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Syntheses of nickel sulfides from 1,2-bis(diphenylphosphino)ethane nickel(II)dithiolates and their application in the oxygen evolution reaction

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ABSTRACT

In this work, four heteroleptic Ni(II)dppe dithiolates complexes, [Ni(NED)(dppe)] (**Ni-NED**), [Ni(ecda)(dppe)] (**Ni-ecda**), [Ni(i-mnt)(dppe)] (**Ni-i-mnt**) and [Ni(cdc)(dppe)] (**Ni-cdc**) (dppe = 1,2-bis(diphenylphosphino)ethane; NED = 1-nitroethylene-2,2-dithiolate; ecda = 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate; i-mnt = 1,1-dicyanoethylene-2,2-dithiolate and cdc = cyanodithioimidocarbonate), have been synthesized and characterized by analytical and spectroscopic techniques (Elemental analysis, vibrational, electronic absorption and multinuclear NMR spectroscopy). Structural characterization of all the four complexes by single crystal X-ray diffraction study suggests distortion in regular square planar geometry at Ni(II) center by coordination with two phosphorus of the dppe and two sulfur of the dithiolate ligands, respectively. The decomposition of all four complexes have been done to produce nickel sulfides and the resulting nickel sulfides have been utilized for electrocatalytic oxygen evolution reaction (OER). The nickel sulfide obtained by decomposing Ni-cdc shows best activity with overpotential $\eta = 222$ mV at $j = 10$ mA cm⁻² and a Tafel slope of 44.2 mV dec⁻¹ while other catalysts shows $\eta > 470$ mV at $j = 5$ mA cm⁻² and $\eta > 600$ mV at $j = 10$ mA cm⁻² at loading of 1.3 mg cm⁻².

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Introduction

The enormous depletion of fossil energy, which in turn had resulted in numerous environmental hazards, have created

zeal amongst researchers especially the materials scientists to explore various renewable and sustainable energies so that they could replace traditional resources for the energy conversion and storage [1–3]. In view of this, the oxygen evolution

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reaction (OER) is an essential electrochemical step to convert renewable to storable chemical energy through the water splitting process [4–6]. The efficient water splitting requires active electrocatalysts to avoid sluggish kinetics associated with the anodic oxygen evolution reaction (OER) that generates high overpotential [7–16] which had been identified as the gridlock of the water splitting for commercial applications. Currently, $\text{IrO}_2/\text{RuO}_2$ are utilized as the benchmark catalysts for oxygen evolution reaction (OER) [17]. However, the high price as well as their scarcity significantly limits their scale-up applications [17]. Therefore, the quest for low-cost, earth-abundant alternative non precious electrocatalysts that can exhibit effective activity and stability toward full water splitting is necessary [18,19].

To date, various non-precious metal catalysts with comparable electrocatalytic activity have been synthesized and explored for water splitting viz. metal phosphides [20–23], sulfides [24–26], and oxides/hydroxides [27–30]. Amongst these electrocatalysts, nickel sulphides which can have various stoichiometries [31–34] viz Ni_xS_y (where $(x:y) = (1:1), (1:2), (3:2), (3 + x:2), (3:4), (4:3 + x), (6:5), (7:6),$ and $(9:8)$) also showed fairly good performance [35–43].

Because of different stoichiometries associated with nickel sulfides they are not only an attractive candidate for OER but can also be utilized in diversified technical applications in electrochemical devices as electrodes or battery materials, as catalysts for hydrogenation reaction, and transformation tougheners for complex ceramics [44–47] and potential thin film solar cells having efficiency comparable to silicon based solar cells [48]. A variety of procedures have been utilized for synthesis of nickel sulfide nanostructures with varied morphologies using different types of precursors [49–69]. Inspired by the existing literature describing the syntheses and applications of nickel sulfides, we also had reported the syntheses of heteroleptic Ni(II) dithiocarbamate (dppe) [70] as well as Ni(II) dithiophosphate (dppe) complex cations with different counter-anions [71]. These complexes have been used as single source precursors for the preparation of nickel sulphides. The impact of the counter-anions on morphology as well as the phase of synthesized nickel sulfides has been observed.

To explore these possibilities and in the search of new precursors to synthesize nickel sulfides, we herein report the syntheses and characterization of four 1,2-bis(diphenylphosphino)ethane nickel(II) dithiolates complexes with different groups and the use of these as single source precursors to get nickel sulfide and finally explored their utility as electrocatalysts in oxygen evolution reactions (OER).

