

Zn-mediated electrochemical allylation of aldehydes in aqueous ammonia

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General methods

Commercial solvents and reagents were used without further purification with the following exceptions: benzaldehyde, furan-2-carbaldehyde, cinnamaldehyde and 3-phenylpropanal were distilled before use, and secondary distilled water was used for the reaction.

Crotyl bromide was purchased from Aldrich; heptanal and cyclohexanecarbaldehyde was purchased from Alfa, 3-methylbenzaldehyde, picolinaldehyde, cinnamaldehyde, 3-phenylpropanal and allyl bromide were products from Alfa; furan-2-carbaldehyde, 4-methoxybenzaldehyde, 2-hydroxybenzaldehyde, 4-chlorobenzaldehyde and 2-oxoacetic acid were purchased from Aladian Corporation in China; zinc foils (98%) were purchased from domestic corporation.

Analytical thin layer chromatography (TLC) plates and the silica gel for column chromatography were phased from Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd.

Proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on Bruker Advance 300 and 500 NMR spectrometers. Chemical shifts of ^1H NMR spectra are reported as in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-*d* ($J = 7.264$, singlet). Multiplicities were given as: s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (n) for a given resonance is indicated by nH. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-*d* ($J = 77.03$, triplet).

Cyclic voltmmetry (CV) analysis was performed on Auto Lab[®] PGSTAT30 (product from Metrohm AG, Switzerland).

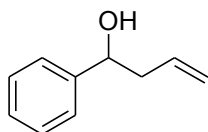
SEM image was performed on SE-30 EXEM.

X-ray diffraction (XRD) data were collected on a PANalytical (Netherlands) X'Pert PRO X-ray diffractometer.

Experimental procedure

General procedure for the allylation of benzaldehyde: A mixture of benzaldehyde (0.5 mmol), allyl bromide (1.0 mmol) in aqueous ammonia (4.5 M, 5 mL, diluted from 1.5 mL of 25% (w/w) ammonia with water) was stirred in a round-bottom flask cell equipped with a pair of zinc electrodes (1.5 cm^2) at room temperature. The suspension was electrolyzed at a constant current (15 mA) until benzaldehyde was completely consumed (2 F mol^{-1} of current was consumed, 1.5-2 hrs). The reaction mixture was quenched by 3 M HCl, and then extracted with diethyl ether ($2 \times 10\text{ mL}$). The combined organic layer was washed with water (5 mL), brine (5 mL) and then dried over anhydrous magnesium sulfate. The organic solvent was removed on a rotary evaporator under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 7:1) and the corresponding homoallylic alcohol was obtained as a colourless liquid (**3a**, 68 mg, 92%). The totally consumed Zn on the electrodes was 43 mg, 0.66 mmol. The authenticities of the products are verified by comparing their ^1H NMR and ^{13}C NMR spectral with reported data.

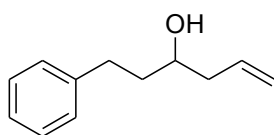
Spectroscopic data of products



1-phenylbut-3-en-1-ol

3a (68 mg, 92%) colourless oil δ_{H} (500 MHz; CDCl_3 ; Me_4Si) 2.16 (1 H, br s, CHOH), 2.47-2.56 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 4.73 (1 H, dd, J 5.4 and 7.6 Hz, CHOH), 5.13-5.19 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.77-5.86 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.26-7.36 (5 H, m, $5 \times \text{Ph}$); δ_{C} (500 MHz; CDCl_3 ; Me_4Si) 43.7, 73.2, 118.2, 125.7, 127.4, 128.3, 134.4, 143.8.

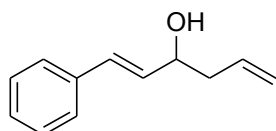
Reference: Yamamoto, Y.; Yatagi, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969.



