Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu



Mahmoud Nasrollahzadeh^{a,*}, Abbas Azarian^b, Ali Ehsani^a, S.Mohammad Sajadi^c, Ferydon Babaei^b

^a Department of Chemistry, Faculty of Science, University of Qom, Qom 37185-359, Iran

^b Department of Physics, University of Qom, Qom, Iran

^c Department of Petroleum Geoscience, Faculty of Science, Soran University, PO Box 624, Soran, Kurdistan Regional Government, Iraq

ARTICLE INFO

Article history: Received 13 November 2013 Received in revised form 24 February 2014 Accepted 31 March 2014 Available online xxx

Keywords: Metals Nanostructures Optical materials Optical properties

ABSTRACT

This paper reports the synthesis and use of Pd/Fe_3O_4 nanowires, as magnetically separable catalysts for ligand-free amidation coupling reactions of aryl halides with benzylurea under microwave irradiation. Then, the in situ hydrogenolysis of the products was performed to afford the *N*-monosubstituted ureas from good to excellent yields. This method has the advantages of high yields, simple methodology and easy work up. The catalyst can be recovered by using a magnet and reused several times without significant loss of its catalytic activity. The catalyst was characterized using the powder XRD, SEM, EDS and UV–vis spectroscopy. Experimental absorbance spectra was compared with results from the Gans theory.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

N-Monosubstituted urea compounds constitute a very important class of organic compounds playing a significant role in a number of natural products and bioactive molecules [1–4].

The classical approaches to substituted ureas are based on the reaction of primary amines with toxic phosgene or its derivatives [5,6], reaction of primary or secondary amines with isocyanates or reaction with sodium or potassium cyanate in aqueous solution in the presence of one equivalent of HCI [7,8], insertion of CO or CO_2 into amino compounds in the presence of different catalysts in organic solvents (at high pressure and temperature) [9–12], acid or base-catalyzed hydration of cyanamides or reaction of *S*,*S*-dimethyl dithiocarbonate with ammonia in water-dioxane [13–16].

However, each of these methods suffer from different drawbacks such as employing expensive, toxic, hazardous and moisture sensitive reagents, harsh reaction conditions, tedious work-ups,

Abbreviations: XRD, X-ray Powder Diffraction; SEM, Scanning Electron Microscopy; EDS, Energy Dispersion X-ray Spectroscopy; FT-IR, Fourier transform infrared spectroscopy; NMR, Nuclear Magnetic Resonance.

Corresponding author. Tel.: +98 25 32850953; fax: +98 25 32103595.

E-mail address: mahmoudnasr81@gmail.com (M. Nasrollahzadeh).

long reaction times, low yields, several-step methods, environmental pollution caused by formation of side products [13-16]. Thus, due to safety considerations, it is desirable to develop a more efficient and convenient method for the synthesis of *N*-monosubstituted ureas that reduce or eliminate the use and generation of hazardous compounds is essential.

Palladium-catalyzed C–N cross-coupling reactions have evolved into a highly versatile and synthetically attractive technique for targeting pharmaceutically useful intermediates [17–19]. While a number of C–N cross-coupling methods to synthesize symmetrical and unsymmetrical diarylureas exist, methods for the formation of monoarylureas are sparse [20,21]. As an alternative approach, we believed a mild and efficient crosscoupling method might be utilized to greatly expand the inventory of available monoarylureas.

Nanotechnology is emerging as a cutting edge technology interdisciplinary with biology, chemistry and material science. Metal nanoparticles have been used widely in recent years due to their unique electronic, optical, mechanical, magnetic and chemical properties which differ greatly from the bulk substances [22]. For these reasons, metallic nanoparticles have been found to be of use in many applications in different fields, such as catalysis, photonics, and electronics. Palladium (Pd) is able to catalyze a wide variety of chemical reactions that are homogeneous and heterogeneous under conditions and therefore it is one of the most





widely used metal catalysts [23]. Due to a higher available catalytic surface, use of heterogeneous catalysts in the form of nanoparticles is increasing. Recently, a variety of magnetic nanoparticles that are amenable for easy separation and recovery have been synthesized and applied as heterogeneous catalysts to a range of chemical reactions [24–27].

