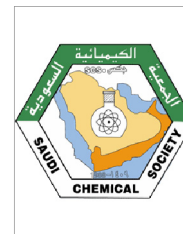




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ORIGINAL ARTICLE

The combined role of heterogeneous catalysis and ultrasonic waves on the facile synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones

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KEYWORDS

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Abstract Pt–MWCNTs nanocomposites are found to be an excellent and efficient catalyst to promote one-pot and three-component coupling reaction of isatoic anhydride, aldehyde and ammonium acetate or primary aromatic amine to produce 2,3-dihydroquinazolin-4(1*H*)-one derivatives under ultrasound irradiation. This novel method has the advantages such as short reaction times, convenient manipulation, excellent yields and the use of effective catalyst.

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1. Introduction

Since the first multi-component reaction was reported in 1850 by Strecker [1], this methodology has emerged as an especially attractive synthetic strategy for rapid and efficient synthesis. Since the products are formed in a single synthetic operation, the structural diversity can be achieved simply by varying the reaction components which shows high atom economy and high selectivity [2,3]. 2,3-Dihydro-4(1*H*)-quinazolinones are important bicyclic heterocycles which have emerged as versatile biologically active compounds possessing applications as diuretic [4], antitumor [5], antibacterial [6], anticonvulsant [7]

and antihypertensive agents [8]. In addition, these compounds can easily be oxidized to their quinazolin-4(3*H*)-one analogues [9–11], which also are important pharmacologically active compounds [12–17]. Due to the significant interest in 2,3-dihydro-4(1*H*)-quinazolinones, several synthetic protocols have been developed for these heterocyclic compounds. The usual procedure involves one pot three-component reaction of isatoic anhydride, aldehydes and amines to synthesize 2,3-dihydro-4(1*H*)-quinazolinones. The reported catalysts for this one-pot procedure are included montmorillonite K-10 [18,19], silica sulfuric acid (SSA) [20,21], zinc(II) perfluorooctanoate [Zn(PFO)₂] [22], MCM-41-SO₃H [23], *p*-toluenesulfonic acid-paraformaldehyde copolymer (copolymer-PTSA) [24], Amberlyst-15 [25], gallium(III) triflate (Ga(OTf)₃) [26], KAl(SO₄)₂·12H₂O (alum) [27], molecular iodine (I₂) [28–30], *p*-toluenesulfonic acid (*p*-TsOH) [31], aluminium tris(dihydrogen phosphate) (Al(H₂PO₄)₃) [32], silica-bonded *N*-propyl-sulfamic acid (SBNPSA) [33], acetic acid [34], SiO₂–FeCl₃ [35], SnCl₂ [36], ceric ammonium nitrate (CAN) [37], ionic liquids [38–40], silica-bonded S-sulfonic acid [41] and Al/Al₂O₃ and Fe₃O₄ nanoparticles [42,43]. However, some reported

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methods have certain disadvantages such as tedious work-up, high reaction temperature and low yields. Therefore, development of a simple and efficient procedure is an important goal in the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones.

On the other hand, transition metal nanoparticles as exclusive materials have wide application in the homogeneous and heterogeneous catalysts. Among metal nanoparticles, Pt nanoparticles (NPs) have attracted significant attention due to their high catalytic activity [44]. It is well known that the specific electrocatalytic activity of platinum nanoparticles is strongly related to the size and dispersion of the particles, the supporting materials, preparation methods and their surface conditions. Highly distributed nanoscale Pt particles with nanometer size particles and narrow size distribution are ideal for high electrocatalytic activity owing to their large surface-to-volume ratio [45–53]. In fact, the choice of a suitable supporting material is an important aspect that may affect the performance of supported electrocatalysts due to interactions and surface reactivity [54,55]. Many researchers have demonstrated that, multi-walled carbon nanotubes (MWCNTs) are attractive supporting materials among the possible supports for Pt NPs catalyst, which can support a high dispersion of Pt nanoparticles owing to their particular morphology and large surface area [56–58]. As a result, several research papers reported that Pt NPs supported on CNTs increase the electrocatalytic activity [59,60] and also electrochemical stability [61,62]. In fact, Pt nanoparticles on the external walls contact easily with the reactant. Accordingly, various approaches have been devised to load platinum nanoparticles onto the surface of CNTs with a high specific surface area, superior catalytic activity and lower catalyst loading. These include wet chemical impregnation [63–65], electrode position [51,66–68], colloidal methods [58,69,70] and ion exchange [71,72].

