

Supplementary on-line material

Novel Approach to the Processing of Meso-macroporous Thin Films of Graphite and *in-situ* Graphite-Noble Metal Nanocomposites†

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1. Experimental procedure

The porous PVDF films are processed from a solution containing 15% PVDF and 12% NH_4NO_3 (AN) in $\text{C}_3\text{H}_7\text{NO}$ (DMF). For the *in-situ* nanocomposites, 1 2% of AgNO_3 (SN) or 2 % of chloroplatinic acid (H_2PtCl_6) (Pt) were added to the solution under stirring. A clean stainless steel substrate (AISI 316) was used as substrate and the PVDF films were deposited by dip-coating. The films were first allowed to dry for 10 minutes at room temperature and subsequently tempered at 150°C for 12h.

Pyrolysis was performed in a tube furnace at 550°C under flowing nitrogen and a ramp of $2^\circ\text{C}/\text{min}$ for both heating and cooling.

The samples were investigated by X-ray diffraction (XRD) (X'Pert Pro, PANalytical, Holland) in grazing incident geometry with fixed angle of 1.5° , step size 0.05° using monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a scanning range (2θ) of $10\text{--}90^\circ$. A Bruker Raman microscope (532 nm laser diode) was used to acquire spectra over a range of $100\text{--}3700 \text{ cm}^{-1}$, with a spectral resolution of $3\text{--}5 \text{ cm}^{-1}$, using a backscattering configuration with a $20\times$ objective. Data were collected on numerous spots on the sample and recorded with a fully focused laser power of 5 mW. Each spectrum was accumulated ten times with an integration time of 15 s. The Raman signal was recorded using a CCD camera. Silicon substrate Raman peak position (520 cm^{-1}) was used to calibrate spectral frequency. The nano-structured surface was characterized using a high-resolution scanning electron microscope (Ultra Plus, ZEISS, Germany). The electrochemical experiments were performed at room temperature in a standard three electrode cell using fresh H_2SO_4 (0.5M) as electrolyte, which is degassed ($>30 \text{ min.}$) prior to each experiment. The cyclic voltammetry (CV) measurements, range between 0.2 V and 0.8 V at different scan rates, were recorded using an electrochemical workstation (Zahner, IM6e, Germany). A Pt mesh and Hydroflex probe (Reversible H_2 reference electrode) were used as counter and reference electrodes, respectively. All potentials are referred to normal hydrogen electrode (NHE).

Fig. 1S: XRD patterns in grazing incidence mode of a graphite-Pt-nanocomposite film. The phases are indexed following: Fe_3O_4 : 01-076-2948; Pt: 01-087-0646; Substrate: 01-071-4649 (fcc-Fe). Notice that there are no peaks corresponding to crystalline graphite or graphite oxide (see reference 13 in the main manuscript).

Fig. 2S: EDS analysis of the *in situ* graphite-Pt-NP-nanocomposite. The fluorine peak is not from residual PVDF but from fluorine that remains as a constituent in the film.

Fig. 3S: Capacitance vs. scan rate of a plain PVDF film.

