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Reactivity of electrochemically synthesised zinc nanofiber in facile reduction of nitro and azide compounds

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Electrochemistry is used in generation of metallic nano zinc wire from aqueous zinc chloride. For this electrochemical process we have designed a unit galvanic cell. During the electrochemical process both aliphatic and aromatic nitro and azide compounds undergo facile reduction to the corresponding amines. $ZnCl_2$ is used as stoichiometric reagent and causes electrochemical deposition of zinc in cathode. During the process wire shaped nano zinc architecture has been formed in cathode which is supposed to be the active reagent for reduction. The cathode deposited material has been characterised by powder XRD, XPS, FESEM, HRTEM, EDX, SQUID etc. The corresponding amines are prepared in good yields. Both zinc salts and aqueous solution can be recycled.

Keywords: Electrochemistry, Nano zinc, $ZnCl_2$, ITO glass, FESEM, SQUID, Nitro/Azide/Amine Reduction

With respect to sustainability electrochemical methods are well accepted because waste materials are eliminated and metal reagents can be reused[1]. On the other hand, aqueous reactions have been widely studied in order to reduce the use of flammable, toxic, or carcinogenic organic solvents[2]. A combination of aqueous and electrochemical conversion will be an excellent green synthetic approach[1,3].

Nanomaterials are deposited on cathode during the electrochemical process. Due to higher surface area nanomaterials show higher reactivity compared to bulk[4]. Synthesis of nanoarchitectures of different metals of a particular shape and size is always important because of their applications in nanotechnology. Metallic nanofibers have a huge number of technological applications. Perhaps the most obvious use for nanofibers is in electronics. Some nanofibers are very good conductors or semiconductors, and could fit millions more transistors on a single microprocessor. As a result, computer speed would increase dramatically. Nanofiber networks exhibit precisely the properties required for MIS silicon solar cells. Closely spaced and conductive metal fibers induce a junction for homogenous carrier extraction, and simultaneously a high optical transparency. Electrochemically synthesized fiber like nanoarchitecture was known in literature because of its wide application in nanotechnology[5]. Here we wish to report the temperature and agitation effect on electrochemical synthesis of metallic zinc nanofiber from aqueous zinc chloride solution (pH 2-2.5). The use of *in situ* generated zinc nanofiber for the facile reduction of nitro and azide functional groups was also explored. Process is efficient and a range of functional groups are stable in these mild reaction conditions. Cathode deposited zinc nanofiber was characterization by XRD, XPS, FESEM, HRTEM, EDX, SQUID.

Transformations of organic nitro and azide compounds to corresponding amines are very important processes in synthetic point of view because of their use as building blocks in natural products or multi step synthesis. Metal-mediated reductions are well-known examples of organic reactions in aqueous media[6]. But metal salts have been used in over stoichiometric ratio in many cases and subsequently end metal salts were generated as junk products. These junk metal by-products are also difficult to separate. In this respect zinc metal is very useful because of its low toxicity and cost. On the other hand lots of methods have been developed in aqueous medium because of its green nature[7]. But, activation of zinc is necessary by physical or chemical methods. In many cases addition of acidic co-reagent is necessary for chemical activation.

Materials and Methods

General procedure

The procedure given bellow was followed in all cases. All products showed satisfactory spectral and analytical data and matched with the literature.

Nitrobenzene reduction to aniline

To a stirred solution of 0.02 M $ZnCl_2$ in 10 ml H_2O-THF (8:2) at pH 2.5, 2 mmol of nitro substrate (A) was added. The stirring mixture was then electrolyzed in a unit cell at a current of 2 V and 20 mA in a beaker equipped with a zinc electrode and a ITO electrode (1x3 cm^2) at 70 ^oC with slow stirring. The electrolysis was stopped when the nitro substrate (A) had been completely consumed (TLC monitoring). After the electrolysis, zinc film was collected and the reaction mixture was concentrated under reduced pressure (i.e. THF was removed by evaporation). Then reaction mixture was diluted with distilled water (5 ml) and the aqueous reaction mixture was extracted twice with DCM (2x10 ml). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (100-200 mesh) and eluted at 1.5-3% MeOH-DCM to afford the desire amine product (P) (Yields~80-97%).