1-phenylhex-5-en-3-ol

3b (71 mg, 70%) colourless oil δ_{H} (300 MHz; CDCl_3 ; Me_4Si) 1.77-1.81 (2 H, m, $2 \times \text{PhCH}_2\text{CH}_2$), 2.16-2.22 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.30-2.35 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.66-2.84 (2 H, m, $2 \times \text{PhCH}_2\text{CH}_2$), 3.67-3.69 (1 H, m, CHOH), 5.13-5.16 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.79-5.85 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.09-7.30 (5 H, m, $5 \times \text{Ph}$). δ_{C} (300 MHz; CDCl_3 ; Me_4Si) 32.0, 38.4, 42.0, 69.9, 118.3, 125.8, 128.3, 128.4, 134.6, 142.0.

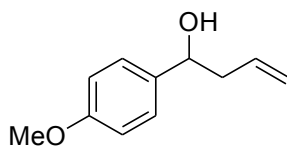
Reference: Schmidt, B. *J. Org. Chem.* **2004**, *69*, 7772.



(*E*)-1-phenylhexa-1,5-dien-3-ol

3c (61 mg, 70%) colourless oil δ_{H} (300 MHz; CDCl_3 ; Me_4Si) 2.28-2.43 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 4.30 (1 H, dd, J 6.0 and 12.3 Hz, CHOH), 5.09-5.14 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.73-5.84 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.18 (1 H, dd, J 6.3 and 16.0 Hz, $\text{CH}=\text{CH}$), 6.54 (1 H, d, J 16.0 Hz, $\text{CH}=\text{CH}$), 7.13-7.46 (5 H, m, $5 \times \text{Ph}$); δ_{C} (300 MHz; CDCl_3 ; Me_4Si) 42.0, 71.7, 118.5, 126.5, 127.7, 128.6, 130.3, 131.5, 134.0, 136.6.

Reference: Kobayashi, S.; Nagayama, S. *J. Org. Chem.* **1996**, *61*, 2256.

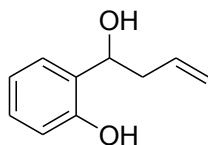


1-(4-methoxyphenyl)but-3-en-1-ol

3d (76 mg, 85%) colourless oil δ_{H} (500 MHz; CDCl_3 ; Me_4Si) 1.94 (1 H, br s, CHOH), 2.41-2.44 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 3.72 (3 H, s, $3 \times \text{OCH}_3$), 4.61 (1 H, t, J 6.3 Hz, CHOH), 5.04-5.09 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.68-5.76 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.80-7.21 (4 H, m, $4 \times \text{Ph}$); δ_{C} (500 MHz; CDCl_3 ;

Me₄Si) 42.8, 54.3, 72.1, 112.9, 117.2, 126.1, 133.7, 135.2, 158.1.

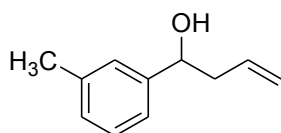
Reference: Dam, J. H.; Fristrup, P.; Madsen, R. *J. Org. Chem.* **2008**, *73*, 3228.



2-(1-hydroxybut-3-enyl)phenol

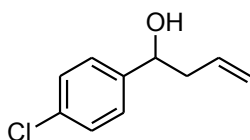
3e (59 mg, 85%) colourless oil δ_{H} (500 MHz; CDCl₃; Me₄Si) 2.48-2.59 (2 H, m, 2 × CH₂CH=CH₂), 2.94 (1 H, br s, CHOH), 4.79 (1 H, dd, *J* 5.0 and 8.2 Hz, CHOH), 5.12-5.15 (2 H, m, 2 × CH₂CH=CH₂), 5.72-5.81 (1 H, m, CH₂CH=CH₂), 6.75-7.11 (4 H, m, 4 × Ph); δ_{C} (500 MHz; CDCl₃; Me₄Si) 42.0, 74.5, 117.1, 119.1, 119.7, 126.4, 127.0, 128.8, 133.8, 155.3.

Reference: Zhang, T.; Shi, M.; Zhao, M. *Tetrahedron* **2008**, *64*, 2412.