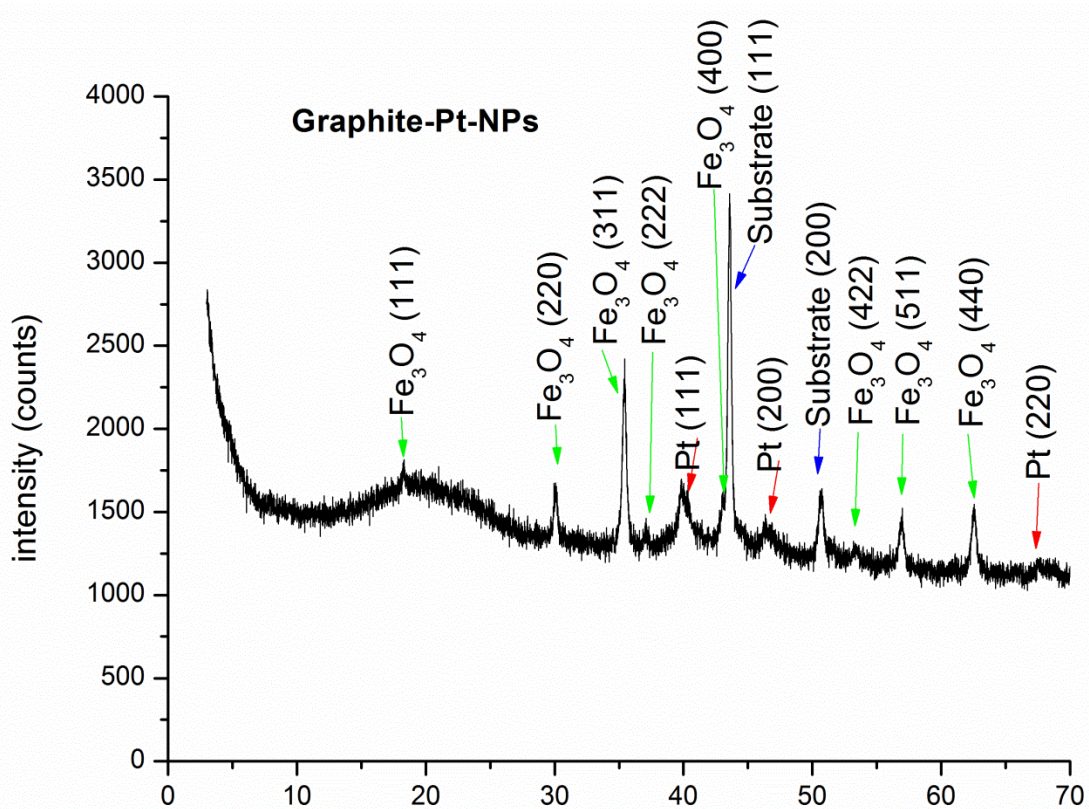


Fig. 1S: XRD patterns in grazing incidence mode of a graphite-Pt-nanocomposite film. The phases are indexed following: Fe₃O₄: 01-076-2948; Pt: 01-087-0646; Substrate: 01-071-4649 (fcc-Fe). Notice that there are no peaks corresponding to crystalline graphite or graphite oxide (see reference 13 in the main manuscript).