Azide reduction to amine

The reactivity of metallic zinc in the aqueous medium is worth mentioning. Here we wanted to report the reactivity of the deposited zinc nanomaterial for the reduction of azides. Materials with nanostructure have a large surface area than the bulk one. It enhances the number of reaction site for the reaction to occur. Keeping it in mind and triggered by our initial success of nitro reduction, we applied the standard condition of nitrobenzene reduction for azide reduction reactions also. In this reaction condition organic azides are reduced to corresponding amines with good to excellent yield.

Characterization techniques

Field emission scanning electron microscopy (FESEM) was used for size and shape of the Zn nanofiber with a supra 40, Carl Zeiss Pvt. Ltd. Instrument and an EDS machine (Oxford link and ISIS 300) attached to the instrument is used to obtain the elemental composition. The chemical states of Zn nanofiber was studied by X-ray photoelectron spectroscopy (XPS) using PHI 5000 Versa Probe II (ULVAC − PHI, INC, Japan) system equipped with microfocused (100 µm, 25 W, 15 KV) monochromatic Al-Kα X-ray source (hν = 1486.6 eV). The phase of Zn nanofiber was studied by X-ray diffraction (XRD) (Philips XPert MRD) at a grazing incidence mode using Cu Kα radiation (45 kV, 40 mA). TEM images have been done by TECNAI G2 20 S-TWIN (200KV) model with Resolution: 2.4A0 of FEI COMPANY, USA. TEM image analysis has been done by TIA (FEI imaging software), EMMENU4, EMTOOLS. Magnetic measurements were carried out by a SQUID magnetometer (Quantum Design, MPMS XL-7) in the temperature range of 5−300 K. Reactions were performed in oven-dried glassware.

Results and Discussion

Designing of unit galvanic cell

A unit galvanic cell has been designed with the help of aqueous zinc chloride solution kept in a simple laboratory glass beaker. Commercial zinc rod has been used as anode and ITO (indium tin oxide) glass plate (3x1 cm^2) has been used as cathode. Zinc rod and ITO glass plate has been short circuited externally by copper wire (Fig. 1a). External bias may be used insted of copper wire to construct the cell (Fig. 1b). It is already proved that galvanic cell using an external bias is much more efficient for organic transformation compared to a short-circuited unit galvanic cell[6]. The zinc rod served as a self-decaying anode and the ITO glass substrate as the cathode (Fig. 1). Throughout the process the pH of the solution was maintained within 2-2.5. This pH of the mixture was found to be optimal for desired zinc film deposition. Regeneration and redeposit of metallic zinc on cathode was done by reducing the spent zinc reagent on cathode. We chose the zinc-mediated reduction of nitro-compounds to corresponding amines. Our idea was to use the *in situ* generated

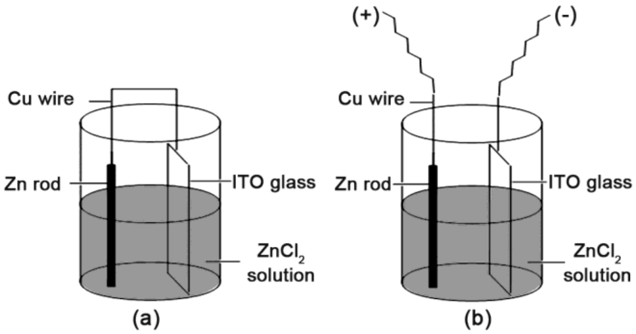


Fig. 1 — Electrochemical set up for the synthesis of thick Zn films.

metallic zinc for reduction reactions. Efficient reduction of nitrobenzene can take place in cathode and we obtained 40% yield of aniline at 40 °C in the first attempt in an undivided galvanic cell after 7 h using no external bias. We concluded that the reduction process in an undivided cell mainly takes place at the cathode where metallic zinc was deposited. In the same reaction conditions only when external bias is applied to 20 mA and 02 V 90% yield of aniline was obtained at 70 °C.