In the course of our researches on the applications of heterogeneous catalysts [28–35], herein we report a simple, inexpensive and two-steps protocol for the preparation of Pd/Fe_3O_4 nanowires by arc discharge of Fe in deionized (DI) water and electroless deposition of palladium. The main advantage of the present method is the direct formation of Fe nanowires from discharge of iron electrodes in water. The catalyst is heterogeneous and reusable, which provides an advantage over the homogeneous Pd-catalyst.

Several methods for preparation of Fe nanowires have been reported. Classical methods for the synthesis of Fe nanowires have involved epitaxy [36], chemical deposition [37], self-assembly [38] and electrochemical methods [39]. In spite of these methods, there are no reports on the preparation of iron nanowires by the electrical arc discharge method. The early works on arc discharge method in liquids were based on the production of carbonaceous nanostructures such as MWCNTs, SWCNTs, SW-CNHs and nano onions [40-43]. In general, electrical arc discharge in water has the advantage in this regard as it produces self-crystallized nanoparticles due to the high temperature caused by joule heating. Moreover, compared with other techniques, electrical arc discharge in water is an attractive method because of the simplicity of the experimental set up, lack of complicated equipment, low impurity and less production steps leading to a high-throughput and cost-effective procedure to generate high yields of nanoparticles.

In the next step, we hereby describe the development of Pd/ Fe_3O_4 nanowires as a novel and stable heterogeneous catalyst for the amidation of aryl halides with benzylurea (Scheme 1). The amidation of aryl halides with benzylurea, followed by hydrogenolysis, provides the corresponding *N*-monosubstituted ureas in high yields.

During this study, we also introduce the effective medium optical constant for decorated nanowires (Fe_3O_4 nanowires decorated by Pd nanoparticles) thin films by comparing the experimental data and calculation results in the spectral range of 300–700 nm. Gans theory and these effective optical constants were used for calculation of extinction cross section of dispersed above nanostructures in water. Our simulation results show that this approach can be used for prediction of optical spectra of decorated nanowires.

2. Experimental

2.1. Instruments and reagents

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by different spectroscopic methods (FT-IR and ¹H NMR spectra), elemental analysis (CHN) and melting

points. The NMR spectra were recorded in acetone and DMSO. ¹H NMR spectra were recorded on a Bruker Avance DRX 250, 300 and 400 MHz instrument. The chemical shifts (δ) are reported in ppm relative to the TMS as internal standard. J values are given in Hz. IR (KBr) spectra were recorded on a PerkinElmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. The elemental analysis was performed using Heraeus CHN-O-Rapid analyzer. TLC was performed on silica gel polygram SIL G/UV 254 plates. X-ray diffraction measurements were performed with a Philips powder diffractometer type PW 1373 goniometer. It was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded in the 2θ range (10–60) with scanning speed of 2° min. Morphology and particle dispersion were investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by EDS performed in SEM. UV-vis spectral analysis was recorded on a double-beam spectrophotometer (Hitachi, U-2900).

2.2. Preparation of Pd/Fe_3O_4 nanowires

Fe nanowires were prepared using a system consisting of two main parts: a high current DC power supply and a reactor including an anode, cathode and a micrometer, which moves the anode in contact with the cathode. In this method, an 8 V DC voltage and 5 A current are applied between two metallic iron electrodes; it was found that the voltage dropped to 5 V during arcing but the current remained constant. Both the anode and cathode were Fe, wire shaped, 2mm in diameter and 99.99% in purity. Initially we brought the two electrodes into contact, leading to a small contact cross section and thus to a high current density. As more iron was ablated from the anode, the plasma expanded and pushed the liquid away, and a gaseous bubble was formed. Melted species can react with plasma and then condense into the liquid. In order to extract the dispersed wires, the solution was dried at a pressure of 10⁻¹ Torr and centrifuged several times and then dispersed on a glass substrate. Deposition of Pd on the surface of Fe nanowires was accomplished via a simple drop-drying process by dropping PdCl₂ solution onto Fe nanowires films and drying them at room temperature. This solution was prepared by ultrasonically solving $0.02\,g\,of\,PdCl_2\,powder\,(5\,N), 99.9\,mL\,DI$ water and 0.1 mL HCl. After Pd deposition, samples were washed with DI water several times and then dried in air. However, Fe nanowires are very air-sensitive and easily oxidize to Fe₃O₄ nanowires in water.

