

Supplementary Materials: PANI-Based Stacked Ferromagnetic Systems: Electrochemical Preparation and Characterization

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1. PANI Electrochemical Characterization

The increase of the PANI’s thickness (deposited on Au from the acidic solution: aniline 0.1 M, H₂SO₄ 1 M) is monitored as a function of the electropolymerization constant current by means of CVs performed in KCl 0.1 on different deposits in the main article (progressively increasing the electropolymerization current, with equal time). Here, results reported in Figure 3 are cross-checked adding the redox probe [Fe(III)(CN)₆]³⁺/[Fe(II)(CN)₆]⁴⁺ in the KCl solution. Figure S1 (b) shows that the semi-quantitative pattern of Figure 3 between the current for the PANI electropolymerization and the currents obtained in the CVs is maintained with the redox probe in solution.

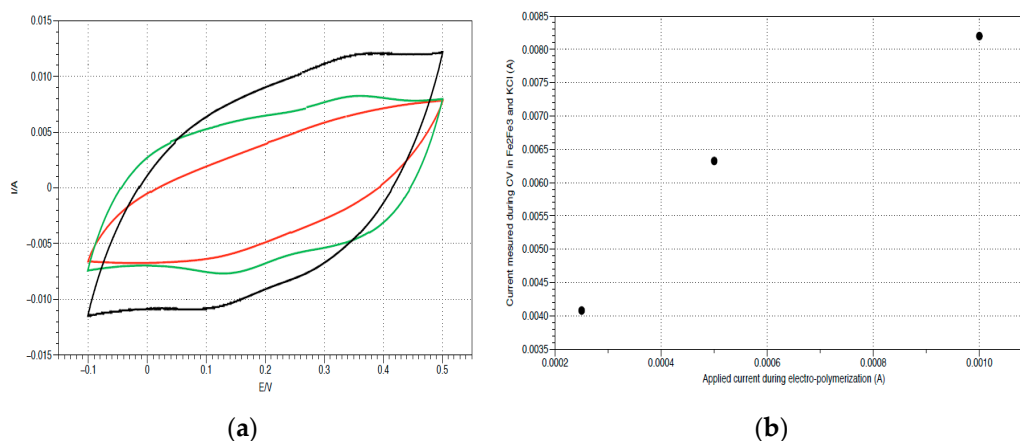


Figure S1. (a) Cyclic voltammetry (CV) curves recorded on PANI/Au WEs. The several colours are associated with separate samples which underwent different currents of electropolymerization, leaving unaltered all the other parameters (electrochemical bath, electropolymerization time of 900 seconds, substrate, electrode area...). **Red curve:** PANI electropolymerization at 0.25 mA for 900 s; **green curve:** PANI electropolymerization at 0.5 mA for 900 s; **black curve:** PANI electropolymerization at 1.0 mA for 900 s. These samples were tested by CV between −0.1 V and 0.5 V vs Ag/AgCl/KCl_{sat}; Pt was the counter electrode. The solution consisted of the Fe²⁺/Fe³⁺ redox probe (K₃Fe(CN)₆ and K₄Fe(CN)₆ 2mM) in support electrolyte (KCl 0.1 M). 0.1 V/s is the scan-rate. (b) Relation between the oxidation peak current of Fe²⁺ recorded in Figure S1 (a) CVs and the value of the imposed current during the electropolymerization of the samples.

2. Magnetite Electrodeposition

Fe_3O_4 was electrodeposited on an Au substrate following a standard procedure [37]: the electrolytic solution consisted of 2 M NaOH, 50 mM $\text{Fe}_2(\text{SO}_4)_3$ and 0.1 M TEA. The Au WE underwent a potentiostatic electrodeposition at -1.3V vs Ag/AgCl for 1800 seconds. The deposition curve is reported below, in Figure S2.