1-*m*-tolylbut-3-en-1-ol

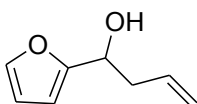
3f (67 mg, 82%) colourless oil δ_{H} (500 MHz; CDCl₃; Me₄Si) 2.11 (1 H, br s, CHOH), 2.31 (3 H, s, CH₃), 2.40-2.48 (2 H, m, 2 × CH₂CH=CH₂), 4.63 (1 H, dd, *J* 5.4 and 7.3 Hz, CHOH), 5.07-5.13 (2 H, m, 2 × CH₂CH=CH₂), 5.71-5.79 (1 H, m, CH₂CH=CH₂), 7.02-7.20 (4 H, m, 4 × Ph); δ_{C} (500 MHz; CDCl₃; Me₄Si) 21.4, 43.7, 73.3, 118.1, 122.8, 126.4, 128.1, 128.2, 134.5, 137.9, 143.8.



1-(4-chlorophenyl)but-3-en-1-ol

3g (64 mg, 70%) colourless oil δ_{H} (500 MHz; CDCl₃; Me₄Si) 2.35-2.45 (2 H, m, 2 × CH₂CH=CH₂), 4.63 (1 H, dd, *J* 5.0 and 7.6 Hz, CHOH), 5.06-5.10 (2 H, m, 2 × CH₂CH=CH₂), 5.66-5.74 (1 H, m, CH₂CH=CH₂), 7.19-7.25 (4 H, m, 4 × Ph); δ_{C} (500 MHz; CDCl₃; Me₄Si) 43.7, 72.5, 118.6, 127.1, 128.4, 133.1, 133.9, 142.2.

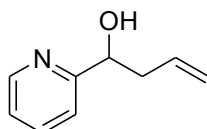
Reference: Makoto, W.; Hidenori, O.; Kinya, A. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1738.



1-(furan-2-yl)but-3-en-1-ol

3h (58 mg, 84%) colourless oil δ_{H} (500 MHz; CDCl₃; Me₄Si) 2.52-2.58 (2 H, m, 2 × CH₂CH=CH₂), 4.68 (1 H, t, *J* 6.3 Hz, CHOH), 5.06-5.13 (2 H, m, 2 × CH₂CH=CH₂), 5.69-5.78 (1 H, m, CH₂CH=CH₂), 6.18 (1 H, d, *J* 3.1 Hz, furyl), 6.26 (1 H, dd, *J* 1.9 and 3.1 Hz, furyl), 7.30-7.31 (1 H, m, furyl); δ_{C} (300 MHz; CDCl₃; Me₄Si) 40.0, 66.9, 106.1, 110.1, 118.5, 133.7, 142.0, 156.0.

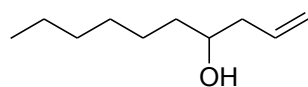
Reference: Wang, Z.; Zha, Z.; Zhou, C. *Org. Lett.* **2002**, *4*, 1683.



1-(pyridin-2-yl)but-3-en-1-ol

3i (46 mg, 84%) yellow oil δ_{H} (300 MHz; CDCl_3 ; Me_4Si) 2.40-2.54 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.55-2.67 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.74-4.80 (1 H, m, CHOH), 5.06-5.15 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.74-5.91 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.15-7.22 (1 H, m, *pyridyl*), 7.26-7.32 (1 H, m, *pyridyl*), 7.63-7.71 (1 H, m, *pyridyl*), 8.52-8.53 (1 H, m, *pyridyl*); δ_{C} (300 MHz; CDCl_3 ; Me_4Si) 42.9, 72.2, 118.0, 120.4, 122.3, 134.1, 136.6, 148.2, 161.3.

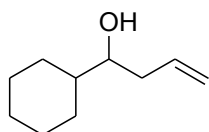
Reference: Kobayashi, S.; Nagayama, S. *J. Org. Chem.* **1996**, *61*, 2256.



dec-1-en-4-ol

3j (39 mg, 50%) colourless oil δ_{H} (300 MHz; CDCl_3 ; Me_4Si) 0.87 (3 H, m, CH_3), 1.15-1.50 (10 H, m, $10 \times \text{CH}_2$), 2.05-2.18 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.23-2.39 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.61 (1 H, m, CHOH), 5.06-5.18 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.74-5.92 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$).