2.3. General experimental procedure for the synthesis of Nmonosubstituted ureas

A Smith process vial was charged with $1.0 \text{ mol}\% \text{ Pd}/\text{Fe}_3O_4$ nanowires, 1.0 mmol of phenylurea, 1.0 mmol of aryl halide and Cs_2CO_3 (1.5 mmol). After sealing the cap and twice purging with N_2 , the vial was irradiated by microwave at $120 \degree \text{C}$ for 1 h in the Smith Synthesizer. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled to room temperature, and a small volume of MeOH (4 mL) was added; the catalyst was



X: I & Br

Scheme 1. Synthesis of N-monosubstituted ureas.

separated by a magnetic separator and the reaction mixture was filtered through a pad of Celite and MeOH (6 mL/mmol), conc. HCl and an equal weight of Pd black were added and the reaction vessel was connected to a Parr medium pressure hydrogenation apparatus (40–50 ψ); then it was stirred at room temperature for 20 h.

The mixture was quenched with 2 M NaOH, filtered, diluted with 30 mL of ethyl acetate and washed with 2 M NaOH. Then the mixture was extracted three times with ethyl acetate (30 mL each). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was subjected to gel permeation chromatography to afford pure products.

The elemental analysis (CHN), IR, ¹H NMR and ¹³C NMR data of the unknown substituted ureas is given as below:

N-(2,5-Dichlorophenyl) urea (Table 3, entry 4): white color; M. p. 222–224 °C; FT-IR (KBr, cm⁻¹) 3495, 3417, 3364, 3340, 3308, 3206, 2826, 1676, 1610, 1586, 1535, 1466, 1410, 1385, 1351, 1263, 1089, 1056, 873, 805, 792, 764, 583, 557, 475, 440, 418; ¹H NMR (300 MHz, DMSO- d_6) $\delta_{\rm H}$ = 8.24 (s, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.55 (s, 2H); ¹³C NMR (75 MHz, DMSO- d_6) $\delta_{\rm C}$ = 154.7, 137.7, 131.7, 129.9, 121.5, 119.5, 118.8; Anal. Calcd for C₇H₆N₂OCl₂: C, 41.00; H, 2.95; N, 13.66. Found: C, 39.84; H, 2.89; N, 13.80.

N-(4-Acethylphenyl) urea (Table 3, entry 5): white color; M.p. 297–298 °C; FT-IR (KBr, cm⁻¹) 3407, 3307, 3215, 1672, 1613, 1584, 1536, 1508, 1410, 1357, 1310, 1273, 1117, 1013, 963, 874, 835, 766, 747, 718, 632, 655, 594, 494, 410; ¹H NMR (300 MHz, DMSO- d_6) $\delta_{\rm H}$ = 8.93 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.02 (s, 2H), 2.47 (s, 3H); ¹³C NMR (75 MHz, DMSO- d_6) $\delta_{\rm H}$ = 196.6, 156.0, 145.7, 130.2, 130.0, 117.0, 26.7; Anal. Calcd for C₉H₁₀N₂O₂: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.47; H, 5.45; N, 15.59.

N-(1-Naphthyl) urea (Table 3, entries 6 and 7): white color; M. p. 221–222 °C; FT-IR (KBr, cm⁻¹) 3444, 33055, 3206, 3052, 2922, 1651, 1608, 1555, 1530, 1505, 1360, 1335, 1278, 1101, 785, 772, 608, 530; ¹H NMR (250 MHz, DMSO-*d*₆) $\delta_{\rm H}$ = 8.70 (s, 1H), 8.17 (s, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.85 (s, 1H), 7.73–7.37 (m, 4H), 6.22 (s, 2H); ¹³C NMR (62.5 MHz, DMSO-*d*₆) $\delta_{\rm C}$ = 157.1, 135.9, 134.5, 128.9, 126.6, 126.4, 126.0, 122.7, 122.3, 117.5; Anal. Calcd for C₁₁H₁₀N₂O₂: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.82; H, 5.34; N, 14.91.

