

Article

Nickel Nanowires: Synthesis, Characterization and Application as Effective Catalysts for the Reduction of Nitroarenes

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Abstract: We have demonstrated a convenient method of synthesizing nickel nanowires (NiNWs), which could be easily tuned to produce materials with a carefully defined nanostructure. By varying the concentration of the Ni precursor, pH of the medium or reaction temperature, we directly affected the diameter of the formed product as well as the yield of the process. The obtained material consisted of straight bundles of NiNWs, which revealed powerful catalytic action for the reduction of nitroarenes to appropriate amine derivatives. A selection of substrates were employed and all of them were successfully converted into the corresponding aromatic amine despite the presence of different substituents on the aromatic ring with high yields, even in large scale reactions. The results showed that NiNW-based catalysts could constitute efficient catalytic systems for the synthesis of aryl amines at industrial levels.

Keywords: nickel nanowires; synthesis; catalytic properties; reduction of nitroarenes

1. Introduction

The discovery of the possibility to create materials with nanoscopic precision has opened another chapter in the history of technology for mankind. We have learned that regular chemical elements, which we have known about for a long time, can have a wide spectrum of previously unknown properties if they take the form of a nanodot, nanotube, nanowire, nanosheet, etc. Moreover, these so-called nanomaterials have often been found to outperform the electrical, thermal, mechanical, or other properties of their corresponding bulk materials.

Nickel nanowires (NiNWs) in particular have emerged as a promising material because of their electrical [1,2], thermal [3,4], and magnetic properties [5–7]. Fundamental research on this topic has already led to the development of prototypes for the application of NiNWs for body motion sensing [8], data storage [9], or bioanalysis [10]. Interestingly, the material has only been explored from the catalytic point of view to a very limited extent. For instance, it has been reported as a successful catalyst for promoting the steam reforming of ethanol [11], partial oxidation of methane to syngas [12], or urea electro-oxidation [13]. This is surprising because recent trends in research regarding the catalytic reaction with transition metals has focused on nickel [14–18]. It is an attractive metal for catalysis since it can adopt a flexible number of oxidation states, Ni(–I), Ni(0), Ni(I), Ni(II), Ni(III), Ni(IV), offering unique reactivity pathways [19–21].

In our study, we focused on the usage of NiNW as an effective catalyst in the reduction of nitroarenes to anilines. This transformation is of great importance for the chemical industry.

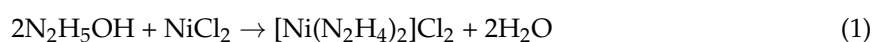
Anilines are among the most important precursors necessary for the production of dyestuffs and pharmaceuticals in the chemical industry. The industrial production of functionalized anilines mainly depends on the non-catalytic reduction of nitroarenes using stoichiometric reducing agents such as sodium hydrosulfite, iron, tin, or zinc in ammonium hydroxide [22–25]. Such processes have major disadvantages like poor selectivity and the generation of toxic wastes. Therefore, the development of a more efficient, selective, and environmentally friendly process to produce anilines is important for both fundamental studies and industrial applications. Catalytic hydrogenation using precious metals such as Rh, Pd, Ru, and Pt as the preferred choice is still not attractive because the cost of producing the catalyst is too expensive. Therefore, the development of a non-noble low cost catalyst has become more intensive in the last decade. Among them, nickel is an attractive metal for that transformation.

In this contribution, we present our results of the synthesis of NiNWs for catalytic applications. First, we studied how pH, temperature, and Ni precursor concentration affected the yield and the shape of the final NiNW product. The results showed that the diameter of the NiNW bundles could be significantly influenced by varying the parameters of the synthesis. To demonstrate the catalytic potential of these nanostructures, we employed them for the reduction of nitrobenzene derivatives to corresponding amines. The presented transformations executed in mild conditions with very high yields prove that NiNWs can be potent catalysts for a wider range of chemical reactions.

