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Titanium dioxide nanowires as green and heterogeneous catalysts for the synthesis of novel pyranocoumarins

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ABSTRACT

Titanium dioxide nanowires were employed as novel, recyclable and safe catalysts in a one-pot three-component condensation of aldehydes, malononitrile, and 4-hydroxycoumarin to produce new and known pyrano[2,3-*c*]chromenes as potent biologically active compounds. A possible catalytic mechanism was also proposed based on the interaction of reactants with TiO_2 nanowires. This expedient new route has advantages, such as the use of a safe and reusable catalyst, simple operation, short reaction times and good to excellent yields.

1. Introduction

Nowadays, almost all the devices and technologies are becoming smaller and smaller in size, with improved properties. Among the developments, catalytic technology is an important field. Enhancing the contact between the reactants and catalyst was dramatically observed with the use of nanocatalysts, since the nanoscale increases the exposed surface area of the active component of the catalyst [1–3]. Among nanomaterials, titanium dioxide (TiO_2) is a biocompatible and environmentally benign catalyst. TiO_2 nanomaterials, including nanoparticles, nanorods, nanowires, and nanotubes, are widely investigated for various applications in photocatalysis, photovoltaics, batteries, smart surface coatings, photonic crystals, sensors, ultraviolet blockers, pigment, and paints [4]. Synthetically, multi-component reactions (MCRs) have emerged as useful methods because the combination of three components to generate new products in a single step is extremely economical [5]. Besides, in medicine, pyranocoumarins are well recognized due to their importance in biological and pharmaceutical researches [6]. Several methods have been reported for the synthesis of pyrano[2,3-*c*]coumarin as biologically active compounds. In general, pyrano[2,3-*c*]coumarin derivatives are accessible via the one-pot three-component reaction of hydroxycoumarins, carbonyl compounds and active methylenes in the presence of basic catalysts [7] In recent studies, the synthesis of pyrano[2,3-*c*]chromenes via a three-component reaction has been described using various reagents, such as sodium dodecyl sulfate (SDS) [8], $H_6P_2W_{18}O_{62}{\cdot}18H_2O$ [9], hexamethylenetetramine [10] magnesium oxide (MgO) [11], diammonium hydrogen phosphate (DAHP), (*S*)-proline [12], KF–Al_2O_3 [13], tetrabutylammonium bromide (TBAB) [14], and triethylbenzylammonium chloride (TEBA) [15]. However, some of these mentioned reports suffer from drawbacks, such as long reaction times, low product yields, harsh reaction conditions, and the use of excessive amounts of catalyst. In this work, a new methodology to obtain novel and known pyrano[2,3-*c*]chromene under ultrasound irradiation, via a one-pot three-component condensation, is reported. In this paper, we introduce a new application of

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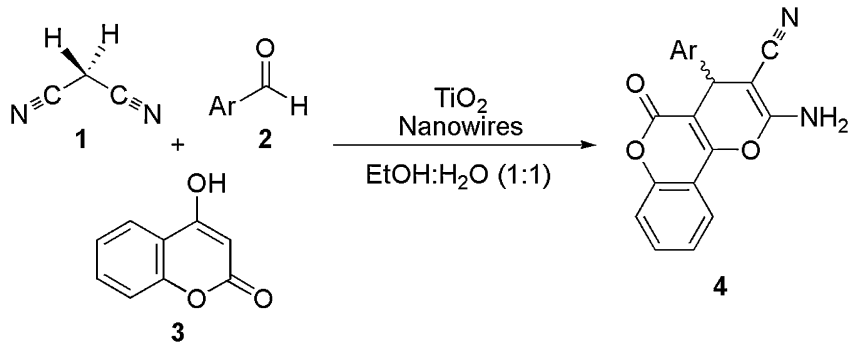

Scheme 1. Synthesis of pyrano[2,3-*c*]coumarins using TiO_2 NWs.

titanium dioxide nanowires as a novel and safe catalyst for the synthesis of novel and known pyranocoumarin derivatives.

2. Experimental

2.1. General procedure for preparation of TiO_2 nanowires

In a typical synthesis, 0.115 g of commercial Degussa P25 powder was mixed with 3.5 mL of 10 M NaOH and 3.5 mL of ethanol. The mixed solution was then transferred into a 35 mL Teflon-lined stainless-steel autoclave. The autoclave was maintained at 180 °C under autogenous pressure for 24 h and then cooled to room temperature naturally. The sample so obtained was filtered off, washed several times with a dilute HCl aqueous solution and water until the pH value of the washing solution was about 7. The TiO_2 nanowires so obtained have diameters in the 60–150 nm range and are a few microns in length [16,17].

