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Ag/Tio$_2$ Nano Thin Films Catalyzed Efficient Synthesis of 6-Amino-4-Aryl-3-Methyl-1,4-Dihydropyrano[*2,3-C*] Pyrazole-5-Carbonitriles At Green Conditions

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ABSTRACT

Ag/TiO_2 nano thin films was found to be efficient and green heterogeneous catalyst for the synthesis of dihydropyrano[*2,3-c*]pyrazole derivatives via a one-pot three-component reaction between 3-methyl-1*H*-pyrazol-5(4*H*)-one or 3-methyl-1(phenyl)-pyrazol-5(4*H*)-one, aldehydes and malononitrile at room temperature. Ag/TiO_2 and TiO_2 films were prepared by spray pyrolysis technique and the effect of substrate temperature and silver incorporation on optical, morphological and structural properties were investigated by XRD, AFM, spectrophotometry and photoluminescent spectroscopy. The results of this study shows adding of Ag to TiO_2 films increased the optical absorption due to plasmonic behavior of Ag free electrons. XRD analysis was revealed the Hexagonal structure with Anatase phase and 101 prefer crystal orientation which is prefer phase for photocatalyst applications.

Keywords: Ag/TiO_2 nano thin films**,** dihydropyrano[*2,3-c*]pyrazole, 3-methyl-1*H*-pyrazol-5(4*H*)-one, 3-methyl-1(phenyl)-pyrazol-5(4*H*)-one, aldehydes, malononitrile

INTRODUCTION

Titanium dioxide is the most popular and efficient semiconductor photo catalyzer due to its strong oxidative ability of photo generated electron-hole pairs on its surface[1-2]. This efficient photo catalysis has been studied extensively due to many industrial applications. Unfortunately, this semiconductor has limited catalytic efficiency due to its wide energy band gap; it is just sensitive to UV radiation. The energy band gap of bulk TiO_2 is 3 eV and 3.2 eV for rutile and anatase phases,

respectively. TiO_2 as a photo catalysis have been widely studied in anatase and rutile phases. Its photo catalytic activity in anatase phase is more than other phases [3].

In recent years nano-composite thin films, due to their industrial application, have been studied by many researchers [4-7]. Ag/TiO_2 nano particles have been widely used in photo electrochemical and photo catalyst applications. One of the most important problems which decrease the photocatalyst efficiency is electron-hole recombination. It is well experienced that noble metal doping reduces the electron-hole recombination rate and hence increases the photocatalytic efficiency. In this work, Ag/TiO_2 nanocomposite films was deposited on microscope glass slides and also insides of beakers by spray pyrolysis technique and the effect of silver incorporation on optical, crystal structure, surface morphology and recombination rate were characterized and reported.

Combinatorial methods employing multicomponent reactions have recently become the focus of considerable interest because of their swift and convenience of synthesis of various classes of compounds.[8, 9] Multicomponent reactions (MCRs), defined as one-pot reactions in which at least three functional groups are joined via covalent bonds, gradually gain importance in synthetic organic chemistry [8-11].

Nitrogen-containing heterocycles, key element and widespread structural motif in many drugs, are important design feature of medicinal agents in medicinal chemistry [12]. Moreover, they can act as biomimetic and active pharmacophores [13]. Pyrazoles are among the most commonly investigated organic nitrogen- containing heterocycles compounds with 5-membered ring. Pyrazoles have many applications in the field of pharmaceutical industry, and medical chemistry due to their biological activities such as antifungal [14], antiviral [15], anticancer [16], and anti-inflammatory properties [17]. Due to these properties, they are widely utilized in the pharmaceutical industry, medicinal chemistry and they are also important core in natural products [18, 19]. In addition pyrazoles have been used for treatment of type 2 diabetes, obesity, thrombopiotinmimetics and antiangiogenesis because of their kinase inhibitory effects [20]. Furthermore, some pyrazoles are employed in polymer and supramolecular chemistry, in the food industry, and as UV stabilizers and cosmetic colorings and in some cases it was observed that these compounds also have liquid crystal properties [21-25]. Dihydropyrano[*2,3-c*]pyrazoles, are one of the most important pyrazole compounds and they have received considerable attention owing to their biological activity and they have been utilize as a template for medicinal chemistry. They exhibited many biological activities like antimicrobial [26], insecticidal [27], and anti-inflammatory [28]. Moreover, dihydropyrano[*2,3-c*]pyrazoles exhibit molluscicidal activity [29], and has been identified as a screening kit for Chk1 kinase inhibitor [30]. Because of the importance of these compounds, a number of methods have been reported for their synthesis in the presence of various catalysts such as ionic liquids [31,32], organic bases [33-36], amberlyst [37], glycine [38], per-6-amino-b-cyclodextrin [39], and iodine [40].