N-(2-Methylphenyl) urea (Table 3, entries 8 and 9): white color; M.p. 196–198 °C; FT-IR (KBr, cm⁻¹) 3438, 3315, 3218, 1650, 1613, 1582, 1547, 1459, 1354, 1289, 1258, 1117, 1041, 844, 747, 596, 480; ¹H NMR (250 MHz, DMSO- d_6) $\delta_{\rm H}$ = 7.79 (t, *J* = 6.4 Hz, 1H), 7.69 (s, 1H), 7.13–7.07 (dd, *J* = 8.0 Hz, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.03 (s, 2H), 2.19 (s, 3H); ¹³C NMR (62.5 MHz, DMSO- d_6) $\delta_{\rm H}$ = 156.6, 138.6, 130.5, 127.4, 126.4, 122.5, 121.4, 18.36; Anal. Calcd for C₈H₁₀N₂O: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.85; H, 6.61; N, 18.52.

3. Results and discussion

3.1. Characterization of catalyst

The catalyst was characterized using the powder XRD, SEM, EDS and UV–vis spectroscopy.

Fe₃O₄ nanowires decorated by Pd nanoparticles were fabricated in two-steps using a simple process. Fe₃O₄ nanowires of several micron lengths were synthesized through arc discharge of iron electrodes in DI water and then they were dispersed on glass substrates and dried in air. Palladium nanoparticles were overlaid on the surface of Fe₃O₄ nanowires via a simple drop-drying process by dropping PdCl₂ solution onto Fe nanowires films and drying them at room temperature. Fig. 1 illustrates typical morphologies of Pd/Fe₃O₄ nanowires obtained at 5 A arc currents. In general Fe tends to form wire-like structures due to its lattice geometry. The presence of a high temperature region and DI water in the reactor



Fig. 1. Typical SEM image of Pd/Fe₃O₄ nanowires.

leads to the formation of a temperature gradient and fast condensation process. In fact, rapid cooling of the products reduces the growth rate of the created nuclei and they do not have enough time to form wire-shaped structures before stabilization. Hence, due to fast condensation there are also other shapes rather than nanowires in our samples. Scanning electron microscopy image illustrate Pd/Fe₃O₄ nanowires with size ranging from 1 to less than 20 μ m in length and about 100 nm in diameter. In addition, Pd particles appear as bright dots over the surface of Fe₃O₄ nanowires with average size of less than 30 nm.

The crystalline structure and phase composition of catalyst was confirmed by X-ray diffraction measurement. The X-ray diffraction pattern revealed that Fe nanoparticles are very oxygen-sensitive and easily oxidized to Fe_3O_4 (Fig. 2). All of the peaks in the X-ray diffraction (XRD) pattern could also be assigned to the corresponding lattice planes of face-centered-cubic (fcc) Pd and Fe_3O_4 crystals in accordance with the bimetallic heterodimer structure.

We used energy dispersive X-ray spectroscopy (EDS) to determine chemical composition of our samples. In the EDS spectrum of catalyst, peaks related to O, Fe and Pd were observed. The atomic and weight ratios are listed in Table 1. The excess amount of oxygen is due to physical absorption of oxygen from environment during sample preparation.

3.2. Optical properties

For non-spherical metallic particles, to calculate the light absorption by them, the orientation with respect to the oscillating electric field must be taken into account. In 1912, Gans derived the extinction cross-section for nanowires, when the dipole approximation holds [44].

In recent years, many papers have been published about surface plasmon resonance (SPR) of nanowires. In most of these articles, the Gans theory was widely used because SPR properties of nanowires is in good agreement with the results of this theory [45].

In this work, we introduce the effective medium optical constant of these thin films by comparing the experimental data and calculation results and then Gans theory which these optical constants were used for the calculation of extinction cross section of dispersed Fe nanowires decorated by Pd nanoparticles in water.



Fig. 2. XRD pattern of Pd/Fe₃O₄ nanowires.

Table 1Atomic and weight ratios of Pd/Fe₃O₄.