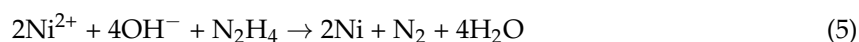
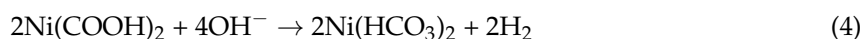
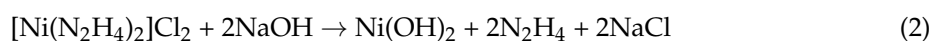
2. Results and Discussion

2.1. Mechanism and Methodology of NiNW Synthesis

To probe the reaction mechanism, initial attempts were carried out according to a method by Eluri et al. wherein hydrazine and sodium hydroxide was introduced to the nickel precursor [26]. A total of 5 mL of 0.1 M NiCl₂ solution in ethylene glycol (EG) was heated up to 60 °C. Then, 0.5 mL of N₂H₄ (aq.) and 1.5 mL of 0.1 NaOH were added to the beaker. Heating of the reaction mixture led to the formation of a blue precipitate (nickel hydrazine complexes) according to the following transformation.



This complex of paramagnetic Ni²⁺ can then arrange along the magnetic field and react in a stepwise fashion to yield a protonanowire [27]. For that to occur at an appreciable time scale, the temperature has to be increased. After increasing the temperature beyond 100 °C (and adding a further 6 mL of 0.1 M NaOH), the precipitate started to darken and reached a greyish color after a couple of minutes, which indicated the successful reduction of nickel ions to metallic nickel by the hydrothermal treatment. The mechanism of the reaction is as follows [26]:



Although the reaction eventually did lead to NiNWs, all of the obtained products were contaminated with the aforementioned blue precipitate. Washing the product with copious amounts of water and isopropanol did not remove the contaminant. Furthermore, the dimethylglyoxime test was used to detect nickel ions gave a bright red color (indicative of the presence of nickel bis(dimethylglyoximate) in the dispersed product), which confirmed that the reaction was incomplete. As a consequence, this synthesis route was abandoned.

We decided to adapt and tune the parameters of the published technique, in which water was essentially eliminated (except for the N₂H₄ solvation water) and ethylene glycol was used instead as the reaction medium [26,28]. This approach afforded NiNWs, which more readily aligned in the

magnetic field (compared to products prepared by the previous method) and no signs of adulteration were observed.

2.2. The Influence of Reaction Conditions on the Microstructure

2.2.1. Temperature

Temperature often has a significant effect on the reaction rates according to the Arrhenius relation and this situation is no different in the case of NiNW synthesis. However, the precise quantification of this influence is difficult because, as we found, NiNW synthesis has an exothermic nature. Combination of the nickel precursor with a reducing agent under basic conditions causes a notable increase in temperature by more than 10 °C (as measured by an on-line thermocouple). We attempted to carry out this process at the starting temperatures of 80 °C, 100 °C, and 120 °C. Low temperature of the reaction mixture (80 °C) resulted in the evident appearance of the blue precipitate, part of which was eventually converted into NiNWs. By increasing the temperature to 100 °C, we were able to significantly reduce the life time of the blue precipitate. It has to be noted that the increase in temperature accelerated the unwanted evaporation of hydrazine, so a trade-off has to be established. We postulate that the optimum temperature is 100 °C.

As shown in Table 1 and Figure 1, the temperature had a very strong effect on the yield of the process and the diameter of the obtained NiNW bundles. The presence of the blue precipitate at 80 °C, indicative of contamination, was directly reflected in the yield of the final product. After purification, the yield of the product was just 33%. With an increase in temperature, the NiNW synthesis not only occurs much faster, but its yield can be increased up to 97% by establishing appropriate thermodynamic conditions. Furthermore, the higher the reaction temperature, the smaller the diameter of the obtained NiNW bundles. It appears that an increase in thermal energy favors the elongation of NiNWs rather than growth in the radial direction.

Table 1. The influence of reaction temperature on the product parameters.

Reaction Conditions					Product Parameters	
V _{NaOH} [mL]	V _{N₂H₄} [mL]	V _{NiCl₂} [mL]	C _{NiCl₂} [M]	T [°C]	Yield [%]	Bundle Diameter [nm]
70	20	10	0.1	80	33	655 ± 122
70	20	10	0.1	100	85	451 ± 87
70	20	10	0.1	120	97	335 ± 121

