Nitrogen-doped carbon-based electrocatalysts synthesised by ball-milling

Roberta Sibul[a], Elo Kibena-Põldsepp[a], Sander Ratso[a], Mati Kook[b], Maike Käärik[a], Maido Merisalu[a,b], Päärn Paiste[c], Jaan Leis[a], Väino Sammelselg[a,b], Kaido Tammeveski[a,*]

[a] Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia
[b] Institute of Physics, University of Tartu, W. Ostwald Str. 1, 50411 Tartu, Estonia
[c] Institute of Ecology and Earth Sciences, University of Tartu, Vanemuise 46, 51014 Tartu, Estonia

ARTICLE INFO

ABSTRACT

Herein, for the first time, ball-milling of carbon materials (e.g. graphite, graphene oxide or graphene) in the presence of dicyandiamide (DCDA) followed by heat treatment at 800 °C was employed to synthesise N-doped carbons for the oxygen reduction reaction (ORR) in alkaline medium. The obtained results highlight that: i) the N-doped nanocarbon catalysts synthesis process employed herein is easy and could be used without hazardous solvents; ii) X-ray photoelectron spectroscopy indicated successful N-doping, iii) N-doped graphite and graphene are Mn-free as confirmed by the ICP-MS analysis, iv) the ORR electrocatalytic activity depends on the carbon source used for the catalyst preparation and v) all the N-doped nanocarbons revealed better ORR performance than the undoped materials.

1. Introduction

The oxygen reduction reaction (ORR) is very important process for example in energy storage and conversion systems (e.g. fuel cells, metal-air batteries) [1]. It is well-known that in fuel cells, the ORR is the bottleneck because of its rather slow kinetics. In order to speed up the ORR process, it is crucial to find a good and inexpensive electrocatalyst. Carbon materials like graphite, graphene and graphene oxide (GO) have been widely used as catalyst support for the ORR because of their low cost and wide potential window in electrochemistry [2]. It has been shown that the modification of carbon nanomaterials (e.g. doping with heteroatoms like nitrogen) expands their applications in the field of electrocatalysis [3].

Much of the ongoing research in electrocatalysis is focused on developing simple, effective and economically viable methods to fabricate active ORR catalysts. In this regard, ball-milling has shown great promise for the synthesis of heteroatom-doped nanocarbons for the ORR. Ball-milling is commonly used to mechanically reduce the size of carbon materials (e.g. GO) [4, 5], followed by modification of carbon substrate by nitrogen precursors and heat-treatment [6]. It is well-known that the properties of ball-milled carbon nanomaterials strongly depend upon the conditions used for ball-milling [7]. In addition, ball-milling along with a suitable precursor for heteroatom doping can functionalise the material with heteroatoms as well [8–11]. N-doped carbon materials have been synthesised by ball-milling of graphite

flakes in the presence of air [12], graphite or multi-walled carbon nanotubes in the presence of urea [13] or GO in the presence of melamine [14].

In this work, a synthesis procedure based on ball-milling is presented to obtain a highly active ORR catalyst. The novelty of this work is that for the first time, ball-milling in the presence of dicyandiamide (DCDA) along with the carbon material (e.g. graphite, GO or graphene) is employed to fabricate N-doped carbon-based catalysts without the use of any hazardous solvent.

2. Experimental

2.1. Synthesis of the N-doped nanocarbon catalysts

50 mg of graphite (natural graphite flakes), graphene (graphene nanoplatelet aggregates from Strem Chemicals) and GO (synthesised according to the modified Hummer's method [15–17]) along with 1 g of dicyandiamide (DCDA) were ball-milled for 2 h using 5 mm ZrO$_2$ balls. Thereafter, pyrolysis of the samples in N$_2$ atmosphere in pre-heated furnace at 800 °C for 1 h was carried out. The N-doped catalysts based on graphite (G), graphene (Gra) and GO are designated as N-G, N-Gra and N-GO, respectively.

2.2. Physico-chemical characterisation

The surface morphology and elemental composition of the undoped and N-doped catalysts were studied by high-resolution scanning electron microscopy (HR-SEM, Helios NanoLab 600, FEI), inductively-coupled plasma mass spectrometry (ICP-MS, Agilent 8800 ICP-MS/MS) and X-ray photoelectron spectroscopy (XPS, SCIENTA SES-100 spectrometer). N_2 adsorption/desorption isotherms of the catalysts were recorded at the boiling temperature of nitrogen using a NovaTouch LX2 Analyser (Quantachrome Instruments). Specific surface area (S_a) and V_μ were calculated from N_2 adsorption isotherms by a quenched solid density functional theory (QSDFT) equilibria model for slit type pores. The total pore volume (V_{tot}) was calculated from N_2 adsorption at P/P_0 of 0.97.

2.3. Electrochemical characterisation

An Autolab potentiostat/galvanostat PGSTAT128N (Metrohm Autolab) controlled with General Purpose Electrochemical System (GPES) software was used for the electrochemical experiments. The three-electrode system consisted of catalyst-coated glassy carbon (GC) as working electrode, Pt wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. The GC disks of geometric area (A) of 0.196 cm^2 were cut from rods (GC-20SS, Tokai carbon) and were embedded into a Teflon sheath. Catalyst inks were prepared in 2-propanol followed by sonication. An aliquot of catalyst suspension was applied to the GC surface (catalyst loading of 0.1 mg cm^{-2}). Electrochemical measurements were carried out in O_2-saturated 0.1 M KOH solution employing the rotating disk electrode (RDE) method at a scan rate (v) of 10 mV s^{-1}. A CTV101 speed control unit connected to an EDI101 rotator (Radiometer) was used for RDE testing.