Element	Series	Norm. C (wt%)	Atom. C (at%)
Iron Palladium	K series K series	26.07 6.18	9.00 1.12
Oxygen	K series	42.35	51.05

$$\alpha_{ext} = \exp(-4\pi K d/\lambda) \tag{4}$$

where, n_0 , n_s , n_f are real parts of the refraction indices of the thin film, the substrate and the air, respectively. Moreover, *d* is the film thickness and *K* is the imaginary part of the refraction index of Pd/ Fe₃O₄ thin films. To obtain the values of *K*, using the extinction coefficient equation as [48]:

$$\alpha_{\text{ext}} = \exp\left(\frac{-4\pi kd}{\lambda}\right) = \frac{T}{1-R}$$
(5)

A typical UV-vis spectrum of the Pd/Fe_3O_4 thin films on glass substrates is shown in Fig. 3.

In order to obtain the real part of refraction indices (n_f) of the Pd/Fe₃O₄ thin films, we have used the prescription given in [46,47] where it is suggested that the following equation may be used to obtain the optical constants of low absorption thin films:

$$T = \frac{16n_0 n_s n_f^2 \alpha_{ext}}{C_1^2 + C_2^2 \alpha_{ext}^2 + 2C_1 C_2 \alpha_{ext} COS(4\pi n_f d/\lambda)}$$
(1)

$$C_1 = (n_0 + n_f)(n_f + n_s)$$
 (2)

$$C_1 = (n_0 - n_f)(n_f - n_s)$$

Details of the Gans theory can be found in literature [49]. According to the Gans theory, the extinction coefficient γ for N particles of volume V is given by the following equation.

$$\gamma = \frac{2\pi N \mathcal{V} \varepsilon_m^{3/2}}{3\lambda} \left[\frac{(2/p_x^2)\varepsilon_2}{(\varepsilon_1 + k_x \varepsilon_m)^2 + \varepsilon_2^2} + \frac{(1/p_x^2)\varepsilon_2}{(\varepsilon_1 + k_z \varepsilon_m)^2 + \varepsilon_2^2} \right]$$
(6)



(3)

Fig. 3. A typical UV–vis absorption spectrum of the Pd/Fe_3O_4 thin films on glass substrates.



Fig. 4. Investigated effective optical constants of Pd/Fe₃O₄.

Table 2

where λ the wavelength of the light, ε_m the dielectric constant of the medium and ε_1 and ε_2 the real and complex part of copper dielectric function related to interacting light. In this theory for each dimension, a geometrical factor (P_i) are given by

$$p_{z} = \frac{1 - e^{2}}{e} \left(\frac{1}{2e} \ln\left(\frac{1 + e}{1 - e}\right) - 1 \right)$$
(7)

$$p_x = p_y = \frac{1}{2}(1 - p_z)$$
(8)

$$e = \frac{\sqrt{L^2 - d^2}}{L} \tag{9}$$

where L and d is the nanowires length and diameter, respectively. For each dimension the screening parameter is

$$K_i = \frac{1}{p_i}(1 - p_i) \tag{10}$$

Here K_i (i = 1, 2, 3) are the same K_x , K_y and K_z in Eq. (6). The result of this process is shown in Fig. 5. It is clear that there is good agreement between calculation and experimental values of absorption spectra of Pd/Fe₃O₄ dispersed in water.

Optimization of reaction conditions in amidation reaction of 2,5-dichlorobromobenzene with benzylurea^a.

Entry	Pd/Fe ₃ O ₄ nanowires (mol.%)	Base	Yield ^b (%)
1	1.0	Cs ₂ CO ₃	89
2	1.0	Na ₂ CO ₃	50
3	1.0	K ₃ PO ₄	80
4	1.0	K ₂ CO ₃	82
5	1.0	0	0
6	0	Cs ₂ CO ₃	0
7	2.0	Cs ₂ CO ₃	88
8	0.7	Cs ₂ CO ₃	72

 $^a\,$ Reaction condition: 1.0 equiv of aryl halide, 1.0 equiv of benzylurea, 1.0 mol.% of catalyst and 1.5 equiv of base, 120 $^\circ$ C, 1 h. $^b\,$ Isolated yield.