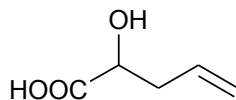
Reference: Jiang, S.; Agoston, G. E.; Chen, T.; Cabal, M-P. and Turos, E. *Organometallics*, **1995**, *14*, 4697.



1-cyclohexylbut-3-en-1-ol

3k (41 mg, 53%) colourless oil δ_{H} (500 MHz; CDCl_3 ; Me_4Si) 0.91-1.32 (4 H, m, $4 \times \text{cyclohexyl}$), 1.56-1.82 (7 H, m, $7 \times \text{cyclohexyl}$), 2.03-2.10 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.23-2.30 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.30-3.35 (1 H, m, CHOH), 5.06-5.10 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.72-5.82 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$)

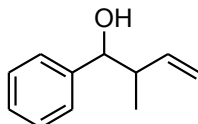
Reference: Li, G.-L. and Zhao, G. *Org. Lett.* **2006**, *8*, 633.



2-hydroxypent-4-enoic acid

3l (28 mg, 48%) colourless oil δ_{H} (300 MHz; CDCl_3 ; Me_4Si) 2.40-2.47 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.54-2.62 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.28 (1 H, dd, J 4.4 and 6.6 Hz, CHOH), 5.11-5.16 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.72-5.81 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$). δ_{C} (300 MHz; CDCl_3 ; Me_4Si) 38.3, 69.8, 119.3, 132.1, 178.3.

Reference: Kaur, P.; Singh, P.; Kumar, S. *Tetrahedron* **2005**, *61*, 8231.



2-methyl-1-phenylbut-3-en-1-ol

3m (76 mg, 94%) colourless oil δ_{H} (300 MHz; CDCl_3 ; Me_4Si) (*syn* isomer) 0.99 (3 H, d, J 6.8 Hz, CH_3), 2.41-2.60 (1 H, m, CHCH_3), 4.59 (1 H, d, J 5.5 Hz, CHOH), 4.98-5.07 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.66-5.86 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.20-7.37 (5 H, m, $5 \times \text{Ph}$). (*anti* isomer) δ 0.85 (3 H, d, J 6.8 Hz, CH_3), 2.41-2.60 (1 H, m, CHCH_3), 4.34 (1 H, d, J 7.8 Hz, CHOH), 5.12-5.22 (2 H, m, $2 \times \text{CH}_2\text{CH}=\text{CH}_2$), 5.66-5.86 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.20-7.37 (5 H, m, $5 \times \text{Ph}$). δ_{C} (300 MHz; CDCl_3 ; Me_4Si) (*syn* isomer) 14.0, 44.6, 77.2, 115.6, 126.5, 127.3, 128.0, 140.3, 142.5; δ_{C} (*anti* isomer) 16.5, 46.3, 77.8, 116.9, 126.8, 127.6, 128.2, 140.6, 142.4.

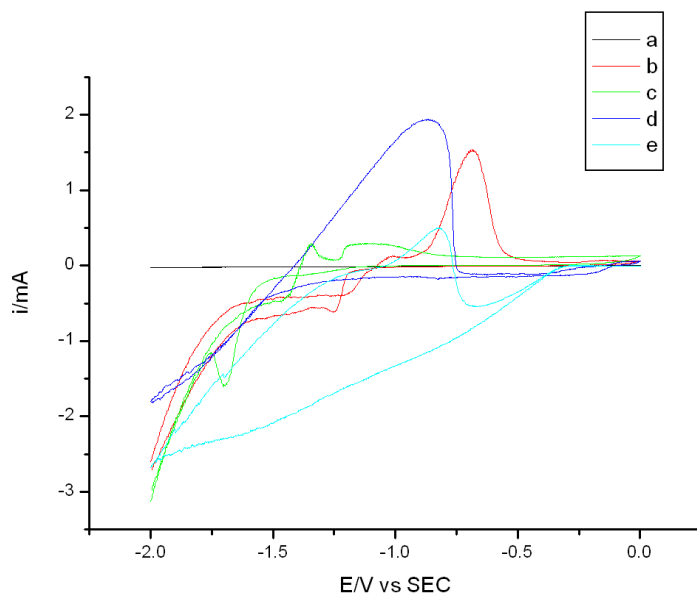
Reference: Wang, Z.; Zha, Z.; Zhou, C. *Org. Lett.* **2002**, *4*, 1683.

