Synthesis and Characterization of Mo$_2$C/MoO$_3$ Nanohybrid as Electrocatalyst for Hydrogen Evolution Reaction

Maria Sarno, Claudia Cirillo*, Eleonora Ponticorvo, Paolo Ciambelli

Department of Industrial Engineering and Centre NANO_MATES, University of Salerno, Via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy
clicirillo@unisa.it

The two-step preparation of core-shell Mo$_2$C/MoO$_3$ nanoplatelets (composed of an MoO$_3$ core covered by 3 nm Mo$_2$C outer layer) is reported. The process consists of the thermolysis of a solid precursor, ammonium molybdate ($\text{(NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), in a reactor fed by nitrogen (200 cm$^3$(STP)/min), heated from room temperature to 700 °C, followed by a controlled Chemical Vapor Deposition (CVD) of CH$_4$, 10 v/v % in nitrogen, for 10 minutes, monitored on-line by continuous gas analyzers.

A Tafel slope of 48 mV/decade was measured for the Mo$_2$C/MoO$_3$ nanohybrid suggesting the Volmer-Heyrovsky mechanism for the nanohybrid-catalyzed HER. MoO$_3$ deserves as a highly nanostructured conductive core, while the thin Mo$_2$C coating serves as both a HER catalyst and a protective layer.

1. Introduction

Hydrogen is being vigorously pursued as an ideal energy carrier and its production by water splitting is attracting growing attention. The electrolysis efficiency is enhanced when Pt is used as the catalyst in acidic media. In particular, the main effective catalysts are Pt-group metals but it remains challenging to look for alternative catalysts that are more abundant and at lower cost. Group VI transition metal carbides exhibit catalytic properties analogous to platinum group metals because of their unique d-band electronic structures. Tungsten carbide has been explored for the Hydrogen Evolution Reaction (HER) providing interesting results, but with a high overpotential if compared with Pt-group metals (Esposito and Chen, 2011). On the other hand, molybdenum carbide was demonstrated able to reduce the overpotential (Chen et al., 2013).

Many approaches including Chemical Vapour Deposition (CVD) (Hanif et al., 2002) and pyrolysis of metal complexes (Wolden et al., 2011) have been developed for the preparation of metal carbides. Among them the more explored is CVD using hydrocarbons (Giubileo et al., 2012) or carbonaceous gases (e.g. CO) and Mo gaseous precursors (MoF$_6$, Mo(CO)$_6$, MoCl$_5$). However, the gas-phase syntheses generally required elaborate equipment, involve the use of expensive and toxic reagents, and the product is usually contaminated by chars from the pyrolysis of carbonaceous gases.

Here we report the preparation of core-shell Mo$_2$C/MoO$_3$ nanoplatelets by a solid precursor thermolysis under nitrogen, followed by a controlled CVD of CH$_4$.

The characterization was obtained by the combined use of different physico-chemical techniques, and the Mo$_2$C/MoO$_3$ nanohybrid was characterized for HER.

2. Experimental

Core-shell Mo$_2$C/MoO$_3$ nanoplatelets were prepared by a solid precursor (ammonium molybdate ($\text{(NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) thermolysis under a nitrogen (200 cm$^3$(STP)/min) flow, in a continuous flow reactor (Di Bartolomeo et al., 2009), from room temperature to 700°C, followed by a controlled CVD (Ciambelli et al., 2004) of CH$_4$ (Sarno et al., 2012b) 10 v/v % in nitrogen for 10 min.
Methane CVD was carried out by feeding, at 700 °C (controlled by a K thermocouple), a methane–nitrogen gas mixture on the reaction bed. The reactor was heated by an electrical oven which temperature was controlled by a temperature programmer–controller (Eurotherm 2408). Cylinder gases (99.998 pure methane and 99.9999 pure nitrogen) were mixed to obtain the methane/nitrogen stream that was fed to the reactor. A constant flow rate of each gas was provided by a mass flow controller. The experimental plant for the synthesis was equipped with on-line ABB analyzers (Sarno et al., 2012a) that permit to monitor the concentrations in the effluent stream (Sarno et al., 2013b) of the following chemicals during the reaction: methane (CH4) the source of carbon, ethylene (C2H4), acetylene (C2H2) and H2.