Synthesis of zinc nanofiber

The metallic zinc deposition from solutions of Zn(II) both in the presence and absence of organic reactants was studied. From 0.02 M $ZnCl_2$ solutions (pH 2-2.5), current 20 mA, ~80 mg of powder was deposited on cathode within 15 min as a thick film (F1) in a unit galvanic cell in presence of an external bias when no organic reaction was performed. Zinc deposition was determined by XRD analysis, EDX, EDX mapping, TEM picture, SQUID etc.

Effect of temperature

Clear increasing linear relationship has been obtained when CCE (cathode current efficiency) was plotted against temperature which shows influence of temperature. From Fig. 2 it can be clearly shown that when bath temperature was increased from 30 °C to 40°C the corresponding CCE also increased from 90.5% to 95.92%. Fig. 2 shows influence of bath temperature on CCE at a current density of 8 mA/cm^2, pH = 2.5, current = 20mA.

For determination of CCE the thickness of deposited zinc was measured by gravimetric analysis. After deposition of zinc in ITO plate, it was rinsed instantly in running tap water then immersed in acetone. Finally, it was dried in warm air and weight was taken to determine the amount of deposited zinc. After that CCE thickness of zinc was calculated by using the following mathematical equation:

$$CCE = (\Delta W/W_{Th}) \times 100\% \qquad \dots(1)$$

Where, CCE is cathode current efficiency (%), ΔW is change in weight after plating (g) and W_{Th} is theoretical weight of deposit (g)

$$\text{Whereas, } \frac{M_{Zn} \times T \times I}{N \times F} \qquad \dots(2)$$

Here I is current (Amp), T is time (s), M_{Zn} is molecular weight of zinc (g/mol), F= Faraday's constant (96,485 C/mol) and N is number of electrons involved in the reaction.

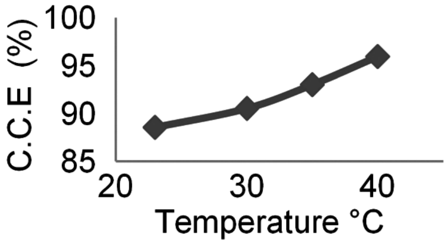


Fig. 2 — Influence of bath temperature on CCE.

Effect of agitation

It can be shown that at constant current density of 8 mA/cm^2, the current efficiency of the bath were found better at lower rates of agitation (Fig. 3). But with increase in agitation the current efficiency was found to decrease. During zinc deposition at limiting current density the concentration of zinc ion near the cathode is reduced instantly and as a result the cathode reaction now shifts from zinc deposition to hydrogen evolution, because in cathode there is always a competition between these two reactions. The Fig. 3 shows the change of CCE with the effect of agitation at current density of 8 mA/cm^2, pH=2.5 and T=23 °C. Thus, due to hydrogen evolution the pH near the cathode increases and thereby forming a mixture of zinc, zinc hydroxides and zinc oxides[8]. So, the agitation may lead to reduce the nucleation rate of zinc on cathode surface. The applied current in term is shared between the two processes: zinc deposition and hydrogen evolution[9,10]. Due to high hydrogen over potential and hydrogen evolution in this bath the main cathode reaction would have been hydrogen evolution. The evolved hydrogen is adsorbed on the cathode surface and could hinder zinc nucleation. So, for effective zinc deposition a higher current density increases both anode and cathode potentials and a large driving force is required to affect zinc depositions[11]. Actually agitation helps to prevent the adsorption of evolved hydrogen on the cathode surface and thereby enhancing the rate of zinc deposition which in term lead to an increase in current efficiency. But it actually does not happen in the present experimental process. The reason may be that

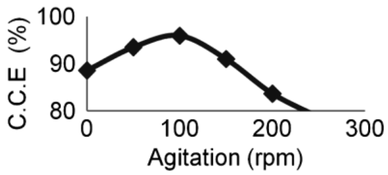


Fig. 3 — Influence of agitation on CCE.

higher agitation does not allow sufficient residence time for zinc ions to be reduced on the cathode surface. Thus, the agitation may have been adverse to the zinc deposition in widespread conditions.