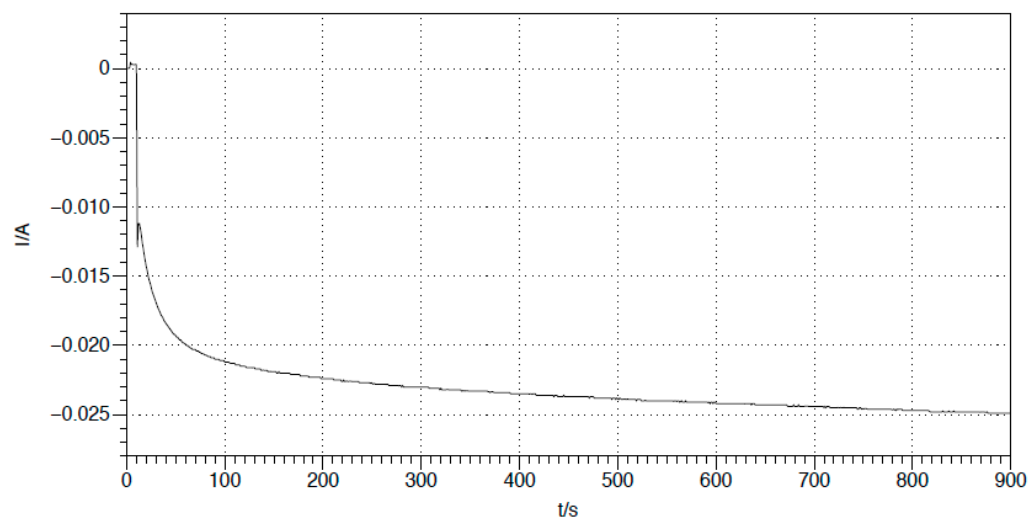


Figure S2. Magnetite (Fe_3O_4) potentiostatic deposition on a Au WE, in a 3-electrodes cell. Pt was used as CE, Ag/AgCl/KCl_{sat} as Ref. The electrolyte consisted in 2 M NaOH, 50 mM $\text{Fe}_2(\text{SO}_4)_3$ and 0.1 M TEA. A constant reduction potential of -1.4 V was applied for 1800 seconds.

3. PANI Profilometry