3.3. Activity of Pd/Fe $_3O_4$ nanowires catalyst for the preparation of N-monosubstituted ureas

The catalytic behavior of the Pd/Fe₃O₄ nanowires was studied for the synthesis of *N*-monosubstituted ureas. Reaction conditions



Fig. 5. Experimental and calculated absorption spectra by effective optical constants of Pd/Fe₃O₄ dispersed in water.

Table 3
Formation of N-monosubstituted ureas.

Entry	Aryl halide	Product	Yield ^a (%)	Reference
1	Br		87	[16]
2		NH2 0	89	[16]
3	Cl-Br	CI V V V V V V V V V V V V V V V V V V V	85	[16]
4	CI CI	CI ON NH2	89 (88,88,87) ^b	This work
5	MeOC-Br	MeOC NH2	85	This work
6	Br	H NH ₂	82	This work
7		H NH ₂	85	This work
8	Me	Me NH ₂	87	This work
9		Me H NH ₂	86	This work
10	Me-Br	Me NH2	84	Commercial
11	Me	Me NH2	86	Commercial
12	MeO-Br	MeO NH2	83	[16]
13	MeO	MeO NH2	85	[16]

^a Yields are after work-up.
 ^b Yield after the fourth cycle.



Fig. 6. FT-IR spectrum (KBr, cm^{-1}) of *N*-(2-methylphenyl) urea.

were optimized for the amidation reaction using 2,5-dichlorobromobenzene as a substrate, and benzylurea and Pd/Fe₃O₄ nanowires as heterogeneous catalysts in the presence of various bases under microwave conditions at 120 °C (Table 2). Control experiments show that there is no effective reaction in the absence of catalyst (Table 2, entry 6). However, addition of the Pd/Fe₃O₄ nanowires to the mixture has rapidly increased the amidation of aryl halides in high yields. Our experiments showed that the base was necessary for the amidation reaction. Among the selected bases, Cs₂CO₃ acted as the most effective one (Table 2, entry 1). Reaction without base did not give any product. The effect of catalyst loading was probed. Catalyst loads of 1.0 mol% were typically required to achieve quantitative conversion with most substrates. The use of lower catalyst loadings resulted in incomplete reactions (entry 8).

We then used the optimal reaction conditions (catalyst (1.0 mol %), aryl halide (1.0 mmol), benzylurea (1.0 mmol) and Cs_2CO_3 (1.5 mmol)) for amidation of different aryl halides under microwave conditions at 120 °C) for 1 h and the results are shown in Table 3. Then, the in situ hydrogenolysis of 1-benzyl-3-arylureas in MeOH and in the presence of conc. HCl and Pd black yielded the desired *N*-monosubstituted ureas from good to excellent yields.

To study the effects of the nature of the substituents, various 1benzyl-3-arylureas were synthesized from the reaction between different aryl halides containing both electron-releasing and electron-withdrawing groups with benzylurea in good to excellent yields. As shown in Table 3, 1-bromo and 1-iodonaphthyl gave the corresponding adduct in good yield (Table 3, entries 6 and 7).

To the best of our knowledge, Pd/Fe₃O₄ nanowires are one of the most general and active catalysts reported so far for the synthesis of *N*-monosubstituted ureas. These results represent a significant advancement in the C–N coupling reaction. Although the mechanism of Pd-catalyzed coupling is not obvious and further studies to elucidate the detailed reaction mechanism are ongoing in our laboratory. It should be noted that Pd/Fe₃O₄ nanowires were absolutely necessary for this reaction as verified by a control experiments where no reaction occurred in the absence of Pd/Fe₃O₄ nanowires or in the presence of only Fe₃O₄ even at a higher reaction temperature for a prolonged reaction time. Based on the most accepted coupling reaction mechanism, Pd nanoparticles are expected to be the reasons for the high catalytic activity of the

catalyst Pd/Fe₃O₄ in comparison with Fe₃O₄. In the other word, the high activity of Pd/Fe₃O₄ catalyst for the synthesis of *N*-monosubstituted ureas could be attributed to the formation of small active Pd nanoparticles on the surface of Fe₃O₄.