Microstructural study

The SEM image (Fig. 4) shows that the thick deposit (F1) was in wire like nanoarchitecture in presence of a external bias (current 20 mA), ~80 mg of powder Zn(0) was deposited as a thick film within 15 min.

Magnetic property

To investigate the static magnetic behaviour of the sample, viz., magnetization (M) *vs*. field (H) curves, M vs. T curve under field cooled (FC) and zero field cooled (ZFC) conditions were recorded in quantum design superconducting quantum interference device (SQUID) magnetometer in the temperature range of 300-5 K and the magnetization was recorded during the rise of temperature. Fig. 5 shows the thermal variations of magnetization (M-T curves) in ZFC and FC conditions and for FC magnetization the sample was cooled from 300 K down to 5 K with an applied field of 500 Oe. From figure it is seen that ZFC magnetization increases slightly with the lowering of temperature from ~ 300 K down to ~ 150 K. But below ~ 150 K down to ~ 30 K, magnetization decreases with the lowering of temperature and attains a minimum value of 0.0015 emu/g at ~ 30 K, and below this temperature down to ~ 5 K magnetization increases rapidly with the lowering of temperature. The sharp rise in magnetization below ~ 30 K is the characteristic of DMS (dilute magnetic semiconductor) material.

Growth mechanism

The 1D growth of the nanofiber is directed by negative charge on ITO plate (cathode) and slowly the whole surface is covered with the Zn nanofiber[12].

Reactivity of zinc nanofiber

Initial success and optimization studies

We found that efficient reduction can take place and in the first attempt we obtained a 40% yield of aniline in an undivided galvanic cell after 7 h at 40 ^{o}C using no external bias (Table 1, entry-1). We concluded that reduction process in an undivided cell mainly takes place at the cathode, where metallic zinc is deposited. The pH of the solution was measured to be ~ 2.5. The reactivity of Zn(0) in the aqueous medium is noteworthy. After the initial success, we applied external bias of current (2 V, 20 mA for 7 h) for the reduction reaction of nitrobenzene. 0.02 M $ZnCl_2$ aqueous solution (pH 2-2.5) was stirred at room temperature for 7 h in a one-compartment galvanic cell (Fig. 1B, ITO glass foil 3x1 cm^2) to afforded 55% yield of the product (Table 1, entry-2). To increase the yield of the allylation reaction organic miscible solvent was added and temperature was increased. The detail standardisation of the reduction reaction has been described in Table 1. The pH of the solution can be varied by varying the concentration of $ZnCl_2$. By changing the pH of the reaction mixture, yield of the amine decreases (entries 3 & 4). So, the pH of the solution was optimised to be 2.5. Yield of the amine increases by increasing the solubility of the organic reactants by adding miscible organic solvent. The effect of THF addition is more prominent

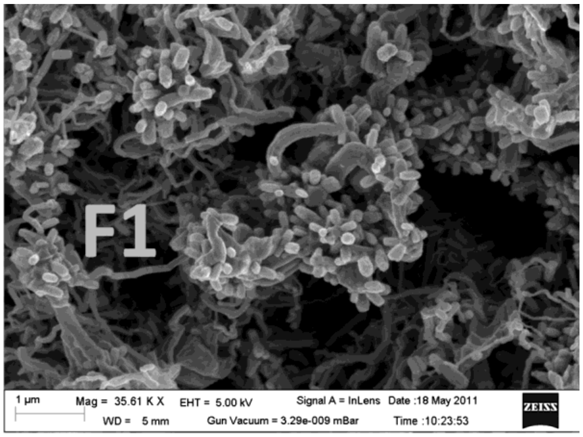


Fig. 4 — FESEM image of Zn nano fiber on the outer surface of ITO in presence of (F1) of external bias.