procedure of electrodeposition

General Electrodeposition procedure: 0.1 M LiClO_4 solution (or 0.1 M NaOH, 0.1 N H_2SO_4 and 4.5 M aqueous ammonia) was electrolyzed at constant current of 15 mA in a round-bottom flask cell equipped with a pair of zinc electrodes (1.5 cm^2) at room temperature for 2 hrs. The Zn powder deposited on the cathode was collected, washed and weighted.

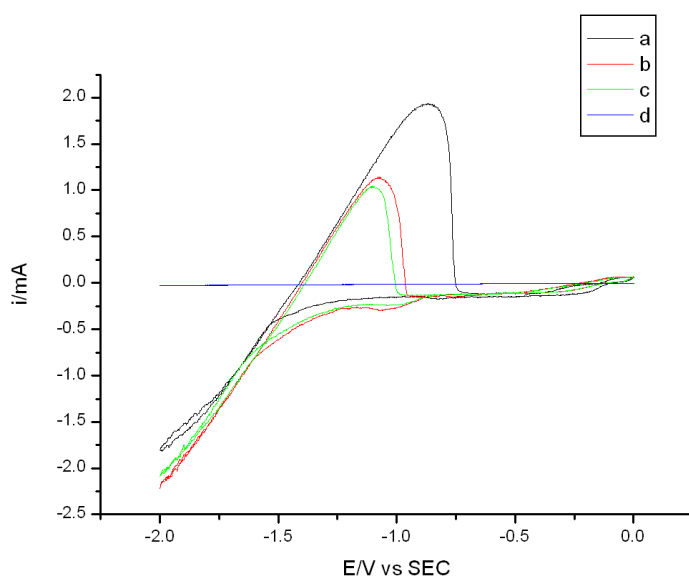
Cyclic voltammograms of Zn^{2+} in different solutions in the absence of reactants

The electrochemistry of Zn deposition from 0.1 N H_2SO_4 , 0.1 M LiClO_4 , 0.1 M NaOH and 4.5 M aqueous ammonia solutions was investigated by cyclic voltmetry (CV) with the same concentration of zinc (II) salt (Figure 2). The available experimental data did not allow full understanding of the deposition mechanism. However, curves of zinc deposition recorded in different solutions exhibited different reduction potentials. As we can see from the following Figure, deposition in 4.5 M aqueous ammonia solution started from - 0.1 V, which was the one who deposited easiest, compared that with 0.1 N H_2SO_4 (-0.3V), 0.1 M LiClO_4 (-1.1V) and 0.1 M NaOH (-1.5V).