In recent years, we investigated the synthesis of these compounds in the presence of diverse green catalysts such as trichloroacetic acid, cellulose, L-proline and in green media. [41-45] In continuation of our research on multi-component reactions, [46-49] herein we would like to describe the synthesis of dihydropyrano[*2,3-c*]pyrazole derivatives, our attention was drawn to the of Ag/TiO_2 nano thin films as an effective and highly reusable catalyst and the synthesis of dihydropyrano[*2,3-c*] pyrazole was investigated in the presence of this catalyst.

RESULTS AND DISCUSSIONS

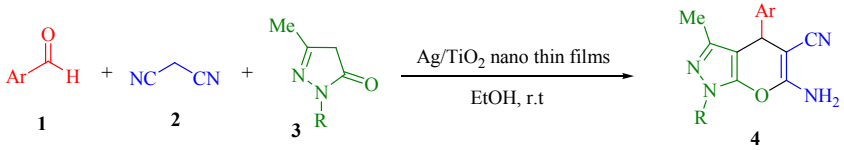
In the opinion of experiment of this new process at first we examined the reaction of aldehydes 1, malononitrile 2 and 3-methyl-1*H*-pyrazol-5(4*H*)-one or 3-methyl-1(phenyl)-pyrazol-5(4*H*)-one **3** in EtOH at room temperature in the proximity of Ag/TiO_2 nano thin films to get the forecasted dihydropyrano[*2,3-c*]pyrazole derivatives. differents temperature and solvent were tested to optimize the reaction position. The results exhibited that the reaction proceeds with good yields when EtOH was used at room temperature. Try again, when we examined the reaction in absence of catalyst, no significant change in the reaction mixture after 48 hours has been seen which showed the catalyst

has good effect on reaction yields. With the optimal conditions in hand, we found the scope of the reaction for the construction of various dihydropyrano[*2,3-c*] pyrazoles.

Finally, we increased the reaction with various aldehydes including both electron withdrawing and electron-donating substituents. The reactions are generally clean, and desired products 4a-r was obtained in good yields. The results are summarized in Table 1.

According to our results, we can propose the reaction mechanism shown in Scheme 2. Initially, Knoevenagel condensation reaction between aldehyde and malononitrile in the presence of catalyst lead to the formation of alkene A. Thereafter, Micheal addition reaction between intermediate A and B lead to intermediate C. Intramolecular cyclization of intermediate C by attack of hydroxyl group to nitrile group in the presence of titanium oxide lead to intermediate E. Finally, imine-enamine tautomerization of E gives desirable product 4.

We also investigated the recycling of the Ag/TiO_2 nano thin films as the catalyst using the model reaction of 3-methyl-1(phenyl)-pyrazol-5(4*H*)-one, malononitrile and 4-methoxybenzaldehyde. When the reaction is done, the crude product was purified by ltration and washed with EtOH (3 × 2 mL) to give the desired products. Then, the vial Ag/TiO_2 nano thin films washed with EtOH and checking the reusability under similar reaction conditions. The results showed that Ag/TiO_2 nano thin films is