A specimen of PANI electropolymerized on an Au electrode (Au|PANI interface) has been electrochemically produced from the acidic solution (aniline 0.1 M, H_2SO_4 1 M) in galvanostatic regime, by applying 0.25 mA for 900 seconds. The thickness of the so obtained sample is evaluated by profilometry measurements, whose results are reported in Figure S3.

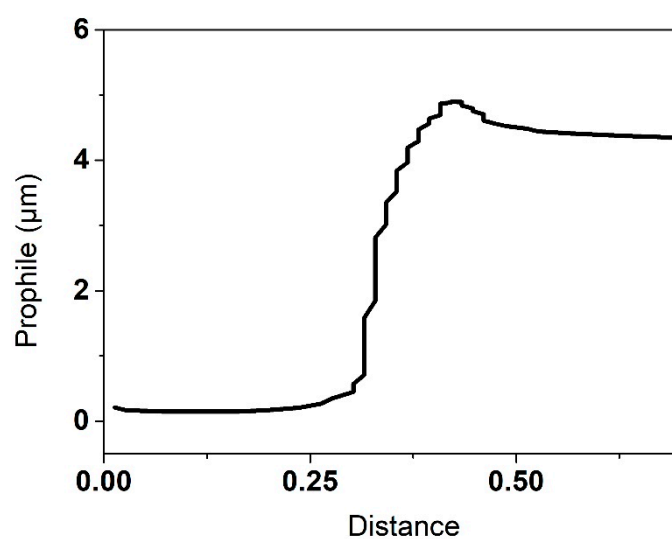
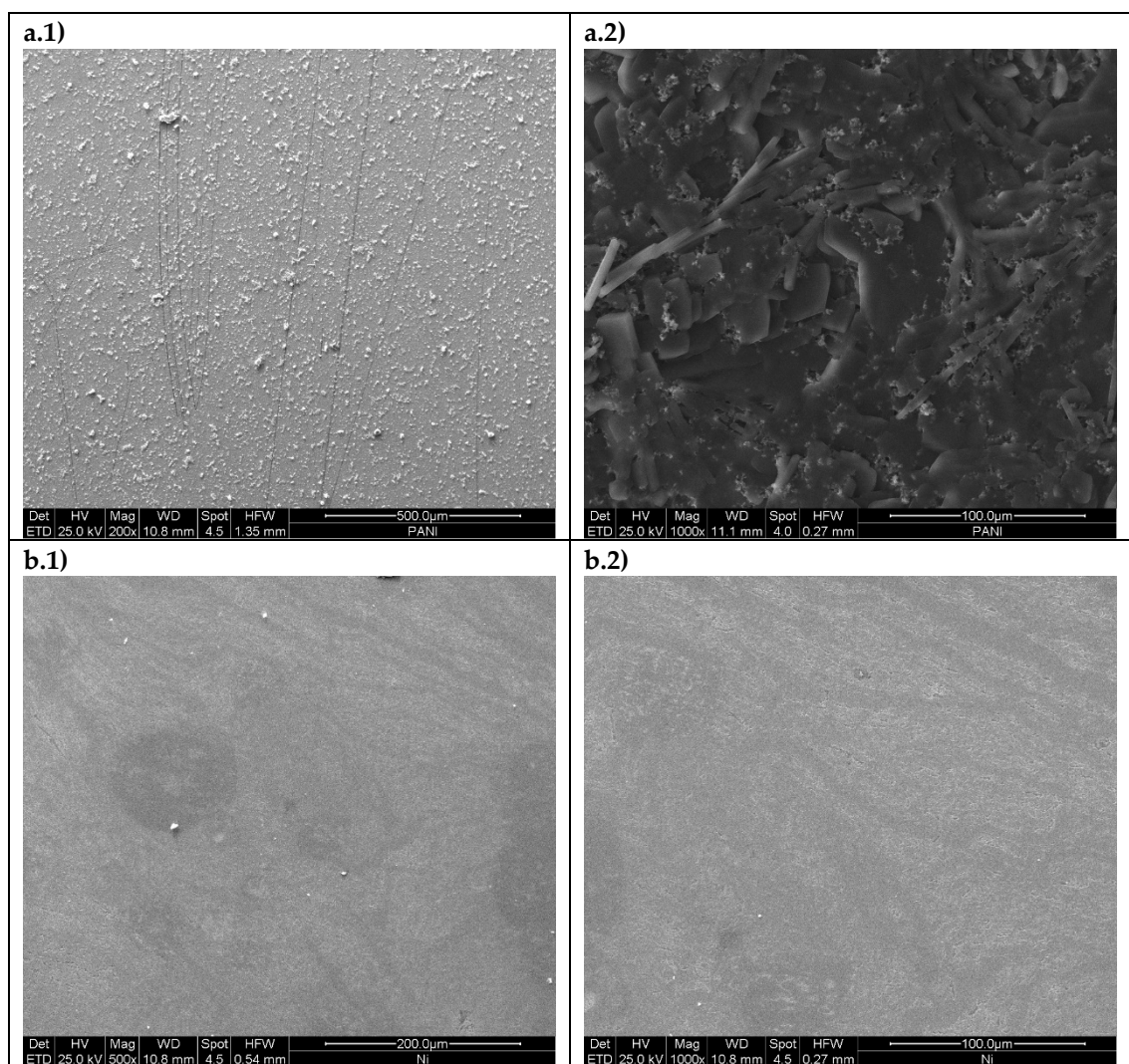