After removal of the solvent and purification, the products were characterized by melting points, elemental analysis (CHN), IR, ¹H NMR and ¹³C NMR. Appearance of the two absorption bands in the range of 3200–3400 cm⁻¹ (NH stretching bands) and one absorption band in the range of 1640–1670 cm⁻¹ (C=O) in the IR spectrum confirmed formation of the *N*-monosubstituted ureas (Fig. 6). The ¹H NMR spectra of the products showed one NH proton signal and another signal for the NH₂ protons. The ¹³C NMR spectra of the products showed one.

3.4. Catalyst recyclability

The reusability of the catalyst was checked in the reaction of benzylurea with iodobenzene under the present reaction conditions (Table 3, entry 4). After the completion of the reaction, the insoluble catalyst was separated from the reaction mixture by the application of an external magnet. The catalyst was washed with ethyl acetate several times, dried in a hot air oven at 100 °C for 2 h and employed for the next reaction. The catalytic activity did not decrease considerably after four catalytic cycles. The reusability of the catalysts is one of the most important benefits and makes them useful for commercial applications.

4. Conclusions

In conclusion, we have developed an efficient protocol for the preparation of Pd/Fe₃O₄ nanowires. The catalyst was characterized by SEM, XRD, EDS and UV–vis spectroscopy and exhibited good activities in ligand-free coupling reactions of aryl halides with benzylurea. This system allows the coupling of electron-rich, -neutral, and -deficient aryl halides from good to excellent yields. This method leads to the advantages of high yields, elimination of homogeneous catalysts, simple methodology and easy work up. The catalyst is eco-friendly catalyst because it produces little waste, and can be recovered by a magnet and successively reused without the significant loss of activity. The optical properties of the catalyst were also studied.

Acknowledgments

We gratefully acknowledge the Iranian Nano Council and University of Qom for the support of this work.

References

- [1] K. Matsuda, Medicinal Research Reviews 14 (1994) 271.
- [2] N.N. Melnikov, J.D. Gunther, Chemistry of Pesticides, Springer-Verlag, Berlin, 1971, pp. 225.
- [3] A. Tsopmo, D. Ngnokam, D. Ngamga, J.F. Ayafor, O. Sterner, Journal of Natural Products 62 (1999) 1435.
- [4] Y. Funabashi, S. Tsubotani, K. Koyama, N. Katayama, S. Harada, Tetrahedron 49 (1993) 13.
- [5] V. Papesch, E.F. Schroeder, Journal of Organic Chemistry 16 (1951) 1879.
- [6] R.L. Clark, A.A. Pessolano, Journal of American Chemical Society 80 (1958) 1658.
- [7] E.A. Jefferson, E.E. Swayze, Tetrahedron Letters 40 (1999) 7757.
- [8] S. Knapp, J.J. Hale, M. Bastos, A. Molina, K.Y. Cheng, Journal of Organic Chemisty 57 (1992) 6239.
- [9] X. Peng, F. Li, C. Xia, Synlett (2006) 1161.
- B. Zhu, R.J. Angelici, Journal of American Chemical Society 128 (2006) 14460.
 Y. Nishiyama, H. Kawamatsu, N. Sonoda, Journal of Organic Chemisty 70 (2005) 2551
- [12] F. Bigi, R. Maggi, G. Sartori, Green Chemisty 2 (2000) 140.
- [13] V.D. Jadhav, E. Herdtweck, F.P. Schmidtchen, Chemisty: A European Journal 14 (2008) 6098.
- [14] D. Schade, K. Topker-Lehmann, J. Kotthaus, B. Clement, Journal of Organic Chemisty 73 (2008) 1025.
- [15] E. Artuso, I. Degani, R. Fochi, C. Magistris, Synthesis (2007) 3497.
- [16] S.H. Kim, B.R. Park, J.N. Kim, Bulletin of the Korean Chemical Society 32 (2011) 716.
- [17] S.A. Lawrence, Amines, Synthesis Properties, and Application, Cambridge University Press, Cambridge, 2004.
- [18] S. Breitler, N.J. Oldenhuis, B.P. Fors, S.L. Buchwald, Organic Letters 13 (2011) 3262.
- [19] A.G. Sergeev, G.A. Artamkina, I.P. Beletskaya, Russian Journal of Organic Chemisty 38 (2002) 538.
- [20] B.J. Kotecki, D.P. Fernando, A.R. Haight, K.L. Lukin, Organic Letters 11 (2009) 947.
 [21] A.G. Sergeev, G.A. Artamkina, V.S. Velezheva, I.N. Fedorova, I.P. Beletskaya,
- Russian Journal of Organic Chemisty 41 (2005) 860. [22] M.C. Daniel, D. Astruc, Chemical Society Reviews 104 (2004) 293.
- [23] A. Molnar, Chemical Reviews 111 (2011) 2251.