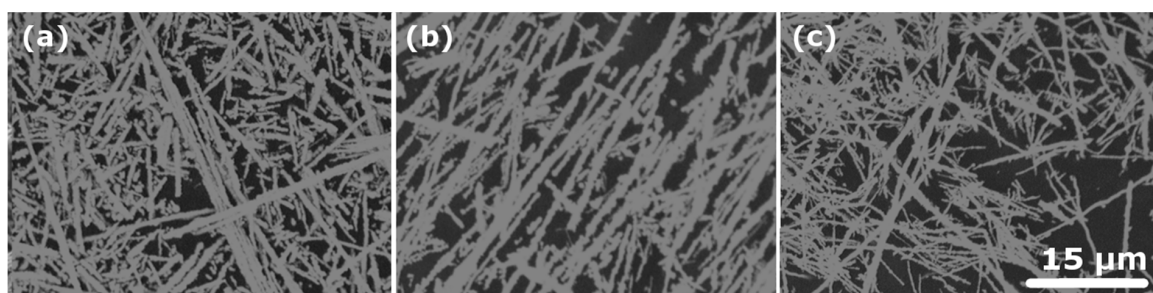


Figure 1. Micrographs of the NiNWs formed at different temperatures: (a) 80 °C, (b) 100 °C and (c) 120 °C.

2.2.2. pH

When looking at the mechanism of the NiNW formation, it is evident that the pH of the reaction medium plays a significant role. We varied the content of hydroxyl anions by changing the volume of the added 0.1 M NaOH solution in EG. With an increase in [OH⁻], we observed a decrease in the NiNW bundle diameter from 426 ± 91 down to 306 ± 57 nm (Table 2). This effect is very similar to the

capping action of polyvinylpyrrolidone in the course of AgNW formation [29]. In that case, the polymer wrapped around the nascent NW and caused the preferential addition of metal nanoclusters from the front, which caused an elongation of NW instead of an increase in bundle diameter. It is possible that the more hydroxyl anions in the medium, the finer the building blocks of NiNWs because under such circumstances, they can be more easily hydrated and thus separated from each other. Increasing the pH improved the yield from 51% (35 mL NaOH) to 85% (70 mL NaOH, Table 1, entry 2) before it decreased to 68% (100 mL NaOH), so there appears to be a sweet spot, at which the synthesis is most effective. The micrographs of the products are shown in Figure 2. The smaller bundle diameter NiNWs appear to be more tightly packed.

Table 2. The influence of pH on the product parameters.

Reaction Conditions					Product Parameters	
V_{NaOH} [mL]	$V_{\text{N}_2\text{H}_4}$ [mL]	V_{NiCl_2} [mL]	C_{NiCl_2} [M]	T [°C]	Yield [%]	Bundle Diameter [nm]
35	20	10	0.1	100	51	426 ± 91
50	20	10	0.1	100	51	387 ± 65
100	20	10	0.1	100	68	306 ± 57

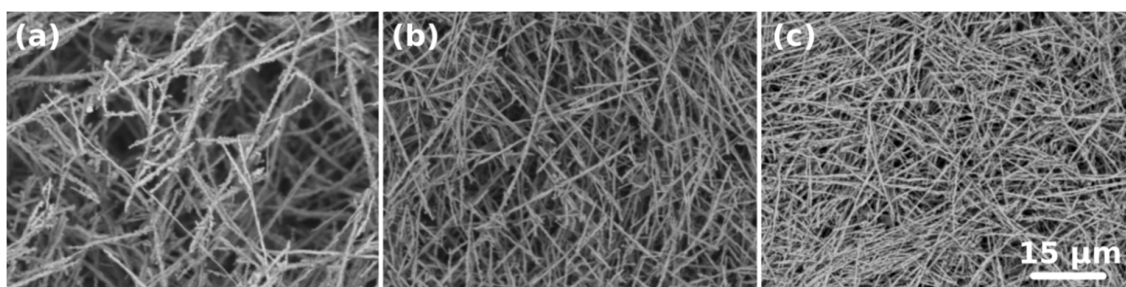


Figure 2. Micrographs of the NiNWs formed after the addition of a selected volume of 0.1 M NaOH: (a) 35 mL, (b) 50 mL, and (c) 100 mL.