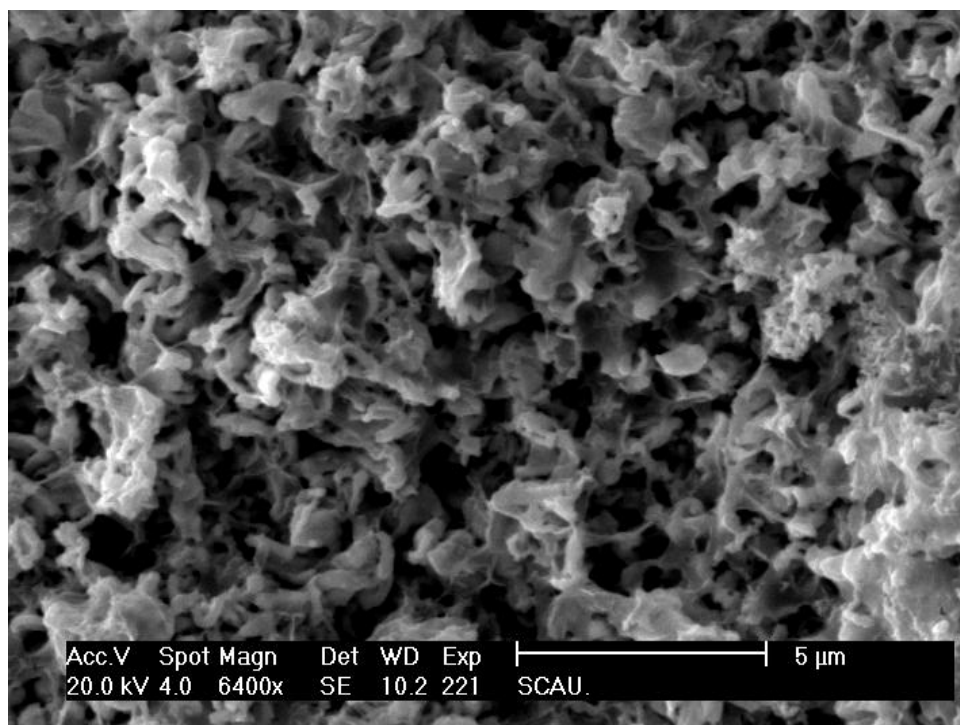
Cyclic voltammograms of the solutions recorded at a scan rate of 50 mV s^{-1} at rt with two platinum electrodes (12 mm^2). (a) H_2O only. (b) 13 mM ZnCl_2 , 0.1 N LiClO_4 . (c) 13 mM ZnCl_2 , 0.1 N NaOH . (d) 13 mM ZnCl_2 , 4.5 M aqueous ammonia solution. (e) 13 mM ZnCl_2 , $0.1 \text{ N H}_2\text{SO}_4$ (a minimal scale represent 5 mA on Y axis for curve e)

Cyclic voltammograms of Zn^{2+} in 4.5 M aqueous ammonia solution in the presence of organic reactants