The characterization was obtained by the combined use of different techniques. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai electron microscope operated at 200 KV with a LaB6 filament as the source of electrons, equipped with an EDX probe. Scanning electron microscopy (SEM) images were obtained with a LEO 1525 microscope. Raman spectra were obtained at room temperature with a micro-Raman spectrometer Renishaw inVia with a 514 nm excitation wavelength (laser power 30 mW) in the range 100 -1100 cm^{-1}. Optical images were collected with a Leica DMLM optical microscope connected online with the Raman instrument. The laser spot diameter was about 10 µm. XRD measurements were performed with a Bruker D8 X-ray diffractometer using CuKα radiation. Thermogravimetric analysis (TG-DTG) at a 10 K/min heating rate in flowing air was performed with a SDTQ 600 Analyzer (TA Instruments) coupled with a mass spectrometer. For the electrochemical measurements 4 mg of catalyst were dispersed in 80 µl of 5 wt.% nafion solution to form a homogeneous ink. Then the catalyst ink was loaded onto a glassy carbon electrode of 3 mm in diameter. Linear sweep voltammetry (using the potentiostat from Amel Instruments) with scan rate of 2 mVs^{-1} was conducted in 0.5 M H2SO4, using saturated calomel electrode as the reference electrode, a graphite electrode as the counter electrode and a loadable glassy carbon electrode as the working electrode.

3. Results and discussion

Figure 1a shows the diffraction pattern recorded for the Mo2C/MoO3 sample. The typical peaks of orthorhombic α-MoO3 (Stoyanova et al., 2009) and β-Mo2C phases were observed (Chen et al., 2013). The Raman spectrum of the sample excited by 514 nm line in air ambient environment is shown in Figure 1b. It is worth to notice that the spectrum has been obtained at 0.1 % of laser power and after 10 s exposition time, because under more stricter conditions the typical Raman spectrum of MoO3 appears generated by the laser, which photon energy closely resonant with the electronic absorption and the band gap energies, determines heating/photochemistry via direct absorption (Cervantes-Gaxiola et al., 2013). The typical bands of MoO3 and Mo2C can be seen in Figure 1b. The laser Raman spectrum of Mo2C (Figure 3a) is very similar to that of MoO3. In particular, the typical vibration frequencies of MoO3 at 994 cm^{-1} and 819 cm^{-1} (Frauwallner et al., 2011) and of Mo2C at 1006 cm^{-1} and 828 cm^{-1} (Xiao et al., 2001), can be seen in our spectrum.

Figure 2 shows the representative SEM images for the Mo2C/MoO3 product, at increasing magnifications. The sample has a platelet elongated shape structure and thickness of few nanometers, as shown in Figure 2b.

![Figure 1: XRD diffraction patterns (a) and Raman spectrum (b) of Mo2C/MoO3.](image-url)
TEM investigations carried out, to provide further insights into the morphology, on the resulting Mo₂C/MoO₃ nanostructures, are reported in Figures 3a and 3b at increasing magnifications. Figure 3a shows a typical TEM image at low magnification for the sample confirming the morphology already observed by SEM (Figure 2b). Figure 3b shows that the nanoplatelets are indeed composed of an MoO₃ core and of an 3 nm Mo₂C outer layer, as confirmed by the selected area diffraction pattern in the Figure 3b insert showing the typical crystallographic in plane square structure ascribable to Mo₂C.

During the precursor thermolysis from room temperature to 700 °C, a weight loss appears below 300 °C, arising from the decomposition of ammonium molybdate (Sarno et al., 2014b), with the formation of MoO₃ (Delporte et al., 1995). At 700 °C, before sublimation that occurs at around 800 °C (Sarno et al., 2014b), the incorporation of C, coming from the decomposition of CH₄, begins by filling MoO₃ anionic vacancies (Frauwallner et al., 2011). In particular, the evolutions of the concentration profiles of CH₄ the source of carbon, C₂H₂, C₂H₄ and H₂ during the isotherm at 700 °C, are shown in Figure 4a.
Figure 4: Profiles of CH₄, C₂H₂, C₂H₄ and H₂ concentrations during the Mo₂C/MoO₃ synthesis at 700 °C (a). TG-DTG profiles of the Mo₂C/MoO₃ as prepared and the corresponding total ion current of CO₂ (b).