Ultrasonic irradiation has been introduced as an eco-environmental technology in green chemistry to improve a large number of organic reactions [73,74]. Ultrasonic energy provides an unusual mechanism to generate high-energy chemistry owing to the extraordinary temperature and pressure generated by the cavitation bubble collapse [75]. The ‘hot-spot’ theory suggests that temperatures up to 5000 K and pressures up to 1000 bar are produced during this collapse [76–78]. The vibration movement of the ultrasonic waves causes growth of cavitation bubbles through the diffusion of solute vapor in the volume of these bubbles. After the growth process, the bubble collapse breaks the chemical bonds of the solute molecules [79]. Moreover, collapsed bubbles can carry smaller particles causing shocks among them and possibly causing surface amorphization which may result in their sintering [80].

To our knowledge, no studies have been reported on the preparation of quinazolinones using ultrasonic energy in the presence of Pt–MWCNTs nanocomposites. Herein, we have developed a novel methodology to prepare 2,3-dihydroquinazolin-4(1*H*)-ones by employing isatoic anhydride, aldehydes and ammonium acetate or primary aromatic amines using Pt–MWCNTs as an efficient catalyst under sonication conditions (Scheme 1).

2. Experimental

All materials were from commercial reagent grade and were used as received. MWCNTs were purchased from Nanotech

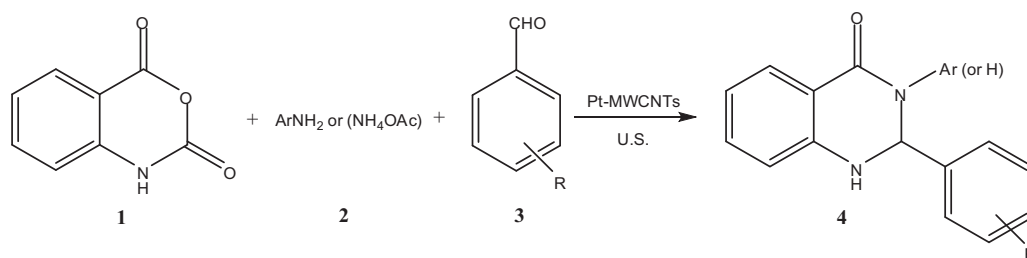
Port Co. (Taiwan). These MWCNTs were produced via the chemical vapor deposition (CVD) method. The outer diameter of MWCNTs was between 10 and 20 nm. Melting points were obtained in open capillary tubes and were measured on an Electrothermal MK3 apparatus and were uncorrected. ^1H NMR and ^{13}C NMR spectra were measured with a Bruker DRX-400 spectrometer using tetramethylsilane (TMS) as an internal standard and DMSO- d_6 as the solvent at room temperature. Chemical shifts (δ) are reported in ppm downfield from TMS and coupling constant (J) values are given in Hz. FT-IR spectra were determined on a Perkin Elmer FT-IR 550 spectrophotometer using the pressed KBr. The progress of the reactions was monitored by thin-layer chromatography (TLC), which was visualized with UV light. The UV spectra were recorded on a UV–Vis Varian Perkin–Elmer UV 550-S spectrophotometer in chloroform. X-ray powder diffraction (XRD) experiment was carried out in a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK α , radiation, $\lambda = 0.154056$ nm), at a scanning speed of $2^\circ/\text{min}$ from 10° to 100° (2θ). The prepared Pt–MWCNTs nanocomposites were also characterized by a TESCAN model VEGA II scanning electron microscope (SEM) operated at a 15 kV accelerating voltage. The Raman spectra were measured on a Bruker SENTERRA spectrometer with spectral range: $200\text{--}3500\text{ cm}^{-1}$ and Laser wavenumber 785 nm. Products were characterized by comparison of their physical and spectral data with those of authentic samples.