3. Results and discussion

3.1. Physical characterisation of undoped and N-doped nanocarbons

The impact of ball-milling on each of the studied materials was rather different as shown by the scanning electron microscopy (SEM) images. For instance, prior to ball-milling, the graphite chunks had a diameter of up to 100 μm (Fig. 1a), while the ball-milling process reduced the size to 1 μm or less (Fig. 1c). SEM images at greater magnification (Figs. 1b,d) clearly show that the initial graphite chunks have a rather smooth surface, where larger single and multi-layered flakes of graphene break apart from the compact structure. The smaller grains that were obtained with ball-milling however are rougher and lack the
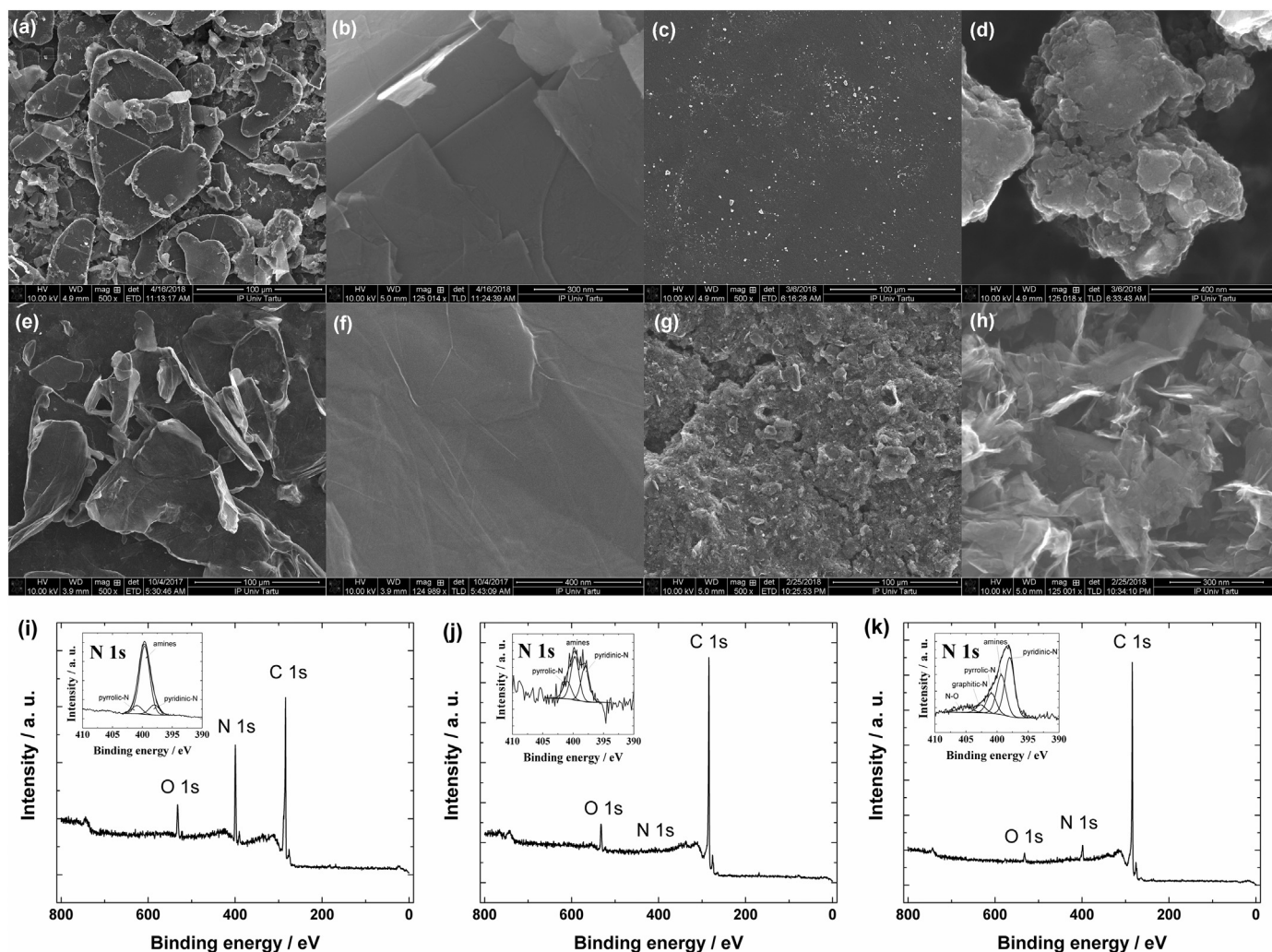

Fig. 1. (a–h) SEM images of (a,b) undoped graphite, (c,d) N-doped graphite, (e,f) undoped GO, (g,h) N-doped GO; (i-k) XPS survey spectra and core-level spectra in the N1s region for N-doped (i) graphite, (j) graphene and (k) GO.