Observing Figure 4a, three temporal phases (Sarno et al., 2014a) can be distinguished:
- Pre-reaction phase (I): the reaction gas is fed to the analyzers. All of the concentration values are close to zero, except for the initial methane concentration, which is 10 v/v %.
- Reaction phase (II): the gases are fed to the reactor, reaching the analyzers after passing through the catalyst bed. After the time necessary to pass the reactor and accounting for the delay time of the analyzers, the steady state methane concentration stabilizes at 9.58 v/v %, while the hydrogen concentration in the effluent stream shows the opposite trend and stabilizes at 0.69 v/v %. No significant C₂H₄ and C₂H₂ concentrations are detected during the entire running time at the chosen temperature (700°C).
- Post-reaction phase (III): the reaction has ended, and the gases are sent directly back to the analyzers (bypassing the reactor). The concentrations of the four gases are the same as those in the pre-reaction phase. The amount of carbon coming from the decomposition of methane is calculated by the conversion of methane (data from Figure 4a) (Sarno et al., 2013a), considering the volumes and densities of MoO₃ and Mo₂C. This result is compatible with the formation of a Mo₂C layer of about 3 nm around the MoO₃ platelet.

In Figure 4b the thermogravimetric (TG-DTG) profiles, of the synthesized Mo₂C/MoO₃ nanohybrid, are reported as function of temperature. As clearly indicated by the corresponding TIC of CO₂ (m/z = 44), two weight losses due to carbon are visible: (i) in the range 200-400 °C, probably due to few percents of carbon impurities, coming from the methane homogeneous decomposition; and in the range 580-800 °C due to the Mo₂C oxidation to form molybdenum trioxide and carbon dioxide (Chen et al., 2013), this is partially superimposed with the sublimation of MoO₃ which begins at around 750 °C, as previously reported (Chen et al., 2013).

The electrocatalytic HER activities of Mo₂C/MoO₃ were investigated. The hybrid material was deposited on a glassy carbon electrode in 0.5 M H₂SO₄ solution using a typical three-electrode setup. As a reference point, a commercial Pt catalyst with known high HER catalytic performances was evaluated (Sarno et al., 2014c). The results are shown in Figure 5. Polarization curve (i-V plot) recorded for Mo₂C/MoO₃ (Figure 5a) showed an overpotential of ~0.13 V for HER, beyond which the cathodic current rose rapidly under more negative potentials. Linear portions of the Tafel plots (Figure 5b) were fit to the Tafel equation (η = b log j + a, where η is the overpotential, j is the current density, b is the Tafel slope), yielding Tafel slopes of ~30 and ~48 mV/decade (iR-corrected) for Pt, and Mo₂C/MoO₃ nanohybrid, respectively. The observed Tafel slope for Mo₂C/MoO₃ suggests that electrochemical desorption is the rate limiting step (Li et al., 2011), the high performance is probably due to the electrocatalytic activity of Mo₂C and an electronic coupling with the highly conductive MoO₃ (Li et al., 2011).
Figure 5: Polarization curves obtained (a), and corresponding Tafel plots (b).

4. Conclusions
Core-shell Mo$_2$C/MoO$_3$ nanoplatelets have been prepared by a solid precursor thermolysis, avoiding the more complicated and dangerous supply of a molybdenum precursor from the gas phase, followed by a controlled CVD of CH$_4$, monitored on-line by ABB analyzers.

The characterization confirms the nature of the material, that shows excellent HER activity, with a Tafel slope of 48 mV/dec compatible with electrochemical desorption as rate limiting step. The Mo$_2$C/MoO$_3$ nanohybrid is able to efficiently drive the HER due to MoO$_3$ working as a highly nanostructured conductive core, while the thin Mo$_2$C coating serves as both a HER catalyst and a protective layer.

References


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