2.1. Synthesis of nanocatalyst

Pt–MWCNTs were prepared according to mentioned procedure in literature [81]. Briefly, the MWCNTs were purified in 2.5 M HNO_3 and 0.5 M H_2SO_4 at 60°C under sonication for 6 h. Then, modified MWCNTs were washed with distilled water to neutral pH and were dried in air at 100°C for 1 h. Then, the modified MWCNTs were added to 0.004 M PtCl_4 aqueous solution and the suspension was sonicated at room temperature for 30 min with the pH value of the solution adjusted to 8–10 by adding NaOH solution. An excess of NaBH_4 was added as reductant to reduce Pt. Then, the pH was maintained above 7. The reaction mixture was sonicated for 10 min and then was left to stand at room temperature for 24 h. Next, the product was filtered and was washed with distilled water and was dried in air at room temperature (Fig. 1).

2.2. General procedure for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones under ultrasound irradiation

Pt–MWCNTs (0.04 g) were added to a mixture of isatoic anhydride (1.00 mmol, 0.13 g), aniline (1.20 mmol) or ammonium acetate (1.10 mmol) and aromatic aldehyde (1.00 mmol) in ethanol (5.00 mL). Then, the reaction mixture was irradiated in a ultrasound bath at temperature of 60°C for appropriate time. After completion of the reaction as indicated by TLC (petroleum ether–EtOAc, 7:3), the reaction mixture was cooled to room temperature, was diluted with hot ethanol and the solid catalyst was separated by filtration. H_2O (5.00 mL) was added and the precipitated product was filtered and was recrystallized from ethanol.



Scheme 1 Ultrasonic activated synthesis of quinazolinone derivatives via multi-component reaction promoted by Pt-MWCNTs nanocomposites.

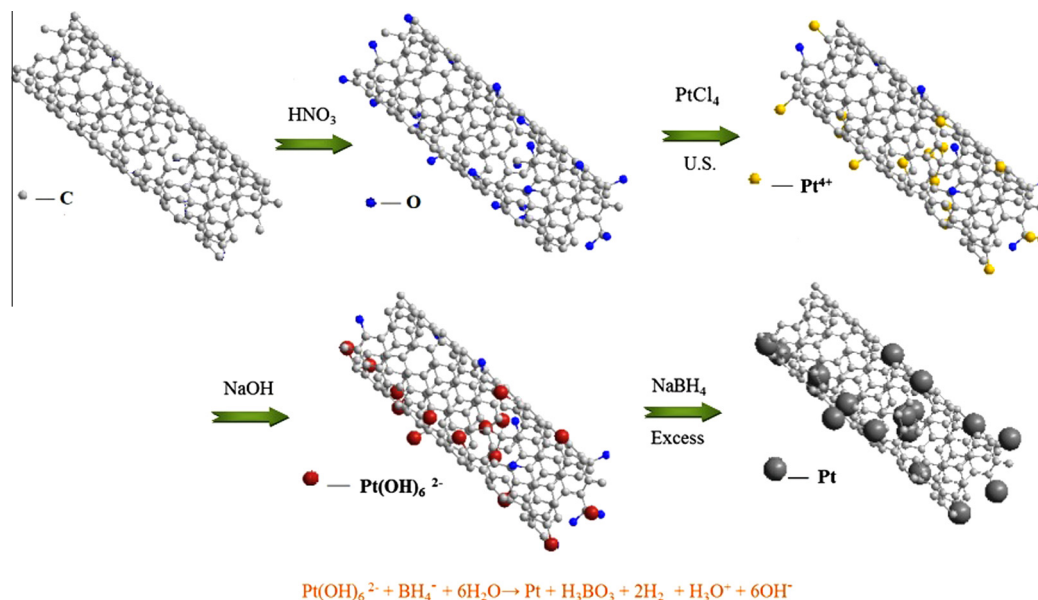


Figure 1 Schematic illustration for the generation of Pt NPs supported on MWCNTs.