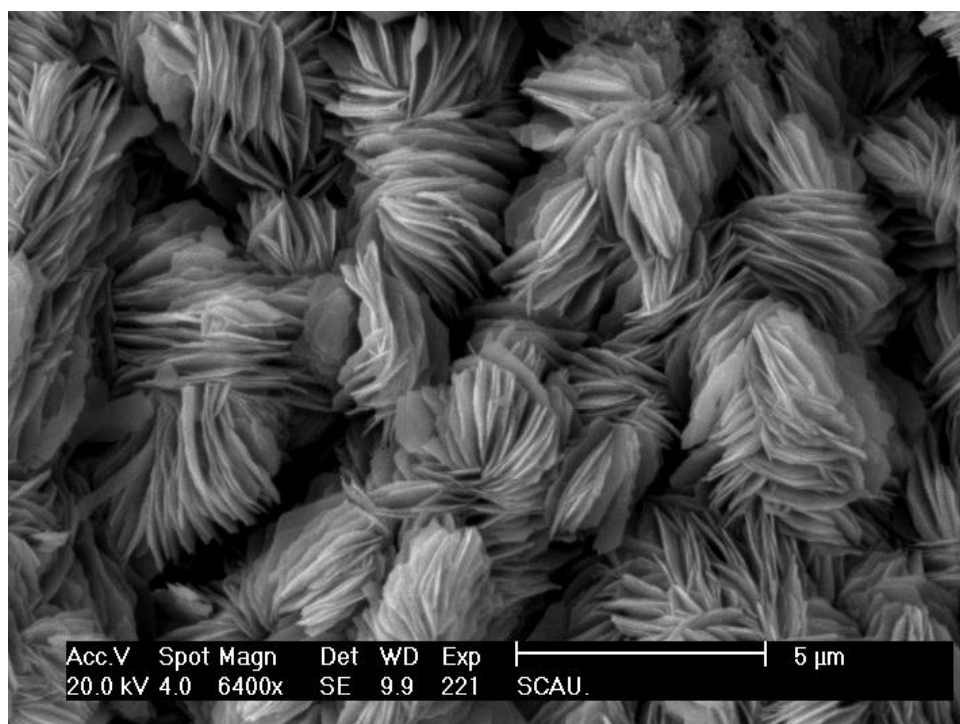


Cyclic voltammograms of the solution recorded at a scan rate of 50 mV s^{-1} and room temperature with two platinum electrodes (12 mm^2). (a) 13 mM ZnCl_2 , 4.5 M aqueous ammonia solution. (b) 13 mM ZnCl_2 , 20 mM allyl bromide, 4.5 M aqueous ammonia solution. (c) 13 mM ZnCl_2 , 10 mM benzaldehyde, 20 mM allyl bromide, 4.5 M aqueous ammonia solution. (d) H_2O only.

SEM image of Zn particles deposited from 4.5 M aqueous ammonia solution and 0.1 N H₂SO₄ solution

