hz, 2H); ¹³C NMR (DMSO-d₆): δ (ppm) 21.7, 28.2, 30.9, 42.4, 117.8, 118.0, 118.4, 119.9, 122.2, 124.7, 125.7, 125.9, 127.2, 127.5, 128.6, 128.7, 128.8, 130.7, 130.8, 130.9, 132.4; MS (EI): m/z 538 (1.9%, M⁺), 335 (76.4), 289 (18.2), 190 (30.0), 167 (28.4), 149 (100), 57 (33.9).

3-(1,3-bis(7-nitro-1H-indol-3-yl)hexyl)-7-nitro-1H-indole (Table 3, entry 16): Orange solid; M.p. 129 °C; Yield: 88%; IR(KBr, Cm⁻¹): 3442, 2925, 1628, 1595, 1384, 1322, 1094, 733, 468; ¹H NMR (300 MHz, DMSO-d₆): δ 0.68 (t, J = 7.2 Hz, 3H), 1.07 (m, 2H), 1.71 (m, 2H), 2.68 (m, 2H), 2.84 (m, 1H), 3.37 (s, 2H), 4.40 (t, J = 8.0 Hz, 1H), 6.99 (m, 2H), 7.26 (s, 1H), 7.45 (d, J = 18.3 Hz, 2H), 7.73 (m, 3H), 7.99 (m, 3H), 11.71 (t, J = 15.6 Hz, 2H); ¹³C NMR (DMSO-d₆): δ (ppm) 13.9, 20.2, 30.9, 33.8, 38.2, 40.9, 117.9, 118.0, 118.4, 119.3, 120.0, 120.6, 125.6, 126.0, 127.3, 127.5, 128.7, 130.7, 130.9, 131.3, 132.3, 132.5; MS (EI): m/z 566 (3.7%, M⁺), 335 (100), 289 (24.1), 218 (74.0), 175 (42.1), 129 (16.8).

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Notes and references

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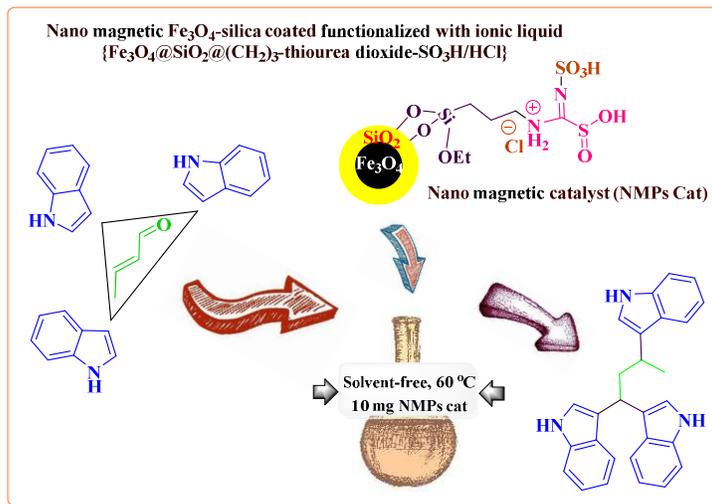
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Graphical Abstract

Synthesis of the first magnetic nano particles with thiourea dioxide-based sulfonic acid tag: Application at the one-pot synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkanes under mild and green conditions



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Synthesis of the first thiourea dioxide-based ionic liquid-stabilized on silica coated Fe_3O_4 magnetic nano particles $\{\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-thiourea dioxide-SO}_3\text{H/HCl}\}$ as an exquisite, extraordinary and effective catalyst for the synthesis of 1,1,3-tri(1*H*-indol-3-yl) alkane derivatives.

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