3. Results and discussion

In the present study, we report a green and valid procedure for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones via one-pot condensation of isatoic anhydride and aromatic aldehydes with NH_4OAc or aromatic primary amines in the presence of Pt-MWCNTs as a heterogeneous catalyst under ultrasound irradiation (Scheme 1). The choice of appropriate reaction conditions is important for a successful synthesis. To study the effect of catalyst on the condensation, the one-pot reaction of isatoic anhydride and benzaldehyde with aniline was chosen as a model reaction under ultrasonic irradiation. As shown in Table 1, Pt-MWCNTs were appropriate to catalyze this reaction and a significant improvement was observed in the yield of quinazolinones in the presence of 0.04 g Pt-MWCNTs. Increase in the amount of catalyst did not improve the yield significantly (Table 1, entry 6). In order to improve the yields, we performed reactions using different quantities of reagents. The optimized reactant ratios were found to be 1: 1.2: 1.1: 1 of isatoic anhydride, aniline or ammonium acetate and benzaldehyde in the presence of 0.04 g Pt-MWCNTs at 60 °C for 8 min. In order to investigate the scope and efficiency of this reaction and to study the effect of substituents on the product formation, we applied the optimal protocol for variety of

amines and aldehydes with isatoic anhydride. It is noteworthy that the reaction proceeds efficiently to furnish the corresponding 2,3-dihydroquinazolin-4(1*H*)-ones in excellent yields. It was observed this method had good tolerance for various substitutions. The results are presented in Table 2. It should be noted that the effect of electronic nature and position of substituent on the phenyl rings did not show strong influence on the reaction and the products were obtained in high yields in short reaction times. In our continued study, it was also found that the reaction times are longer and the yields are lower in the absence of ultrasonic irradiation. The results of these reactions are compared under ultrasound irradiation and in an oil

Table 1 Optimization of amount of catalyst for the three component synthesis of compound 4a.

Entry	Catalyst (g)	Time (min)	Yield (%)
1	0.00	40	20
2	0.01	30	55
3	0.02	25	75
4	0.03	15	85
5	0.04	8	95
6	0.05	8	95

Table 2 Comparison of time and yields on the formation of compounds **4a–4j** using ultrasound irradiation and conventional heating promoted by Pt–MWCNTs.

Entry	Product	Amine (Ar or NH ₄ OAc)	R	Reflux conditions		Ultrasonic irradiation		M.p. (°C)	
				Time (min)	Yield (%)	Time (min)	Yield (%)	Obs.	Lit.
1	4a	Ph	H	35	80	8	95	214–215	214–216 [82]
2	4b	Ph	4-OMe	30	70	12	93	204–206	205–207 [83]
3	4c	4-MeC ₆ H ₅	4-F	40	75	15	90	240–242	241–243 [43]
4	4d	Ph	4-Cl	41	71	10	90	223–225	222–224 [84]
5	4e	4-Me C ₆ H ₅	4-Me	45	65	20	89	244–246	243–247 [41]
6	4f	4-Cl C ₆ H ₅	4-OMe	30	70	15	91	245–247	244–247 [85]
7	4g	5-Cl,2-OH C ₆ H ₅	4-Cl	45	65	25	88	235–236	235–237 [41]
8	4h	NH ₄ OAc	3-NO ₂	25	85	10	95	196–198	195–196 [84]
9	4i	NH ₄ OAc	2-Cl	25	80	12	96	204–205	203–205 [86]
10	4j	NH ₄ OAc	4-OH,3-OMe	30	80	20	90	226–228	226–227 [87]

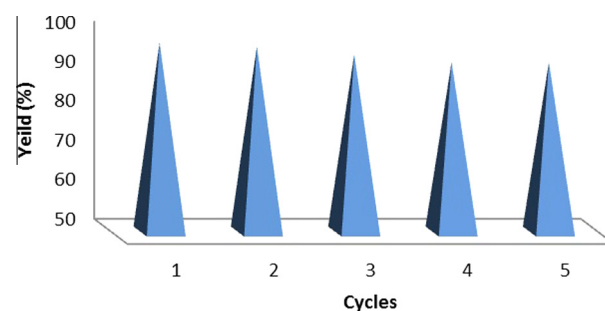
Table 3 Screening different solvents in the model reaction.

Entry	Solvent	Time (min)	Yield (%)
1	MeOH	15	92
2	PhMe	30	53
3	CH ₂ Cl ₂	35	49
4	MeCN	20	85
5	EtOH	8	95
6	THF	40	37

bath and are shown in Table 2. It can be concluded that the synthesis of compounds **4a–4j** is faster and the yields are higher than conventional heating methods. It was apparent that the ultrasound irradiation accelerated this transformation under milder conditions. Its reason may be the phenomenon of cavitation produced by ultrasound waves. Thus the unique combination of Pt–MWCNTs and ultrasound leads to better conversions and a decreased reaction time for this transformation.