- [24] M.A. Willard, L.K. Kurihara, E.E. Carpenter, S. Calvin, V.G. Harris, International Materials Reviews 49 (2004) 125.
- [25] M. Zhu, G. Diao, The Journal of Physical Chemisty C 115 (2011) 24743.
- [26] M. Zhu, C. Wang, D. Meng, G. Diao, Journal of Materials Chemisty A 1 (2013) 2118.
- [27] M. Zhu, G. Diao, Nanoscale 3 (2011) 2748.
- [28] P. Fakhri, B. Jaleh, M. Nasrollahzadeh, Journal of Molecular Catalysis A: Chemical 383-384 (2014) 17.
- [29] D. Habibi, M. Nasrollahzadeh, H. Sahebekhtiari, Journal of Molecular Catalysis A: Chemical 378 (2013) 148.
- [30] M. Nasrollahzadeh, A. Ehsani, A. Rostami-Vartouni, Ultrasonics Sonochemisty (2014) 21 275.
- [31] A. Ehsani, F. Babaei, M. Nasrollahzadeh, Applied Surface Science 283 (2013) 1060.
- [32] A.R. Modarresi-Alam, M. Nasrollahzadeh, F. Khamooshi, Sci. Iran. 15 (2008) 452.
- [33] D. Habibi, S. Heydari, M. Nasrollahzadeh, Journal of Chemical Research 36 (2012) 573.
- [34] D. Habibi, M. Nasrollahzadeh, L. Mehrabi, S. Mostafaee, Monatshefte für Chemie 144 (2013) 725.
- [35] A. Ehsani, S. Adeli, F. Babaei, H. Mostaanzadeh, M. Nasrollahzadeh, Journal of Electroanalytical Chemistry 713 (2014) 91.
- [36] H.M. Hwang, J.H. Kang, J. Lee, J.Y. Choi, H.H. Lee, Electrochemical and Solid-State Letters 11 (2008) K7.
- [37] W.-S. Lin, Z.-J. Jian, H.-M. Lin, L.-C. Lai, Journal of Chinese Chemical Society 60 (2013) 85 et all.
- [38] D.J. Sellmyer, M. Zheng, R. Skomski, Journal of Physics: Condensed Matter 13 (2001) R433.
- [39] J. Zhang, W.M. Tong, H. Ding, H.B. Wang, H. Wang, Integrated Ferroelectics 141 (2013) 24.
- [40] I. Alexandrou, H. Wang, N. Sano, G.A.J. Amaratunga, Journal of Chemical Physics 120 (2004) 1055.
- [41] D. Bera, G. Johnston, H. Heinrich, S. Seal, Nanotechnology 17 (2006) 1722.
 [42] D. Bera, S.C. Kuiry, M. McCutchen, S. Seal, H. Heinrich, G.C. Slane, Journal of
- Applied Physics 96 (2004) 5152.
- [43] N. Sano, Materials Chemisty and Physics 88 (2004) 235.
- [44] R. Gans, Annals of Physics 37 (1912) 881.
- [45] S. Eustis, M. El-Sayed, The Joural of Physical Chemistry B 109 (2005) 16350.
- [46] S.Z. Shang, K. Yi, Z.X. Fan, Applied Surface Science 242 (2005) 437.
- [47] S. Wang, X. Fu, G. Xia, J. Wang, J. Shao, Z. Fan, Applied Surface Science 252 (2006) 8734.
- [48] J.R. Reitz, F.J. Milford, Foundations of Electromagnetic Theory, Addison-Wesley, Reading, MA, 1960.
- [49] C.F. Bohren, D.R. Huffman, Absorption and Scattering of Light by Small Particles, John Wiley & Sons, New York, 1983.