2.2.3. NiNW Precursor Concentration

We found that the nickel concentration had a significant influence on the bundle diameter of the synthesized NiNWs. The higher the Ni concentration, the larger the bundle diameter of the produced NiNWs (Figure 3). It appears as if under high concentration conditions, the nucleating NiNW seeds grow larger and extrude NWs of the corresponding geometry. Moreover, high Ni ion concentration makes the addition of Ni from the radial direction more preferable when compared with the desired addition from the front. A decrease in Ni concentration mitigates the problem of this side reaction and the bundle diameter of the formed NWs decreases accordingly. By lowering the concentration of Ni ions from 0.5 M to 0.01 M, we were able to reduce the bundle diameter from 498 ± 103 to 316 ± 53 nm (Table 3). Moreover, the NiNW precursor concentration did not appear to have an effect on the yield of the process.

Table 3. The influence of NiNW precursor concentration on the product parameters.

Reaction Conditions					Product Parameters	
V_{NaOH} [mL]	$V_{\text{N}_2\text{H}_4}$ [mL]	V_{NiCl_2} [mL]	C_{NiCl_2} [M]	T [°C]	Yield [%]	Bundle Diameter [nm]
175	50	5	0.5	100	77	498 ± 103
175	50	25	0.1	100	85	451 ± 87
175	50	50	0.050	100	95	363 ± 55
175	50	100	0.025	100	95	354 ± 65
175	50	250	0.010	100	88	316 ± 53

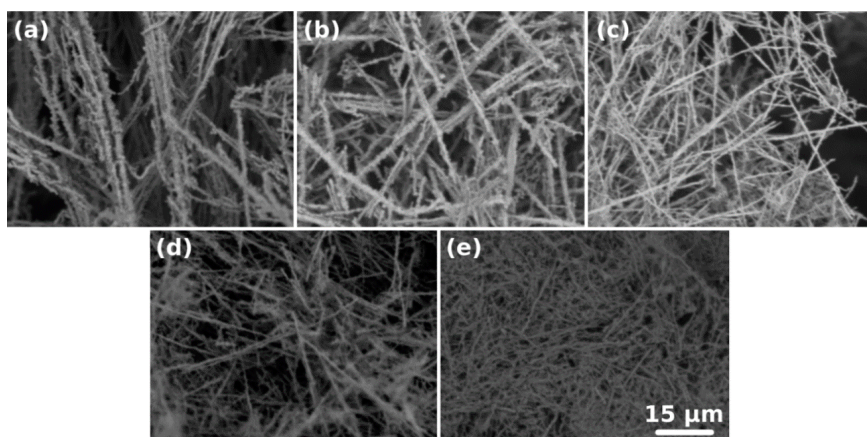


Figure 3. Micrographs of the NiNWs formed after the addition of a selected volume and concentration of 0.1 M NiCl_2 : (a) 5 mL/0.5 M, (b) 25 mL/0.1 M, (c) 50 mL/0.050 M, (d) 100 mL/0.025 M, and (e) 250 mL/0.010 M.

2.2.4. Alternative Reducing Agents

As the mechanism of the reaction shows, the addition of hydrazine is crucial because it enables the formation of some crucial intermediate nickel complexes. However, the use of hydrazine as a reducing agent is inconvenient because it tends to evaporate from the mixture, which must be kept at a high temperature for the reaction to take place at an appreciable rate. We explored a selection of nitrogen-bearing weak reducing agents as possible alternatives: ethylenediamine [30], aniline [31], and ammonia [32]. None of these reductants, however, enabled the synthesis of NiNWs (0% yield). After their addition, we obtained a violet solution, dark brown solution, and white precipitate, respectively.

We suspected that hydrazine as a ligand is somehow important for the reaction course (and also has a sufficiently potent reducing power), so we decided to try hydrazine sulfate as the alternative. Hydrazine sulfate is a solid at room temperature and since we operated in basic conditions, free hydrazine could be liberated in the controlled fashion, when needed. This would alleviate the problem of hydrazine evaporation during the heating up of the reaction mixture. Although the reaction did lead to NiNWs, very low yield (ca. 5%) and a high degree of contamination makes it an unviable route towards these nanostructures.

2.3. NW Composition

Crystallographic studies showed that the NiNWs resembled very much regular Ni (Figure 4). Reflections from (111), (200), (220) and (311) planes were observed. We did not detect signs of NiO on the surface.