For further optimization of the reaction conditions, we then turned our attention to investigate the effect of different solvents on this conversion. The significant rate enhancements were observed when reactions were carried out in ethanol compared with other organic solvents (Table 3). Thus, in order to develop a better reaction system and further optimization, more studies were performed. The possibility of recycling the catalyst was investigated in the model reaction and the activity of the catalyst and yield of the product did not show any significant decrease even after four runs. The results are shown in Fig. 2. In all these cases, the reactions provided a rapid synthetic route, furnishing satisfactorily the respective products that could be isolated and characterized by spectroscopic methods. The structures of all products were characterized on the basis of spectroscopic data particularly ¹H and ¹³C NMR spectra.

The representative SEM images of the prepared Pt–MWCNTs catalyst is shown in Fig. 3. It can be observed from SEM images of Pt–MWCNTs that well-dispersed and spherical Pt particles were anchored on the external walls of MWCNTs and the aggregation of alloy nanoparticles was not apparent. Generally, the high dispersion of the Pt nanoparticles on the MWCNTs supports is owing to the existence of uniform surface functional sites on all nanotubes that can be formed in the chemical-wet oxidation of nitric and sulfuric acid.

**Figure 2** Study of recyclability of catalyst in the synthesis of compound **4a**.

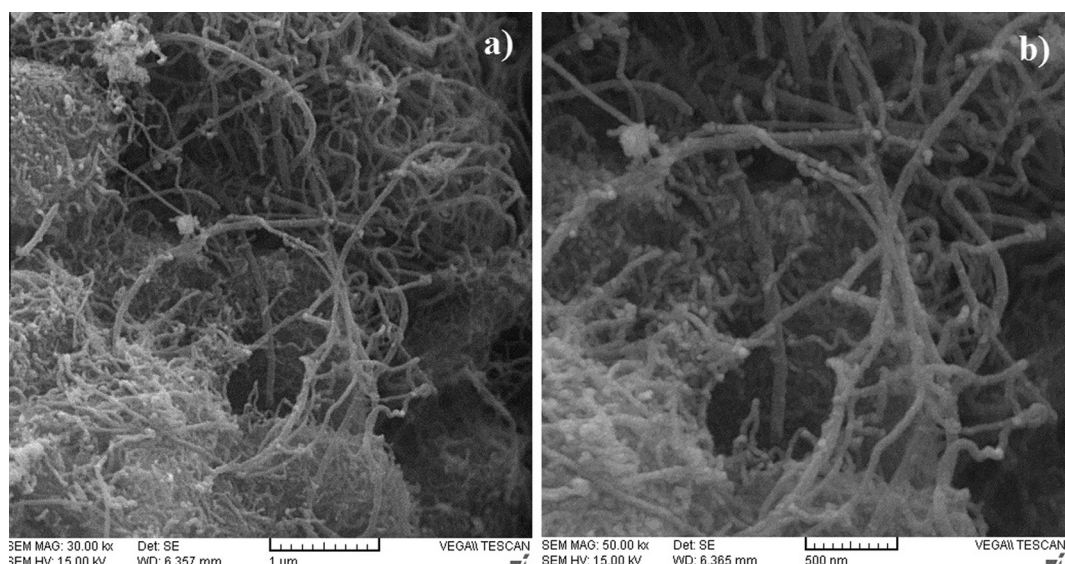


Figure 3 Scanning electron microscopy (SEM) images of Pt-MWCNTs.

The crystalline nature of the Pt nanoparticles was further established by recording the X-ray power diffraction (XRD) pattern of the Pt deposited on MWCNTs sample (Fig. 4). The obvious diffraction peaks at $2\theta \approx 25.92^\circ$ (002) and

43.24° (100) correspond to the graphitic structure of MWCNTs. The other three peaks $2\theta = 40.18^\circ$, 46.64° and 67.80° can be indexed to the (111), (200) and (220) crystalline planes of Pt NPs, respectively, which indicate the Pt