1 2 3 4

Scheme 1: Synthesis of dihydropyrano[2,3-c]pyrazole derivatives 4a-r

Table 1: Synthesis of dihydropyrano[2,3-c]pyrazole derivatives 4a-r

Entry	Ar	R	Product	Time (min)	yield (%)[a]	O.b. m.p (°C)	Lit. m.p [°C]
1	C_6H_5	Ph	4a	60	85	166-168	168-170 [43]
2	4-Br-C_6H_4	Ph	4b	40	85	213-215	213-215[43]
3	4-NO_2-C_6H_4	Ph	4c	18	97	170-171	169-171[43]
4	2-Cl-C_6H_4	Ph	4d	20	90	181-183	181-183 [45]
5	4-OH -C_6H_4	Ph	4e	35	70	220-221	219-221[45]
6	2,4-$Cl_2C_6H_3$	Ph	4f	20	90	235-237	235-237 [43]
7	4-OMe-C_6H_4	Ph	4g	35	80	211-213	210-212 [43]
8	2,5-$(CH_3O)_2C_6H_3$	Ph	4h	25	85	209-211	210-212[43]
9	3-OEt,4-OHC_6H_3	Ph	4i	20	80	157-159	158-160 [45]
10	4-Cl-C_6H_4	Ph	4j	30	85	194-195	190-192 [43]
11	3-NO_2-C_6H_4	Ph	4k	22	95	197-199	195-197 [43]
12	biphenyl-4-yl	Ph	4l	25	80	192-194	193-194 [45]
13	naphthyl 2- carbaldehyd	Ph	4m	20	85	197-199	198-200 [45]
14	C_6H_5	H	4n	70	70	166-168	169-170 [43]
15	4-OMe-C_6H_4	H	4o	40	85	176-177	174-175 [44]
16	2-Cl-C_6H_4	H	4p	45	85	142-144	143-145 [45]
17	4-OH -C_6H_4	H	4q	40	75	223-225	224-226 [43]
18	4-Br-C_6H_4	H	4r	20	80	174-176	175-177 [45]

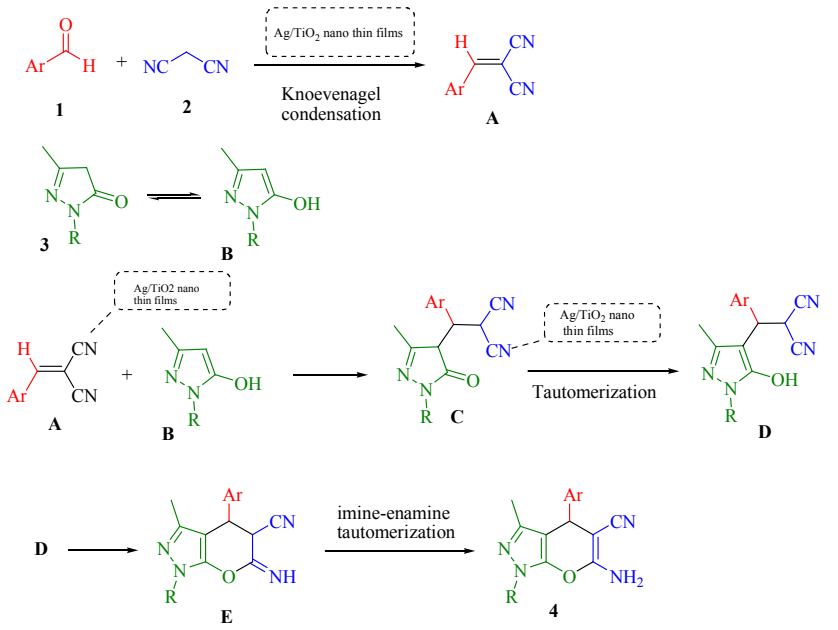
[a] Yields refer to the isolated pure products.

a stable catalyst in reaction media and reused four times without significant loss of its catalytic activity (Fig. 1). Catalyst could be recovered because all eighteen derivatives of dihydropyrano[*2,3-c*]pyrazole were synthesis from only one Ag/TiO_2 nano thin films.