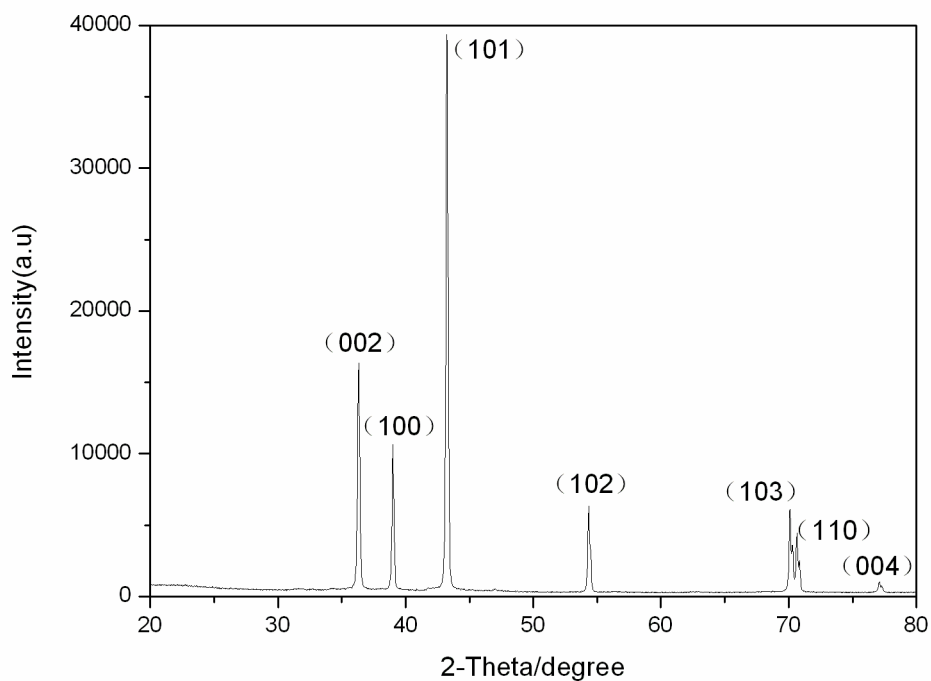


SEM image of Zn particles deposited from 4.5 M aqueous ammonia solution

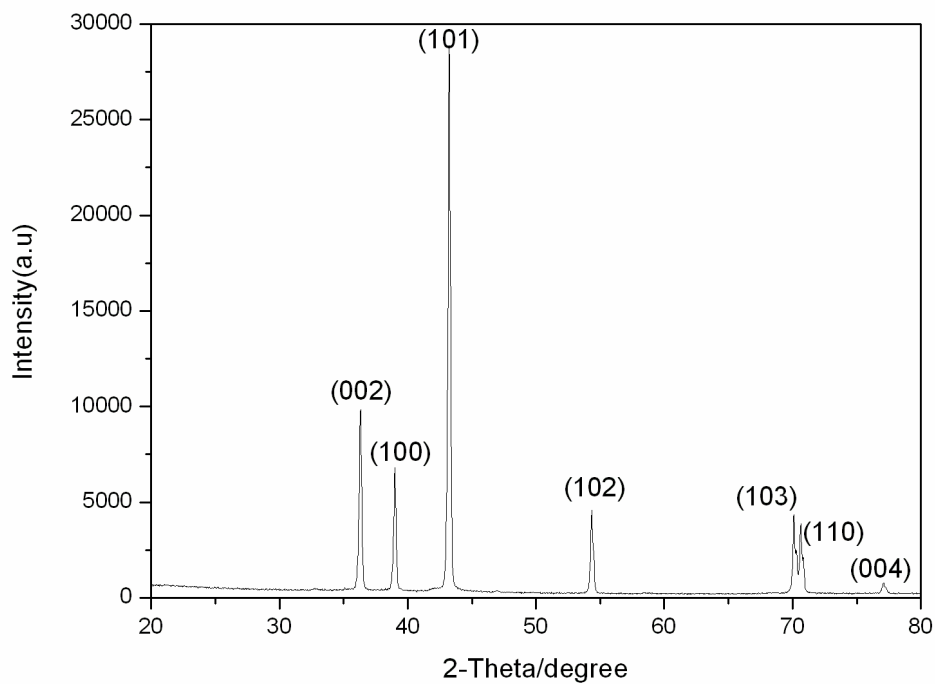


SEM image of Zn particles deposited from 0.1 N H₂SO₄ solution

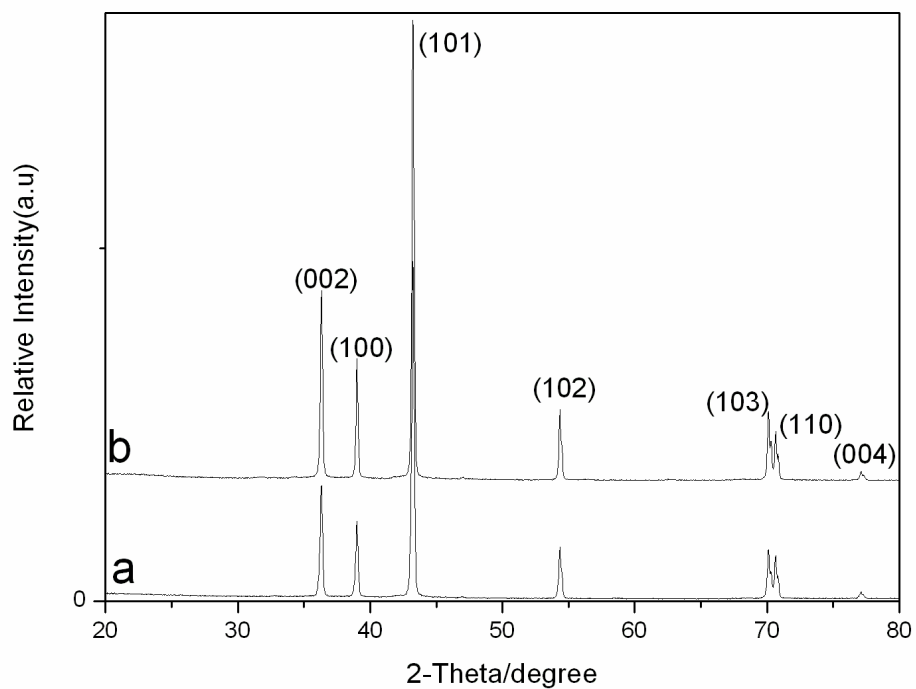
X-ray diffraction spectrum of Zn particles prepared in 4.5M aqueous ammonia solution and 0.1 N H₂SO₄ solution



X-ray diffraction spectrum of deposits from 4.5 M aqueous ammonia solution



X-ray diffraction spectrum of Zn particles deposited from 0.1 N H₂SO₄ solution



Comparison of X-ray diffraction spectrum of deposits from 4.5 M aqueous ammonia solution and 0.1 N H_2SO_4 solution
(a) from 4.5 M aqueous ammonia solution
(b) from 0.1 N H_2SO_4 solution

Copies of NMR spectrum for products