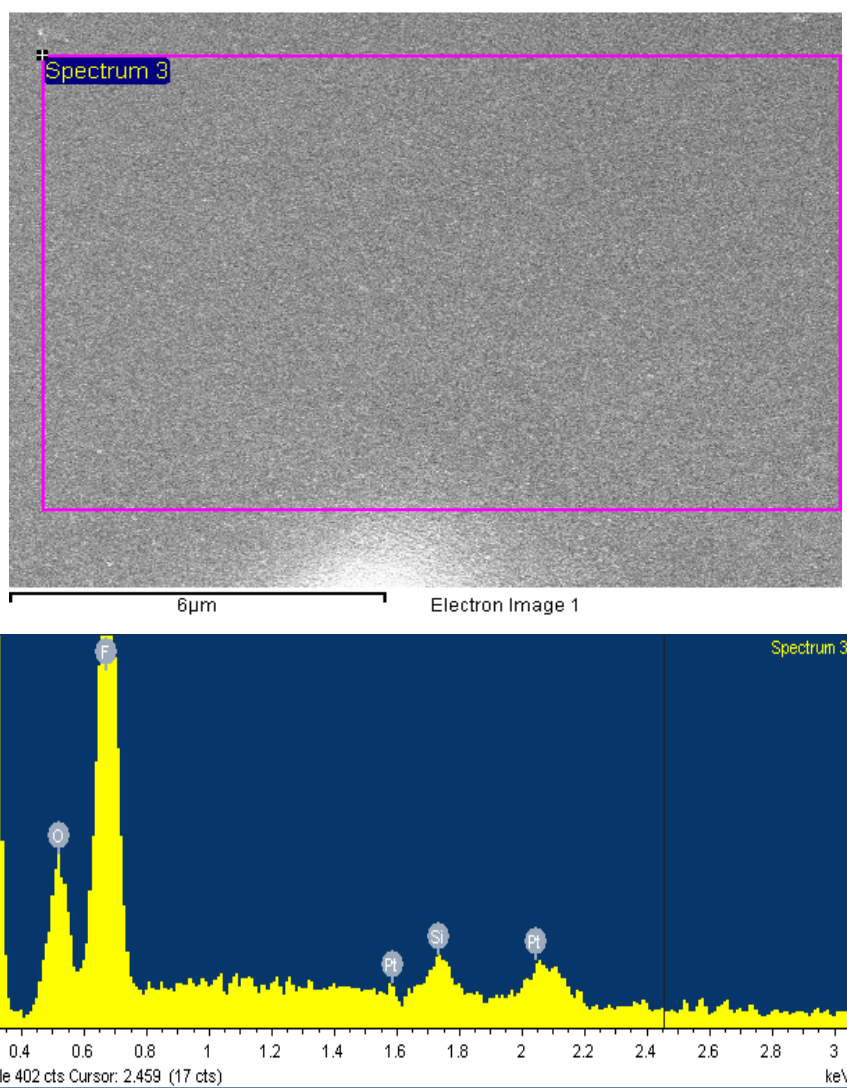


Fig. 2S: EDS analysis of the in situ graphite-Pt-NP-nanocomposite. The fluorine peak is not from residual PVDF but from fluorine that remains as a constituent in the film.

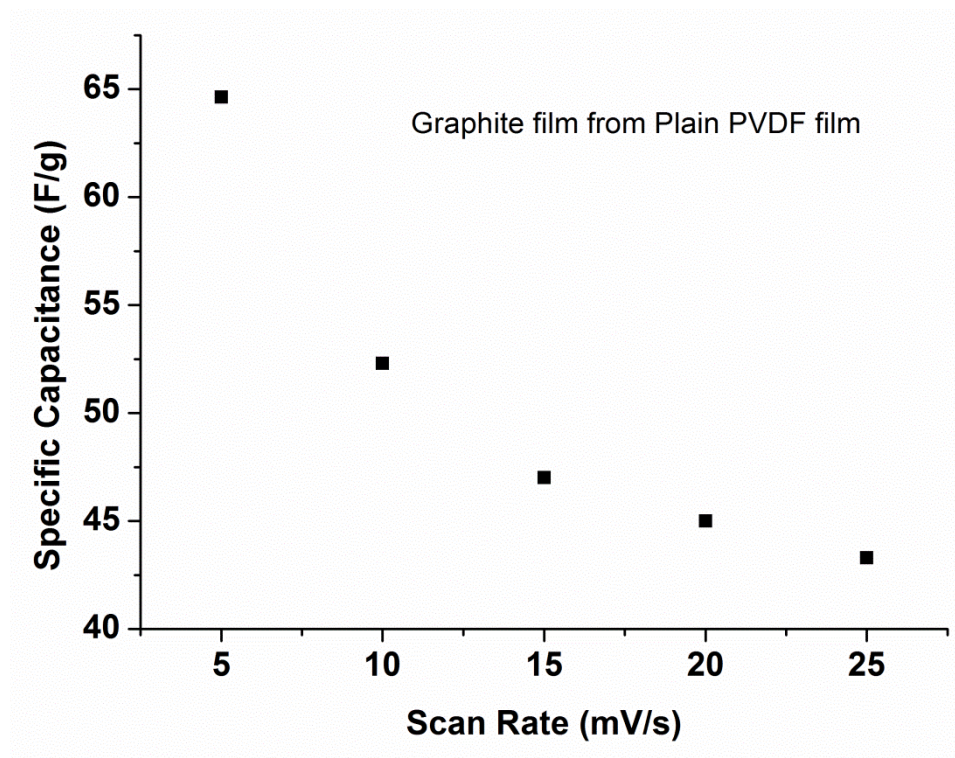


Fig. 3S: specific capacitance of a plain PVDF film as function of the scan rate