2.2. General procedure for the synthesis of pyrano[2,3-*c*]coumarin

Malononitrile (**1**) (1.1 mmol), aromatic aldehyde **2** (1 mmol), 4-hydroxycoumarin (**3**) (1 mmol), and TiO_2 NWs (0.03 mmol) were added to a 10-mL mixture EtOH/H_2O (50/50) in a 25-mL pyrex flask and refluxed for an appropriate time (Table 2). The reaction progress was controlled by thin layer chromatography (TLC) using hexane/EtOAc (1:1). After completion of the reaction, the solvent was removed under vacuum, the crude products **4** were obtained after recrystalization from EtOH.

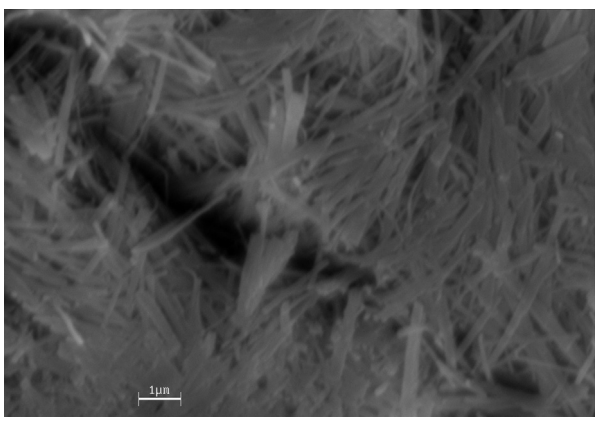

Fig. 1. SEM image of TiO_2 nanowire.

2.3. Spectral data of some compounds

2.3.1. Compound (**4i**)

IR (KBr): 3396, 3321, 3195, 2202, 1706, 1671, 1607, 1381, 1053 cm^{-1}. ^1H NMR (DMSO, 400 MHz): δ 7.90 (dd, 1H, J = 7.8, 1.2 Hz), 7.75–7.70 (m, 1H), 7.52–7.43 (m, 6H), 7.30–7.28 (m, 2H), 4.50 (s, 1H) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 159.55, 157.94, 153.70, 152.18, 146.02, 132.99, 130.69, 130.39, 130.05, 126.94, 124.65, 122.54, 121.68, 119.05, 116.57, 112.98, 103.15, 57.31, 36.59. Anal. Calcd. for $C_{19}H_{11}BrN_2O_3$: C, 57.74; H, 2.81; N, 7.09%. Found: C, 58.05; H, 2.68; N, 7.16%.

2.3.2. Compound (**4j**)

IR (KBr): 3408, 3280, 3175, 2203, 1705, 1674, 1602, 1381, 1055 cm^{-1}. ^1H NMR (DMSO, 400 MHz): δ 7.90 (dd, 1H, J = 7.8, 1.2 Hz), 7.76–7.72 (m, 1H), 7.55–7.48 (m, 4H), 7.55–7.19 (m, 3H), 5.19 (d, 1H, J = 1.6 Hz). ^{13}C NMR (DMSO, 100 MHz): δ 159.38, 158.77, 152.11, 133.18, 133.09, 129.93, 129.83, 124.84, 124.70, 124.66, 122.29, 118.73, 116.68, 115.25, 112.56, 38.83 ppm. Anal. Calcd. for $C_{19}H_{10}ClFN_2O_3$: C, 61.89; H, 2.73; N, 7.60%. Found: C, 61.90; H, 2.55; N, 7.72%.

2.3.3. Compound (**4k**)

IR (KBr): 3391, 3180, 2196, 1712, 1674, 1608, 1381, 1240, 1054 cm^{-1}. ^1H NMR (DMSO, 400 MHz): δ 7.90 (dd,

Table 1
Effect of solvent and catalyst on the synthesis of **4a** under refluxing conditions (90 °C); reaction time: 60 min.

Entry	Catalyst (mol%)	Solvent	Yield (%)
1	5	CH_2Cl_2	50
2	5	CH_3Cl	50
3	5	EtOH	85
4	5	MeOH	85
5	5	H_2O	65
6	–	H_2O/EtOH	Trace
7	1	H_2O/EtOH	50
8	3	H_2O/EtOH	90
9	5	H_2O/EtOH	90
10	10	H_2O/EtOH	85