Experimental section

Materials

All the complexes were synthesized under ambient conditions using dry solvents. The chemicals nickel chloride hexahydrate (Sigma Aldrich, USA), bis(diphenylphosphino)ethane (dppe) (Sigma Aldrich, USA), nitromethane (Sigma Aldrich, USA), ethyl cyanoacetate (Sigma Aldrich, USA), malononitrile

(Sigma Aldrich, USA) and cyanamide (Sigma Aldrich, USA), carbon disulfide (Merck Chemicals), and potassium hydroxide (Merck Chemicals), were purchased and used without further purification.

Physical measurements

Multinuclear NMR (^1H , ^{13}C and ^{31}P) spectra were recorded on a BrukerAvance III HD FTNMR spectrophotometer. Tetramethylsilane (TMS) was used as internal standard for ^1H and ^{13}C and phosphoric acid for ^{31}P NMR. Exeter analytical Inc. Model CE-440 CHN analyser was utilized for microanalysis. SPECORD 210 PLUS BU spectrophotometer utilized to record the UV–Vis spectra of the complexes in methylene dichloride solutions. Structural characterization of the decomposition products were performed using powder X-ray diffraction (PXRD) measurements on a Bruker AXS D8 Discover X-ray diffractometer equipped with Ni-filtered $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$). For SEM measurement, small amount of the prepared composites were dispersed in ethyl alcohol by ultrasonication for few minutes. Scanning electron microscopy (SEM) imaging was carried out using Ultra55 FE-SEM Karl-Ziess instrument. Oxford EDS spectrometer attached with the FE-SEM was utilized for the energy dispersive X-ray spectroscopic (EDS) study.

Synthesis of [Ni(NED) (dppe)] (Ni-NED), [Ni(ecda) (dppe)] (Ni-ecda), [Ni(i-mnt) (dppe)] (Ni-i-mnt) and [Ni(cdc) (dppe)] (Ni-cdc)

All complexes have been prepared using similar experimental procedure: To the stirred methanolic solutions of K_2NED (0.213, 1 mmol)/ K_2ecda (0.187 g, 1 mmol)/ $\text{K}_2\text{i-mnt}$ (0.218 g, 1 mmol)/ K_2cdc (0.194 g, 1 mmol) was added dropwise a methylene dichloride solution of $[\text{Ni}(\text{dppe})\text{Cl}_2]$ (0.528 g, 1 mmol). Final solution was allowed to stir for 2 h and solution was finally dried using rotary evaporator. The brown-red (Ni-NED)/yellow-orange (Ni-ecda)/orange (Ni-i-mnt)/yellow-brown (Ni-cdc) precipitates were collected and dried. Precipitates were then dissolved in 10 mL of methylene dichloride, filtered through silica crucible having celite pad and reprecipitated using diethyl ether. The precipitates were collected by dissolving diethyl ether and washed thrice with diethyl ether and dried in vacuum.

Characterization data

Ni-NED: Brown-red solid (0.682 g, 92.03% yield); M.P. 260 °C; IR (KBr , cm^{-1}): 1512 (C=C), 1432 (NO_2), 1297 (N–O), 1103 (CS_2). ^1H NMR (300 MHz, CDCl_3 , δ): 7.97 (o- C_6H_5), 7.26 (m- C_6H_5), 7.04 (p- C_6H_5), 3.49 (=C–H), 2.51 (CH_2 – CH_2). ^{13}C NMR (75.50 MHz, CDCl_3 , δ): 184.0 (C–S), 133.8 (o- C_6H_5), 133.0 (m- C_6H_5), 131.0 (p- C_6H_5), 127.9 (C=C), 25.6 (CH_2 – CH_2). ^{31}P NMR (121.54 MHz, CDCl_3 , δ): 62.8. Elemental Analysis. Calcd. For $\text{C}_{28}\text{H}_{25}\text{O}_2\text{S}_2\text{P}_2\text{NiN}$ (%): C, 56.78; H, 4.25; N, 2.36; S, 10.83. Found: C, 57.11; H, 4.18; N, 2.54; S, 11.13.

Ni-ecda: Yellow-orange solid (0.553g, 77.34%); M.P. 250 °C; IR (KBr , cm^{-1}): 2250 (C≡N), 1700 (COO), 1446 (C=C), 1100 (CS_2). ^1H NMR (300 MHz, CDCl_3 , δ): 7.79 (o- C_6H_5), 7.76 (m- C_6H_5), (p- C_6H_5), 4.16 (– CH_2 –), 2.36 (4H, CH_2 – CH_2), 2.12 (3H, S, CH_3). ^{13}C NMR (75.50 MHz, CDCl_3 , δ): 163.58 (C–S), 133.85 (o- C_6H_5), 132.0 (m- C_6H_5), 129.0 (p- C_6H_5), 128.0 (CN), 127.9 (C=C), 66.1 (– OCH_2 –), 28.0 (CH_2 – CH_2). ^{31}P NMR (121.54 MHz, CDCl_3 , δ): 57.4. Elemental

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