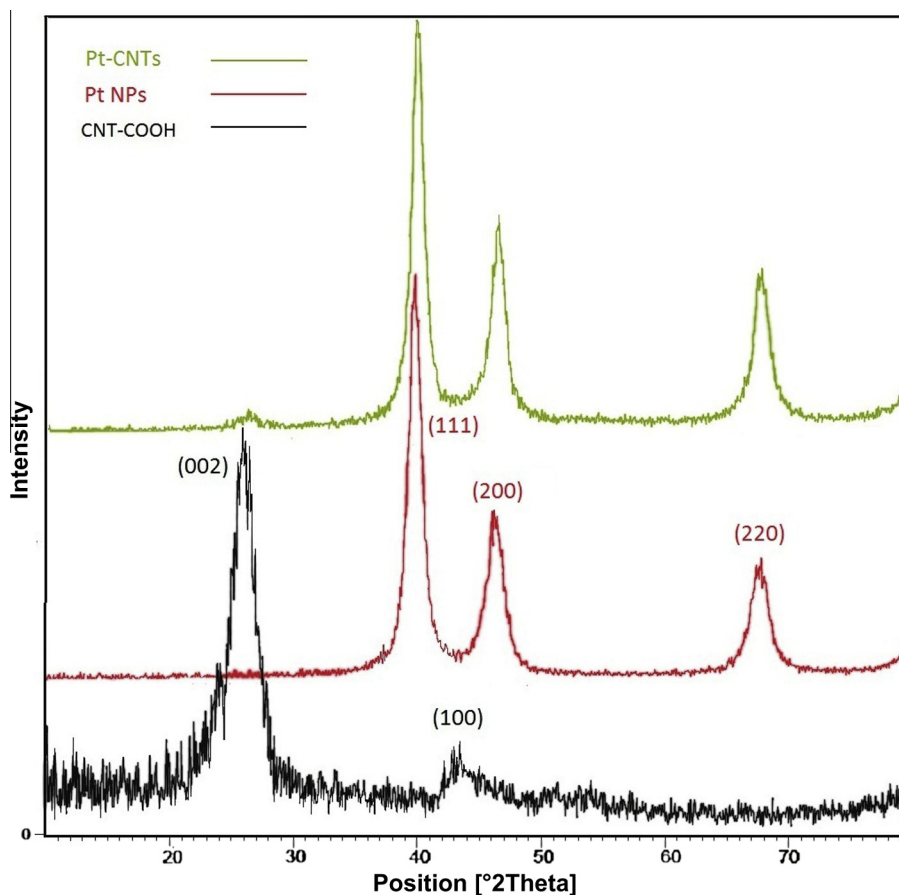


Figure 4 XRD patterns of acid treated MWCNTs, Pt nanoparticles and Pt-MWCNTs composite.

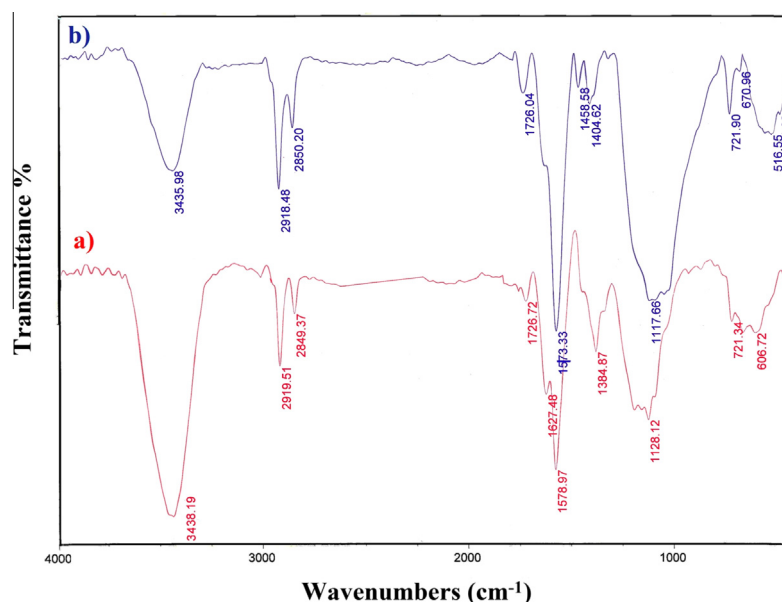


Figure 5 FT-IR patterns of (a) acid treated MWCNTs and (b) Pt-MWCNTs composite.