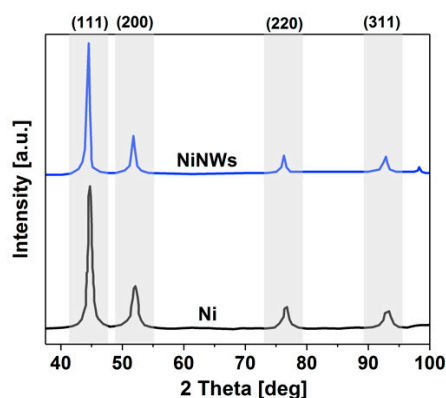


Figure 4. XRD patterns of NiNWs and Ni reference.

2.4. Catalytic Performance

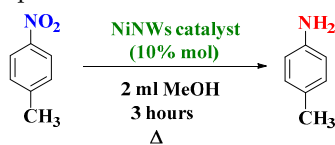
After satisfactory characterization, the catalyst NiNW (of mean 363 ± 55 nm bundle diameter) was further applied in the targeted selective reduction of nitroarenes. Although several methods have been reported for the reduction of nitrobenzene derivatives, they generally require expensive catalysts using precious metals like Rh, Pd, Ru, and Pt and need an extended time period for complete conversion. The analysis in Table 4 shows that NiNWs are very attractive from the financial point of view when compared with other routinely employed catalysts available on the market. The cost of a NiNW catalyst is more than four times lower than the price of Pd/C, Rh/C, or Pt/C (all 5% mol).

Table 4. Comparison of NiNWs and other traditional catalytic systems used for reduction of nitroarenes ^a.

Catalyst [%mol]	Equation of $N_2H_4 \cdot H_2O$	Temp. [°C]	Time [h]	Yield [%]	Cost of Catalyst for Reduction of 1 mol of 4-bromonitrobenzene [\$]	Ref.
Pd/C 5%	10.0	90	0.25	92	410	[33]
Rh/C 5%	1.0	40	3.0	90	290	[34]
Pt/C 5%	10.0	85	1.0	95	520	[35]
NiNWs	10.0	90	3.5	96	64	This work

^a Price for Pd/C, Rh/C, and Pt/C was taken from the website of VWR International. For NiNWs, the cost of precursors was also taken from the same vendor and the price of the final NiNW product was calculated based on the results of this work. The data have been normalized to the cost of the catalyst for the reduction of 1 mol of 4 nitrobenzene (experimental details in the referenced publications) and is presented in US dollars.

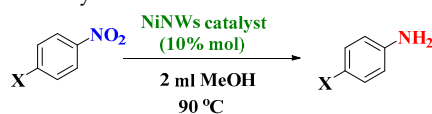
In the present work, we developed a mild reduction procedure that used a small amount of a low-cost non-noble catalyst (NiNW), followed with a simple work-up protocol. Initially, the reduction reaction was performed using 4-nitrotoluene as the model substrate with hydrazine hydrate as the hydrogen source at 65 °C (Table 5). After stirring for 3 h with the NiNW catalyst, the conversion was 5%. However, both the conversion and selectivity almost reached 100% after stirring for 4 h under higher temperature conditions (100 °C). The results demonstrated that the present catalytic system could be used to reduce the nitro group to an amino one. Encouraged by this promising result, we decided to examine the suitability of different reducing agents (sodium borohydride, formic acid, ammonium formate) as hydrogen sources in a reductive catalytic system with our catalyst (Table 5). Simultaneously, we proceeded to optimize the temperature of the reaction by studying the reduction of 4-nitrotoluene. In Table 5, we show the yields of a selected model compound (4-toluidine) obtained using different reducing agents at various temperatures. To our delight, we observed that hydrazine hydrate was the most effective reducing agent (10 mol-excess compared to nitroarenes). This affords a quantitative conversion into 4-toluidine within 3 h (Table 5, entry 3) with 94% yield. Hydrazine hydrate is a friendly reducing agent because decomposition produces only gaseous nitrogen and water as by-products. Moreover, no by-products such as azoxy-, azo- or 1,2-diarylhydrazine were detected in the obtained amines (analysis of ¹H NMR spectra). Other explored reducing agents did not afford the product in high yield or the reaction did not proceed (indicated with n.r. standing for no reaction) at all, regardless of the temperature conditions employed.

Table 5. Optimization of the reaction conditions ^a.

