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SUPPORTING INFORMATION

Hydrothermal-assisted synthesis of an iron nitride-carbon composite as a novel electrode material for supercapacitors

Agata Śliwak, Adam Moyseowicz and Grażyna Gryglewicz*

Department of Polymer and Carbonaceous Materials, Faculty of Chemistry,
Wrocław University of Science and Technology, Poland

*Corresponding author: grazyna.gryglewicz@pwr.edu.pl (Grażyna Gryglewicz).

Experimental details

Materials synthesis

Fe_2N@AC-H was prepared as follows. Firstly, 250 mg of AC was impregnated with an appropriate amount of an aqueous solution of iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) to yield an Fe_2O_3 loading of 50 wt% after mixing by a magnetic stirrer for 1 h. Then, the pH of the mixture was adjusted using a 10% v/v ammonia solution, and the mixture was placed into a stainless-steel autoclave (4590 Micro Stirred Reactor, Parr Instrument Company). Hydrothermal treatment was performed at 180 °C for 5 h under an autogenous pressure of ~9 bar. After the reaction, the autoclave was allowed to cool to room temperature. The obtained product was centrifuged, washed with distilled water several times until reaching neutral pH, and dried at 80 °C for 12 h. Subsequently, the iron-loaded sample was placed as a thin layer at the bottom of a quartz boat, which was then inserted into the centre of a horizontal reactor. The reactor was heated to

800 °C at a heating rate of 5 °/min under a nitrogen flow of 9 L/h. Afterwards, ammonia (6 L/h) was introduced into the reactor for 2 h. Then, the reactor was cooled to room temperature under a nitrogen flow.

Fe_2N and Fe_2N@AC were prepared using the classic chemical method for comparison. The synthesis of Fe_2N was performed as follows. An appropriate amount of $Fe(NO_3)_3 \cdot 9H_2O$ was treated at 80 °C for 12 h. The resultant product was placed at the bottom of a quartz boat, which was then placed into the centre of a horizontal reactor. Calcination was performed at 350 °C for 4 h under a nitrogen flow (9 L/h). Then, the reactor was heated to 800 °C, and ammonia was introduced, maintaining the same process conditions as for the Fe_2N@AC-H composite. For the synthesis of Fe_2N@AC, the AC sample was loaded with an appropriate amount of an aqueous iron nitrate solution via wet impregnation to result in 50 wt% Fe_2O_3 in the sample. Further processing was analogous to that in the Fe_2N preparation, including the calcination and ammonia treatment stages.

Materials characterization

The crystalline properties of the materials were studied by X-ray diffraction (XRD) using an Ultima IV Rigaku analyser equipped with a 2 kW X-ray tube (40 kV per 30 mA) using Cu $K\alpha 2$ radiation ($k = 0.154056$ nm). The porous structure of the materials was examined by N_2 sorption at 77 K and CO_2 sorption at 273 K using an Autosorb IQ gas sorption analyser (Quantachrome). The specific surface area was calculated from the N_2 adsorption data using the BET equation. The amount of nitrogen adsorbed at a relative pressure of $p/p_0 = 0.96$ was used to determine the total pore volume (V_T). The micropore volume (V_{DR}) was estimated from the Dubinin-Radushkevich equation. The mesopore volume (V_{mes}) was calculated as the difference between V_T and V_{DR}. The pore size distribution was calculated from the N_2 isotherm adsorption data by applying the quenched solid density functional theory method (QSDFT). The CO_2 isotherms were used to determine the ultramicropore volume $V_{DR,CO2}$. The ultramicropore surface was calculated according to the following equation:

$$S_{CO2} = \frac{2000\, V_{DR,CO2}}{L_{0,CO2}} \quad (1)$$

The pore size distribution was calculated from the CO_2 isotherm data by applying the non-linear density functional theory method (NLDFT). The morphology of the materials was observed using a Merlin Zeiss field-emission scanning electron microscope (FESEM) operating at an accelerating voltage of 3 kV. The high-resolution transmission electron microscopy (HRTEM) observations of the iron nitride-carbon composites were performed using a FEI TITAN^3 G2 60-300. Thermogravimetric (TG) analysis of the composites was performed using TGA/DSC 1 Analyzer (Mettler Toledo) under an air flow of 100 mL/min, with a heating rate of 5 °C/min, from a room temperature to 800 °C. X-ray photoelectron spectroscopy (XPS) was performed to obtain a detailed elemental surface analysis using a PHI 5000 VersaProbe. The sample charging was corrected using the C1s peak at 284.6 eV as an internal standard. Curve fittings were performed using an iterative least squares algorithm (CasaXPS software) with a Gaussian–Lorentzian (70/30) peak shape and Shirley background removal.

Electrochemical measurements

The electrodes in the pellets form with a geometric surface area of 0.9 cm^2 were prepared by mixing 80 wt.% active material (Fe_2N, Fe_2N@AC or Fe_2N@AC-H) with 10 wt.% polyvinylidene fluoride (PVDF, Kynar Flex 2801) as a binding agent and 10 wt.% carbon black. The electrochemical measurements were performed in a T-type Swagelok® three-electrode assembly using Hg|HgO and mesophase pitch-based AC as the reference and counter electrodes, respectively. The electrodes were separated by a glassy fibrous membrane. An aqueous solution of 6 M KOH was used as the electrolyte. To preserve comparable experimental conditions, gold current collectors were applied. The electrochemical properties of the obtained materials were determined using a VSP electrochemical workstation (Biologic, France). Cyclic voltammetry was carried out at voltage scan rates of 1-100 mV/s. The galvanostatic cycling method was used at current regimes between 0.5 and 20 A/g. The capacitances were expressed in Farads per mass of active material in one electrode. The specific capacitance values (C, *F/g*) were calculated from the galvanostatic discharge curves and from the cyclic voltammograms in accordance with equations (2) and (3), respectively.

$$C = \frac{\int I dt}{U m_{el}} \qquad (2)$$

$$C = \frac{\int I dt}{v m_{el}} \qquad (3)$$

where I is the current (A), U is the operating cell voltage (V), t is the time (s), v is the scan rate (V/s), and m_{el} is the mass of the active material in the electrode (g).