To show the value of the present procedure in comparison with reported results in the other documents, we compared result of Ag/TiO_2 nano thin films with reported catalysts in the synthesis of derivatives of dihydropyrano[*2,3-c*]pyrazole, such as γ-alumina [50], TEAA (triethylammonium acetate) [51], trichloroacetic acid [52], imidazole [53], ceric sulfate [52], ultrasound irradiation [54], nanosized magnesium oxide [55], L-proline [56], H_3PO_4/Al_2O_3 [57], cellulose [58] (Table 2). As it is shown in Table2, Ag/TiO_2 nano thin films remarkably improved the synthesis of 1,4-dihydropyrano[*2,3-c*]- pyrazole in different terms, for example in terms of reaction conditions.

Experimental

All reagents were purchased from Merck and Sigma-Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison physical data with authentic samples and spectroscopic data (IR and NMR). The NMR spectra were recorded on a Bruker Avance DRX 300 MHz instrument. IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer and Avance, respectively.



Scheme 2: Proposed mechanism for the synthesis of dihydropyrano[2,3-c]pyrazole

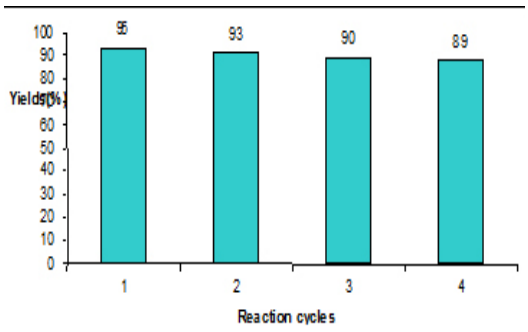


Fig. 1: The recycling of the Ag/TiO_2 nano thin films as catalyst

General procedure for the synthesis of 3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile derivatives

To a magnetic stirred solution of aromatic aldehydes 1 (1.0 mmol), malononitrile 2 (1.0 mmol) and 3-methylpyrazol-5(4*H*)-one 3 (1.0 mmol) in EtOH (2 mL) Ag/TiO_2 nano thin films was added at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the crude solid product was filtered for separation of product and washed with EtOH (3×2 mL) to give the pure product. All of the products are known.

Table 2: Comparison the result of Ag/TiO_2 nano thin films with other catalysts reported in the literature for preparation of 6-amino-4-aryl-3-methyl-1,4-dihydropyrano [*2,3-c*]pyrazole-5-carbonitriles

Entry	Catalyst	Conditions	Time(min)	Isolated Yield (%)a
1	γ-Alumina (15mol%)	H2O, 100°C	50	80
2	(TEAA) ionic liquid (40 mol %)	r.t	20	97
3	Trichloroaceticacid (10 mol %)	Solvent free,100 °C	5	85
4	Imidazole (50 mol%)	H_2O, 80°C	20	89
5	$Ce(SO_4)_2$ (10 mol %)	Solvent free,100 °C	5	80
6	Ultrasound irradiation	H2O, 50 °C	30	92
7	Nanosized MgO (62 mol %)	Acetonitrile, r.t	10	96
8	L-proline (5mol%)	EtOH, reflux	10	87
9	L-proline (5mol%)	H_2O, reflux	10	90
10	H_3PO_4/Al_2O_3 (0.08 mol %)	Solvent free,100 ºC	7	97
11	Cellulose	Solvent free,100 °C	10	96
12	Ag/TiO_2 nano thin films	EtOH, rt	18	97

Selected spectroscopic data of some products are given below:

6-amino-1,4-dihydro-3-methyl-4-(2,4-dichlorophenyl)-1-phenylpyrano[*2,3-c*]pyrazole-5-carbonitrile (4f): IR (KBr, cm^{-1}): 3458, 3325, 2198, 1660; ^1H NMR(400 MHz, (DMSO-d_6): δ = 1.77 (s, 3H, CH_3), 5.15 (s, 1H, CH), 7.32-7.43 (m, 5H, NH_2 and ArH), 7.47-7.51 (m, 2H, ArH), 7.61 (s, 1H, Ar H), 7.77 (d, 2H, *J*=8.0 Hz, ArH).