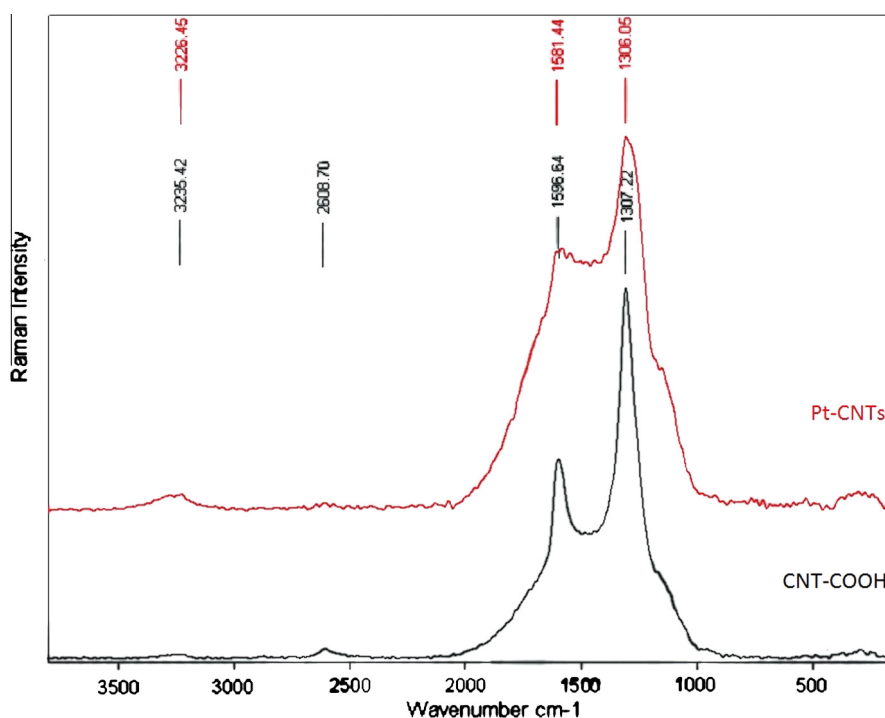


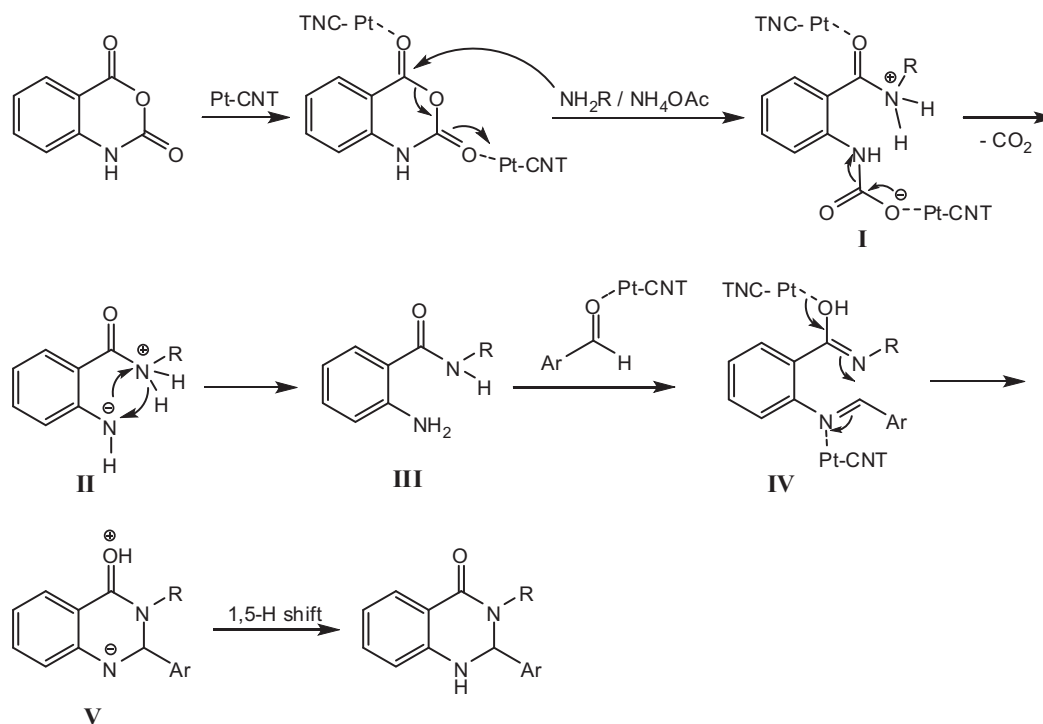
Figure 6 Raman spectra of oxidized MWCNTs and Pt-MWCNTs nanocomposites.

nanoparticles are composed from pure crystalline Pt. According to the Scherrer equation, the particle size of the decorated Pt nanoparticles was about 20–22 nm.