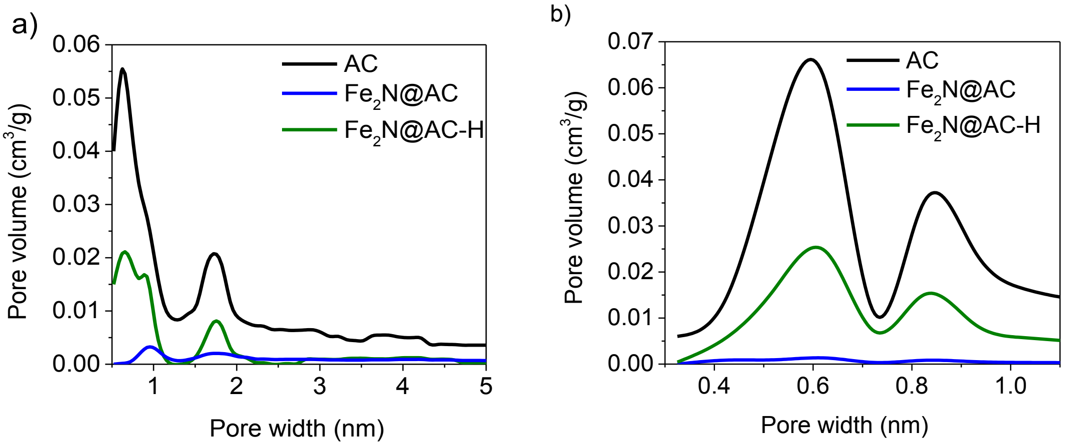

Figure S1. Pore size distribution determined from the N_2 (a) and CO_2 (b) sorption isotherms.

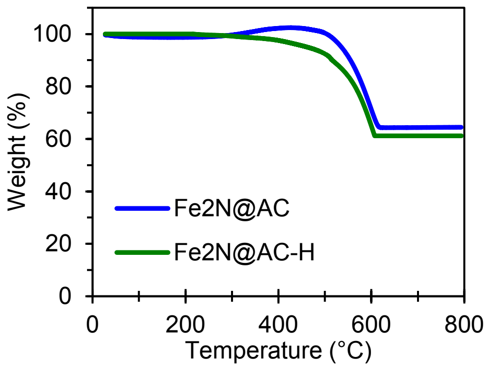

Figure S2. TG curves of Fe$_2$N@AC and Fe$_2$N@AC-H in air at 5°C/min.

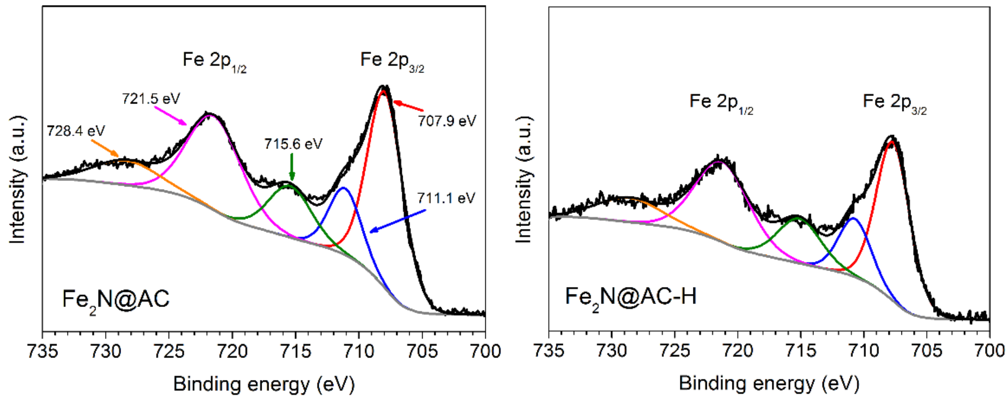

Figure S3. Deconvoluted Fe2p spectra of Fe$_2$N@AC and Fe$_2$N@AC-H composites.

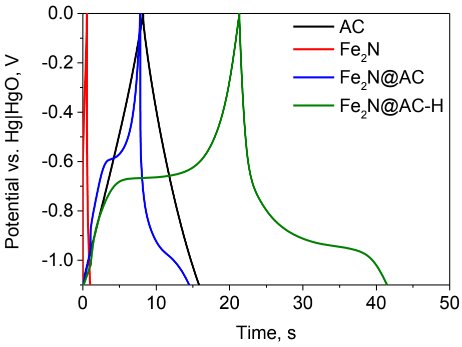

Figure S4. Galvanostatic charge/discharge curves of the electrodes based on AC, Fe$_2$N and their composites, measured at a current density of 20 A/g.

Table S1. Iron oxide and calculated iron nitride contents from TG analysis of composites.

Sample	Fe_2O_3 content after TG analysis, wt.%	Calculated Fe_2N content from Fe_2O_3, wt.%	Fe content on the surface from XPS analysis, at.%
Fe_2N@AC	64.4	50.7	21.9
Fe_2N@AC-H	61.2	48.2	7.6