6-amino-1,4-dihydro-3-methyl-4-(4-methoxyphenyl)-1-phenylpyrano[*2,3-c*]pyrazole-5-carbonitrile (4g): IR (KBr, cm^{-1}): 3392, 2933, 2197, 1663; ^1H NMR(400 MHz, (DMSO-d_6): δ = 1.80 (s, 3H, CH_3), 3.64 (s, 3H, OCH_3), 4.64 (s, 1H, CH), 6.92 (d, *J*= 8.0 Hz, 2H,Ar), 7.19 (br, 2H, NH_2), 7.20 (d, *J*= 8.0 Hz, 2H, Ar), 7.33 (t, *J*= 8.0 Hz,1H, Ar), 7.50 (t, *J*= 8.0 Hz, 2H, Ar), 7.80 (d, *J*= 8.0 Hz, 2H, Ar).

6-amino-1,4-dihydro-3-methyl-4-(3-ethoxy-4-hydroxyphenyl)-1-phenylpyrano[*2,3-c*]pyrazole-5-carbonitrile (4i): IR (KBr, cm^{-1}): 3420, 3329, 2195, 1653; ^1H NMR (400 MHz, (DMSO-d_6): δ = 1.29-1.32 (t, 3H, *J*=7.2 HzCH_3), 1.84 (s, 3H, CH_3), 3.95-4.01 (q, 2H, *J*=7.2 Hz CH_2), 4.59 (s, 1H, CH), 6.62-7.80 (m, NH_2 and Ar), 8.86 (s, 1H,OH).

6-amino-1,4-dihydro-3-methyl-4-(biphenyl-4-yl)-1-phenylpyrano[*2,3-c*]pyrazole-5-carbonitrile (4l): IR (KBr, cm^{-1}): 3471, 3328, 2185, 1645; ^1H NMR (400 MHz, (DMSO-d_6): δ = 1.76 (s, 3H, CH_3), 4.87 (s, 1H, CH), 7.30-7.94 (m, NH_2 and Ar)

6-amino-1,4-dihydro-3-methyl-4-(naphthalen-2-yl)-1-phenylpyrano[*2,3-c*]pyrazole-5-carbonitrile (4m): IR (KBr, cm^{-1}): 3390, 3200, 2180, 1655; ^1H NMR (400 MHz, (DMSO-d_6): δ = 1.76 (s, 3H, CH_3), 4.88 (s, 1H, CH), 7.29 (br, 2H, NH_2), 7.33-7.96 (m, 12H, Ar).

6-amino-1,4-dihydro-3-methyl-4-(4-methoxyphenyl)pyrano[*2,3-c*]pyrazole-5-carbonitrile (4o): IR (KBr, cm^{-1}): 3455, 3320, 2190, 1654; ^1H NMR(300 MHz, (DMSO-d_6): δ = 1.79 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 4.55 (s, 1H, CH), 6.85 (br, 2H, NH_2), 6.88 (d, J= 9.0 Hz, 2H, Ar), 7.07 (d, *J*=9.0 Hz, 2H, Ar), 12.03 (s, 1H, NH).

6-amino-1,4-dihydro-3-methyl-4-(2-chlorophenyl)pyrano[*2,3-c*]pyrazole-5-carbonitrile (4p): IR (KBr, cm^{-1}): 3470, 3240, 2180, 1638; ^1H NMR (300 MHz, (DMSO-d6): δ = 1.77 (s, 3H, CH_3), 5.08 (s, 1H, CH), 6.99 (br, 2H, NH_2), 7.18-7.43 (m, 4H, Ar), 12.16 (s, 1H, NH).

CONCLUSION

In this research, we used Ag/TiO_2 nano thin films for first time as a catalyst for the Synthesis of dihydropyrano[*2,3-c*]pyrazole derivatives. The efficient features of this protocol are simple

performing reaction, cleaner reaction, use of green and reusable nano catalyst. Satisfactory yields of products, as well as a simple isolation and reduced reaction times of the products make it a useful protocol for the green synthesis.

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