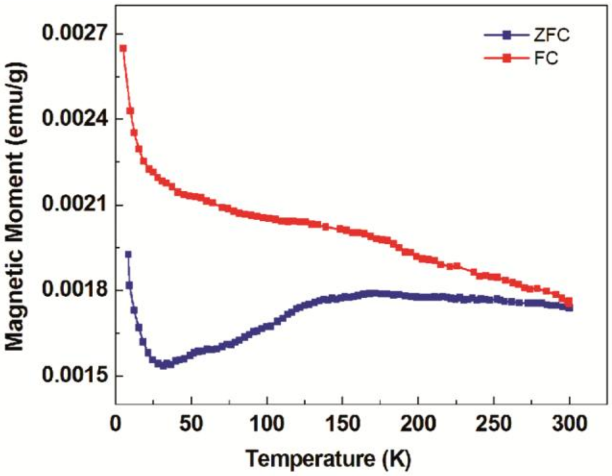
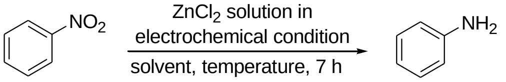


Fig. 5 — magnetization (M) *vs.* field (H) curves, M *vs*. T curve under field cooled (FC) and zero field cooled (ZFC) conditions were recorded in SQUID.

compared to DMF and MeOH (entry 7 *vs.* entries 5 & 6). Reducing the amount of the THF solvent, results in lower yield of the product (entry 7 *vs.* 8).

Table 1 — Standardisation of reduction of nitro substrate



S. N.	Electrochemical Conditions	Solvent	Temp (°C)	Yield (%)
1	Without external bias, pH 2.5	H_2O	40	40
2	2 V, 20 mA, 3.9 F/mol, pH 2.5	H_2O	40	55
3	2 V, 2 mA, 3.9 F/mol, pH 2	H_2O	40	45
4	2 V, 2 mA, 3.9 F/mol, pH 4	H_2O	40	30
5	2 V, 20 mA, 3.9 F/mol, pH 2.5	H_2O-MeOH (8:2)	40	61
6	2 V, 20 mA, 3.9 F/mol, pH 2.5	H_2O-DMF (8:2)	40	63
7	2 V, 20 mA, 3.9 F/mol, pH 2.5	H_2O-THF (8:2)	40	80
8	2 V, 20 mA, 3.9 F/mol, pH 2.5	H_2O-THF (9:1)	40	65
9	2 V, 20 mA, 3.9 F/mol, pH 2.5	H_2O-THF (8:2)	70	90

Condition: Nitrobenzene 4 mmol, solvent 10 ml H_2O-THF (8:2) containing 0.02 M $ZnCl_2$

The effect of any acid base additives like NaOH, HCl, HOAc is found to be negative probably because they changes the pH of the solution. The effect of other additives like NH_4Cl and NH_4Br is found to be negligible. By increasing the temperature of the reaction mixture up to 70 °C the yield of the reaction increases to 90% (entry 7 *vs.* 9). Optimized reaction conditions are those given in entry 9.

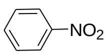
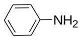
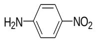
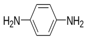
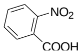
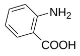
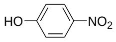
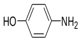
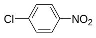
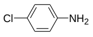
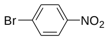
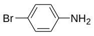
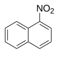
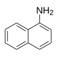
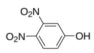
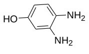
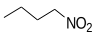
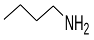
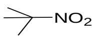
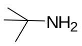
Generality of the nitro or azide reduction reactions