FTIR examination of the acid treated MWCNTs and Pt-MWCNTs catalysts are presented in Fig. 5. The peaks at 3438 and 1726 cm^{-1} are assigned to stretching vibration of COOH group. The peak at 1627 cm^{-1} is assigned to the C=C stretching vibration of MWCNTs. The absorption bands at 2919 and 2849 cm^{-1} are attributed to the stretching vibrations of methylene (CH_2). Stretching modes of Pt-C in

the characteristic frequencies at 1458, 516 and 721 cm^{-1} can be seen from the FTIR spectrum of Pt-MWCNTs.

The decoration of MWCNTs by Pt nanoparticles is also confirmed by Raman spectra (Fig. 6). The peak at 1307 cm^{-1} corresponds to amorphous carbon and the defects of pentagons' or heptagons' structure of carbon (D-line) and the peak at 1596 cm^{-1} indicates the crystalline structure of MWCNT and the sp^2 hybridized carbon in the graphitic structure (G-line). The intensity ratio of D-band to G-band (I_D/I_G ratio) is used to study the structural properties and crystallinity of



Scheme 2 Possible mechanistic route for preparation of quinazolinone derivatives.

MWCNTs. Based on the Raman curves, decrease of the I_D/I_G ratio from 1.86 in the oxidized MWCNTs to 1.42 in Pt-MWCNTs composites indicates that the restoration of sp^2 structure (reduction of $C=C$ bonds) has occurred in MWCNTs surface and functionalization has been done successfully.

The plausible general mechanistic pathway for this transformation has been outlined in Scheme 2. It is conceivable that the supported metal is coordinated to the oxygen atom of the carbonyl groups in different stages of the reaction activating them for the nucleophilic attack of the amine and amide nitrogen atoms. The reaction can be mechanistically considered to proceed via the initial activation of the isatoic anhydride, then the *N*-nucleophilic amine attack on the carbonyl unit to produce an intermediate **I**, which in turn affords intermediate **II** through decarboxylation reaction. The proton transfer of intermediate **II** affords 2-amino-*N*-substituted-amide **III**. The tautomerization of amide group in intermediate **III** could be catalyzed in the presence of the supported metal. Subsequently, the reaction of activated aldehyde with 2-amino-*N*-substituted-amide **III** proceeds to afford the imine intermediate **IV**. The imine moiety in intermediate **IV** is also activated by catalyst. Cyclization of **IV** to intermediate **V** occurs via intramolecular nucleophilic attack of nitrogen on imine carbon. Then, 1,5-proton shift gives the corresponding products.

4. Conclusions

In conclusion, we applied a newly developed synthetic methodology to synthesize 2,3-dihydroquinazolin-4(1*H*)-ones through the one-pot three-component cyclocondensation of isatoic anhydride, ammonium acetate (or primary aromatic amines)

and aldehydes under ultrasound irradiation. To this end, the focus of our study is the use of Pt-MWCNTs nanocomposites, which are relatively nontoxic and efficient. In addition, in order to obtain the stabilized and high reactive Pt-MWCNTs nanocomposites and to decrease Pt nanoparticle agglomeration in the MWCNTs surface, ultrasound is applied to prepare these nanocomposites. Cavitation can be useful to form stable dispersion of the nanoparticles in the coatings. The present reagent system has not previously been investigated for such condensation. The development of this novel catalyst affords an alternative reagent to prepare these pharmacologically important quinazolinones in good yields. The green procedure, recyclability of catalyst, high yields, short reaction times, simple work-up procedures and use of commercially available starting materials make the present method an interesting approach toward the synthesis of dihydroquinazolinones.

Acknowledgment

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