No.	[H]	Temp. [°C]	Yield [%]
1	N ₂ H ₄ *H ₂ O	65	5
2	N ₂ H ₄ *H ₂ O	75	30
3	N ₂ H ₄ *H ₂ O	90	94
4	N ₂ H ₄ *H ₂ O	100	92
5	NaBH ₄	65	10
6	NaBH ₄	75	15
7	NaBH ₄	90	18
8	NaBH ₄	100	18
9	HCOOH	65	n.r.
10	HCOOH	75	n.r.
11	HCOOH	90	n.r.
12	HCOOH	100	5
13	HCOOH	120	31
14	NH ₄ COOH	65	n.r.
15	NH ₄ COOH	75	n.r.
16	NH ₄ COOH	90	n.r.
17	NH ₄ COOH	100	n.r.
18	NH ₄ COOH	120	n.r.

^a Reaction conditions: Substituted nitroarenes (2.0 mmol), N₂H₄*H₂O (20.0 mmol), NiNW catalysts (10 mol% Ni), MeOH (2 mL), 90 °C. Products were isolated and determined by NMR. Optimum reaction conditions are highlighted.

In the next step, a selection of nitro-substrates were examined under the optimized reaction conditions (Table 6). Selective reduction of various substituted nitroaromatics to their corresponding aminoarenes occurred in high yields. Moreover, under our developed protocol, hydrazine exhibited chemoselectivity rather than classical reduction conditions as with hydrogen or sodium borohydride. We did not observe dehalogenation by-reaction of 4-bromonitrobenzene under our procedure with hydrazine and NiNWs.

Table 6. Synthesis of the substituted anilines ^a.

No.	Substrate	Time [h]	Product	Yield [%]
1		3.0		94
2		3.5		92
3		3.5		96
4		4.0		94

^a Reaction conditions: Substituted nitroarenes (2.0 mmol), N₂H₄*H₂O (20.0 mmol), NiNW catalysts (10 mol% Ni), MeOH (2 mL), 90 °C. Products were isolated and determined by NMR.

In all of the reductions in our protocol, the work-up of anilines was extremely simple. The reaction mixture was diluted using a large amount of ethyl acetate. Then, it was washed twice by water and

organic solvent was evaporated at diminished pressure. Finally, pure derivatives of anilines were obtained with yields exceeding 90%.

We also tested if this reaction system could be scaled up by one order of magnitude to evaluate its possible commercial potential. 4-nitrobenzoic acid was successfully converted into the corresponding amine with 94% yield (Supplementary Information). The positive outcome of this experiment at a gram scale is very encouraging because it proves that NiNWs can be used as powerful catalysts already beyond the laboratory scale.

3. Experimental

3.1. Materials and Methods

To synthesize NiNWs, the following chemicals of analytical grade were employed: nickel chloride hexahydrate (Acros Organics, Geel, Belgium), hydrazine monohydrate (64 %wt, Acros Organics, Geel, Belgium), hydrazine monohydrate (50 %wt, Acros Organics, Geel, Belgium), formic acid (85% aqueous solution, Acros Organics, Geel, Belgium), ammonium formate (Acros Organics, Geel, Belgium), sodium borohydride (Merck, Darmstadt, Germany), 4-Nitrotoluene (Merck, Darmstadt, Germany), 4-Bromonitrobenzene (Acros Organics, Geel, Belgium), nitrobenzene (Merck, Darmstadt, Germany), 4-Nitrobenzoic acid (Acros Organics, Geel, Belgium), methanol (SureSeal®, Acros Organics, Geel, Belgium), ethyl acetate (Chempur, Piekary Slaskie, Poland), ethylene glycol (Chempur, Piekary Slaskie, Poland), sodium bicarbonate (Chempur, Piekary Slaskie, Poland), and sodium hydroxide (Chempur, Piekary Slaskie, Poland).

The standard reaction conditions were as follows. 175 mL of 0.1 M NaOH solution in ethylene glycol (EG) was combined with 50 mL of 50 %wt N_2H_4 hydrate and the mixture was heated up to 120 °C. Then, 25 mL of 0.1 M $NiCl_2$ solution in EG was dripped into the mixture in the presence of a neodymium magnet able to hold 55 kg of load (kept in another beaker). Immediately formed NiNWs (in the form of a dark grey suspension) were attracted to the magnet. The method is shown in Figure 5. After the reaction, the NiNWs were separated from the liquid medium and washed thoroughly with water and isopropanol. We could not discern the presence of any other obvious sources of contamination such as precipitates of another color. Where indicated in the text, the conditions of the reaction were modified to tune the microstructure of the obtained product.