Reduction of aryl and aliphatic nitro compounds to corresponding amines is one of the important methods for the amine preparation. The reduction of aromatic and aliphatic nitro groups to anilines and aliphatic amines, respectively is performed with our electrochemical cell with good yields and selectivity in short reaction times. The method is highly successful for reduction of both aliphatic and aromatic nitro compounds with good to excellent yields. We applied external bias of current (2 V, 20 mA for 7 h) for the reduction of nitrobenzene. Amine was found to be the only product of reduction. The optimization reactions showed that using 0.02 molar equivalents of $ZnCl_2$ in a mixture of H_2O: THF (4: 1), pH 2.3-2.5 are the best conditions for the complete conversion of nitrobenzene into aniline. We applied the optimal conditions for the reduction of other nitro compounds (Table 2). We applied the optimal conditions for the

Table 2 — Reduction of nitro to amines

$$R{-}NO_2 \longrightarrow R{-}NH_2$$

A P

S. N.	Substrate	Time (h)	Product	Yield (%)	BP/MP (°C)	Reported (°C)
1.		2		90	183-184 BP	184
2.		2		93	143-145 MP	143-145
3.		3		96	146-148 MP	146-148
4.		4		92	188-190 MP	168
5.		2		94	70-72 MP	68-72
6.		4		96	63-65 MP	60-64
7.		2		95	49-51 MP	47-50
8.		5		88	221-223 MP	223
9.		6		94	77-78 BP	78
10.		7		91	45-46 BP	44-45

Conditions: nitro substrate 4 mmol, solvent 10 ml H_2O-THF (8:2), 0.02 M $ZnCl_2$ solution, 2 V, 20 mA, pH 2.5, 70 °C reduction of a variety of nitro compounds to their corresponding amines. The product amines were obtained in high to excellent yields within 2–7 h. The chemoselective reduction of nitro group in the presence of carboxylic acid was proven with the reduction of 2-nitrobenzoic acid to anthranilic acid in 96% yield (Table 2, entry 3). The complete reduction of arenes with two nitro groups was also achieved perfectly by this protocol. Attempts to perform chemoselective reduction of one nitro group in the presence of the other were unsuccessful. Primary and tertiary aliphatic nitro compounds were reduced to their corresponding amines in excellent yields at same conditions (Table 2, entries 9-10).

Similarly aliphatic and aromatic azides are reduced to corresponding amines following the same reaction conditions (Table 3). Aliphatic azides such as benzyl or substituted benzyl azides are reduced to corresponding amines (entries 1-3, 8). Aryl azides or substituted aryl azides are equally efficient to be reduced to corresponding amines (entry 7). Acyl azides are smoothly reduced to corresponding amides (entries 5 & 6). Aromatic and aliphatic sulfonyl azides are easily reduced to corresponding sulfonamides (entries 4 & 9). The mechanism of this protocol is not clearly understood; however, in our experiments, some results are noteworthy. In all reductions, the immediate deposition of a fine grey shiny metal was observed on ITO cathode. We rationalize that reduction of nitro compounds is probably due to formation of the gray deposition of metallic zinc.

Recycling of the reagent

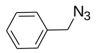
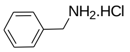
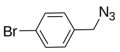
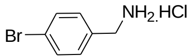
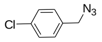
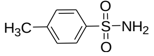
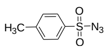
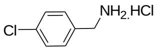
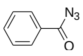
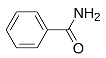
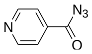
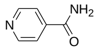
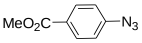
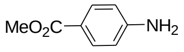
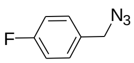
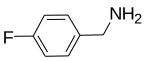
Recycling of the $ZnCl_2$ reagent can be easily achieved for this electrochemical process. After extraction of the reaction mixture with diethyl ether remaining aqueous layer can be reused for the next cycle without further purification. To reuse the remaining $ZnCl_2$ solution, some THF (v/v, 25%) should be added to get good yield of the amine product for the next cycles. The yield of the second and third cycles is very much similar to the 1st cycle. Up to the 5th cycle decrease of the yield of amines is not very significant (Table 4).