Figure S3. Profilometry analysis performed on a Au|PANI interface. The PANI was electropolymerized on the Au substrate through a galvanostatic electrochemical procedure: 0.25 mA were applied for 900 seconds.

The profile baseline is calibrated to 0 at the level of the Au substrate. The tip of the profilometer meets the PANI coating at around 0.25 distance on the x-axis, and measures a step-like altitude difference of about 5 μm .

4. SEM Surfaces Analysis

The different coatings involved in the fabrication of the Au|PANI|Ni and Au|Fe₃O₄|PANI devices are studied separately, by means of SEM microscopy. Figure S4 displays acquisitions at 200 \times and 1000 \times magnification for each layer independently, which were electrochemically deposited directly on Au substrates, following the procedures described in the main manuscript.



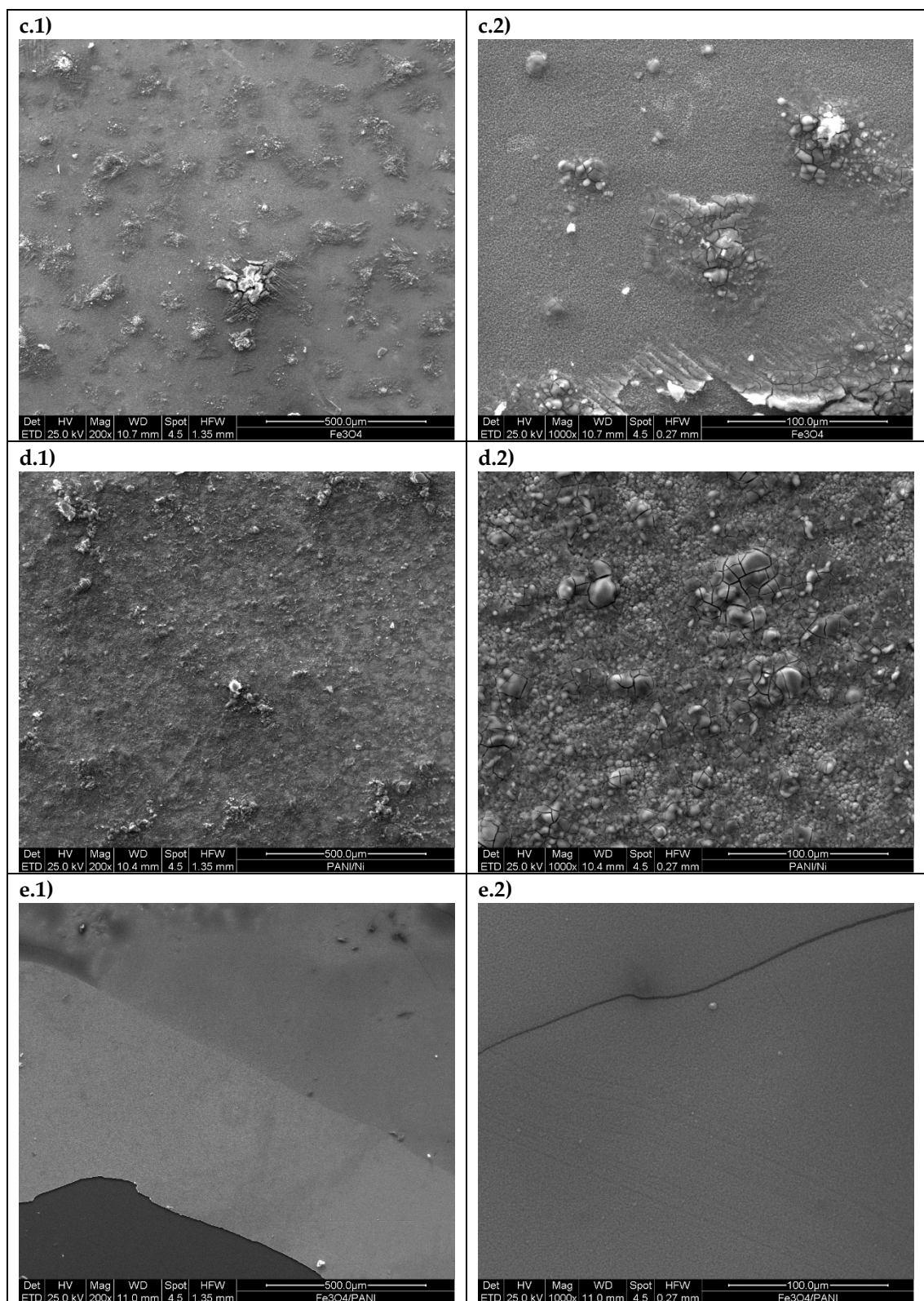


Figure S4. SEM images at 200 \times and 1000 \times magnification (respectively, (1) and (2)) acquired with secondary electrons. (a) acidic solution PANI; (b) Nickel; (c) Fe_3O_4 ; (d) Ni on top of PANI; (e) PANI on top of Fe_3O_4 .

4. PANI Thickness Calculation

The thickness of the acidic solution PANI (1 M H₂SO₄, 0.1 M aniline) has been estimated also by means of Monte Carlo simulations based on the results of EDS microanalysis data [46]. Multiple Au/PANI specimens, with different PANI thicknesses (ranging from 1 μm to 10 μm) have been simulated with DTSA-II software [38]. Au K-ratio values were then calculated, considering that the substrate signal's drop is proportional to the PANI coating thickness. So, the corresponding data have been fitted in order to obtain a calibration curve (Figure S5) which can be used to determine the PANI thickness. For example, in the case of the coating produced with a 900 seconds electropolymerization at 0.5 mA, the resulting thickness is calculated to be 7.3 μm .

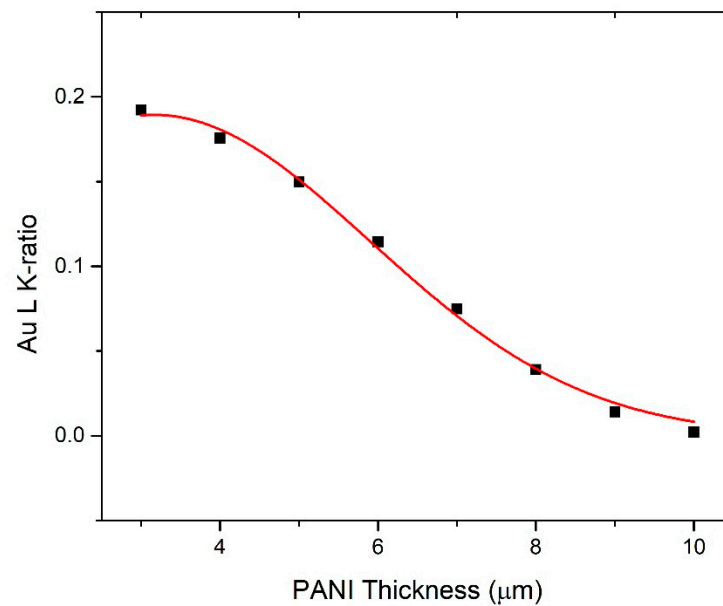


Figure S5. Au K-ratio based calibration curve, for the calculation of the overlying PANI coating.

References

46. Giurlani, W.; Innocenti, M.; Lavacchi, A. X-ray Microanalysis of Precious Metal Thin Films: Thickness and Composition Determination. *Coatings* **2018**, *8*, 84, doi: 10.3390/coatings8020084.