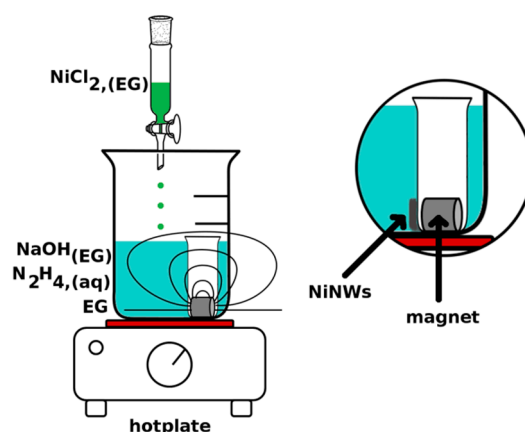


Figure 5. The method of synthesis used in the study. Only a selection of magnetic field lines are shown for the sake of clarity.

To carry out the reduction, the catalyst (10% mmol) was placed in a 10 mL glass reactor (Schlenk tube), followed by the addition of methanol (2 mL), nitroarene (1.0 mmol), reducing compound, and methanol. Then, the reaction was vigorously stirred for an appropriate time at elevated temperature (details of the synthesis are indicated in the text).

The microstructure of the material was probed by scanning electron microscopy (SEM) using a HITACHI TM3000 (Tokyo, Japan) with 5 kV acceleration voltage. The results are represented as the diameter of NiNW bundles as observed by SEM and measured using ImageJ software v. 1.52 (University of Wisconsin, UW, USA). To attain the statistical significance, tens of individual bundles were measured each time and the results are shown as mean \pm standard deviation.

The X-ray diffraction (XRD, Philips PW1050, Eindhoven, Netherlands) gauged the chemical identity of the NWs ($2\theta = 35\text{--}100^\circ$, 0.05° step, 2 s acquisition time).

NMR spectra were recorded at 298 K on an Agilent-MR NMR (Palo Alto, CA, USA; 400 MHz for 1 h and at 100.5 MHz for 13°C).

The progress of the reaction was monitored by TLC using silica-gel-coated aluminum plates with a fluorescence indicator (Merck, SiO₂ 60, F254) and visualized by UV light (254 nm and 365 nm) or dipping into an iodine chamber (well-closed chamber with a few crystals of elemental iodine and 10 g of silica gel).

Melting points (m.p.) were determined with a Boetius apparatus and are uncorrected.

Mass spectrometry were determined with an API 4000Q TRAP tandem mass spectrometer detector equipped with an electrospray ionization (ESI) source (Applied Biosystems/MDS SCIEX, Foster City, CA, USA).

More experimental details can be found in the Supplementary Information.

3.2. Catalytic Tests

3.2.1. General Procedure of Reduction of Nitroarenes

The appropriate nitrobenzene derivative (1.000 eq.) was added to a Schlenk tube and was dissolved in methanol (each 1 mL per 1 mmol of nitrobenzene derivative). Next, the loaded nickel nanowires catalyst (0.10 eq.) and reaction mixture was stirred at 50°C . Then, hydrazine hydrate (100%) was added slowly with a syringe and subsequently the temperature was raised to 90°C (vigorous hydrogen gas evolution was observed). The resulting mixture was stirred for an additional 3 to 4 h and cooled to room temperature. Then, it was diluted with ethyl acetate (each 15 mL per 1 mmol of substrate) and washed with saturated sodium carbonate (each 5 mL per 1 mmol of substrate) and twice with distilled water (each 5 mL per 1 mmol of substrate). The organic solution was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to give pure aniline derivatives. The purity of the product was sufficient as indicated by NMR spectra analysis.