Comparative reactivity study of different types of zinc depending up on surface morphology

The high activity of deposited Zn towards the reduction of simple aryl and aliphatic nitro compounds to corresponding amines might be attributed to its special fiber like 3D nanoarchitecture.

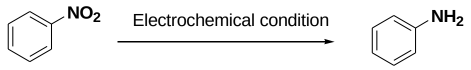
Table 3 — Reduction of azide to amines

$$R{-}N_3 \longrightarrow R{-}NH_2$$

S. N.	Substrate	Time (h)	Product	Yield (%)	BP/MP (°C)	Reported (°C)
1.		2		88	MP.258-260	255-257
2.		2		90	MP:258-260	279
3.		3		86	MP:260-262	259
4.		3		90	MP136-139	138.5
5.		4		75	MP 126-128	130
6.		2		94	MP 125-127	129-130
7.		3		92	MP 108-110	110
8..		4		85	MP 282-284	282-284
9.	$CH_3SO_2N_3$	2	$CH_3SO_2NH_2$	78	MP 84-86	88

Conditions: azide substrate 4 mmol, solvent 10 ml H_2O-THF (8:2), 0.02 M $ZnCl_2$ solution, 2 V, 20 mA, pH 2.5, 70 °C

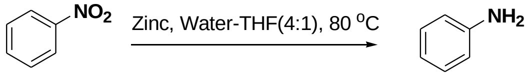
Table 4 — Recycling of the reagents[a]



S. No.	Cycle No.	Yield (%)
1	1st	90
2	2nd	84
3	3rd	82
4	4th	80
5	5th	78

Conditions: 0.02 M $ZnCl_2$ in 10 ml H_2O-THF (8:2) at pH 2.5, 2 mmol of nitro substrate (A), current 2 V and 20 mA, 70 °C

Table 5 — Comparative reactivity study of different types of zinc depending up on surface morphology:[a]



S.N.	Zinc reagents	Time (h)	Nitro reduction Yield (%)
1	Rieke zinc synthesized	17	69
2	Zinc powder 325 mesh (SRL)	17	56
3	Zinc powder 200 mes (Merck)	17	46
4	Zinc granules 30 mesh (Sigm Aldrich)	17	22
5	Zinc foil 0.38 mm (commercial)	17	trace
6	Zinc (F1, this work)	17	85

Conditions: nitrobenzene 2 mmol, zinc 2 mmol and H_2O-THF(4:1) 3 ml

A preliminary comparative reactivity study of different types of zinc depending up on surface morphology was carried out using Rieke zinc, commercial zinc powders, granules, foils etc. under non electrochemical conditions (Table 5). F1 showed the highest reactivity (Yield=85%) towards the reduction of nitrobenzene in water-THF (4:1). Under non-electrochemical conditions, the reduction reaction mediated by F1 was less effective compared to that in electrochemical process (yield 90%). However, in the non-electrochemical process, pH value during the reaction was not acidic (pH 6.5-7).

Conclusions

The effect of agitation and temperature on electrochemical synthesis of fiber like metallic zinc nanoarchitecture and their characterization is reported. To the best of our knowledge, electrochemical synthesis of fiber like nano architecture of metallic zinc from aqueous $ZnCl_2$ solution has been reported for the first time from our laboratory. An efficient aqueous electrochemical synthesis of amines from simple nitro compounds and azides has been developed by the electrochemical process. Amines are synthetically important building blocks for complex molecules. The deposited zinc(0) powder with nanofiber architectures played an important role in the synthesis of aromatic and aliphatic amines. Green nature rendered this methodology as an attractive synthetic route to zinc nanofiber as well as amines. We are deeply engaged in understanding the exact nature of the intermediates and mechanism of the reduction reaction. Further scope to explore the reactivity of the zinc nanofiber is underway in our laboratory.

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Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(08)1076-1083_SupplData.pdf.

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