3.2.2. Large-Scale Reduction of 4-Nitrobenzoic Acid

4-Nitrobenzoic acid (3.34 g, 20.0 mmol) was added to a Schlenk tube and dissolved in anhydrous methanol (20 mL) under a N₂ atmosphere (Schlenk line). Next, the loaded nickel nanowires catalyst (118 mg, 2.0 mmol) and reaction mixture was stirred at 50°C . Then, hydrazine hydrate (64% aqueous solution, 11.6 mL, 200.0 mmol) was added slowly with a syringe and subsequently the temperature was raised to 90°C (vigorous hydrogen gas evolution was observed). The resulting mixture was stirred for an additional 3 to 4 h and cooled to room temperature. Then, it was diluted with ethyl acetate (300 mL) and washed with saturated sodium carbonate (50 mL) and twice with distilled water (50 mL). The organic solution was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to give pure 4-aminobenzoic acid (2.58 g, 18.8 mmol, 94%). The purity of the product was sufficient as indicated by NMR spectra analysis.

3.2.3. Obtained Products

4-Methylaniline (2a). Following the general procedure above, the title compound (503 mg, 94%) was isolated as a white solid. Yield: 94%; m.p. $42\text{--}43^\circ\text{C}$; (lit. mp = $42\text{--}43^\circ\text{C}$); ¹H NMR (400 MHz, DMSO-d₆) δ 2.12 (s, 3H), 4.75 (bs, 2H), 6.46 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 20.11, 114.06, 123.96, 129.22, 146.04; MS (EI) m/z: 108.08 [M + H]⁺.

Aniline (2b). Following the general procedure above, the title compound (172 mg, 92%) was isolated as a colorless oil. Yield: 92%; b.p. 84 °C (lit. bp = 84 °C); ¹H NMR (400 MHz, DMSO-d₆) δ 4.97 (bs, 2H), 6.49 (tt, J = 7.3, 1.1 Hz, 1 H), 6.56 (dd, J = 8.5, 1.1 Hz, 2 H), 7.00 (dd, J = 8.5, 7.3 Hz, 2 H); ¹³C NMR (101 MHz, DMSO-d₆) δ 113.87, 115.65, 128.78, 148.56; MS (EI) m/z: 93.13 [M + H]⁺.

4-Bromoaniline (2c). Following the general procedure above, the title compound (495 mg, 96%) was isolated as a white-yellow solid. Yield: 96%; m.p. 62–63 °C; (lit. mp = 62–64 °C); ¹H NMR (400 MHz, DMSO-d₆) δ 5.23 (bs, 2 H), 6.51 (d, J = 8.8 Hz, 2 H), 7.12 (d, J = 8.8 Hz, 2 H); ¹³C NMR (101 MHz, DMSO-d₆) δ 106.00, 115.75, 131.28, 148.03; MS (EI) m/z: 172.02 [M + H]⁺, 174.02 [M + 2 + H]⁺.

4-Aminobenzoic acid (2d). Following the general procedure above, the title compound (386 mg, 94%) was isolated as a white solid. Yield: 94%; m.p. 188–189 °C; (lit. mp = 186–189 °C); ¹H NMR (400 MHz, DMSO-d₆) δ 5.84 (bs, 2 H), 6.54 (d, J = 6.6 Hz, 2 H), 7.61 (d, J = 6.7 Hz, 2 H), 11.39 (vbs, 1 H); ¹³C NMR (101 MHz, DMSO-d₆) δ 112.59, 116.93, 131.21, 153.10, 167.48; MS (EI) m/z: 159.12 [M + Na]⁺.

4. Conclusions

The nickel nanowires proved to be effective catalysts for the transfer hydrogenation of nitroarenes to the corresponding amine derivatives, using hydrazine as hydrogen donor. The reactions were carried out in mild conditions with very high yield, regardless of the substituents present on the aromatic ring. We also confirmed that these transformations could be executed on an enlarged scale. This indicates that this catalytic system could be useful for transformations at the industrial scale. The presented solution is very attractive as it can substitute traditionally employed metals such as Rh, Pd, Ru, and Pt for catalytic hydrogenation. These species are very expensive in contrast with NiNWs, which can be produced using cheap and widely available precursors. Finally, it is important to mention that NiNWs are stable in the ambient as opposed to other forms of Ni such as Raney nickel, which is pyrophoric, and thus dangerous. Improved safety and high catalytic activity make NiNWs attractive as catalysts for a wide range of chemical transformations.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/11/566/s1>. Experimental procedures for the synthesis of amine derivatives, and melting point data as well as copies of NMR spectra (¹H and ¹³C).

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