

Supporting information

A general potentiodynamic approach for red phosphorous and sulfur nanodots incorporation on reduced graphene oxide sheets: Metal-free and binder-free electrodes for supercapacitor and hydrogen evolution activities

Mohd. Khalid and Hamilton Varela

Institute of Chemistry of São Carlos, University of São Paulo, POBox 780, 13560-970, São Carlos, SP, Brazil, E-Mail (HV): hamiltonvarela@usp.br,
(MK): mkansarister@gmail.com



Fig S1. Digital photograph of the homogeneous suspension of P-rGO, S-rGO, and PS-rGO of 1:1.

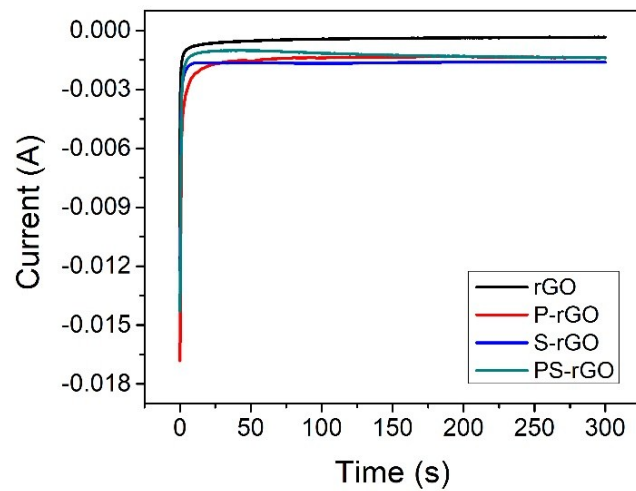


Fig. S2 curves current versus time for P-rGO, PS-rGO, S-rGO, and pristine rGO during potentiodynamic deposition.

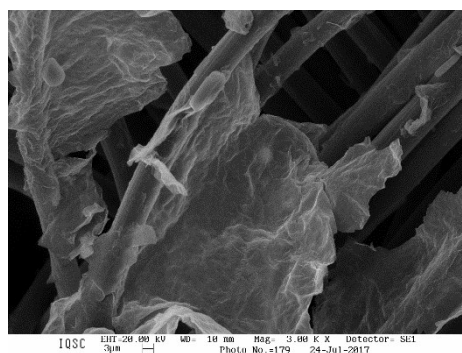


Fig. S3 SEM image of S-rGO on carbon fabric.

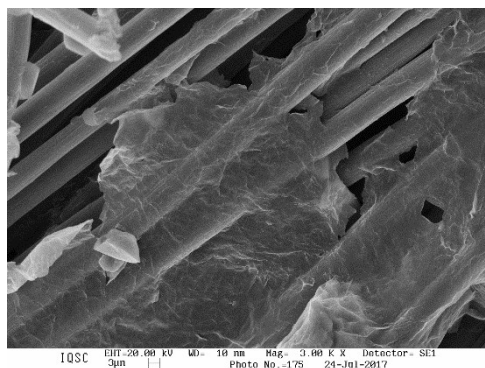


Fig. S4 SEM image of PS-rGO on carbon fabric

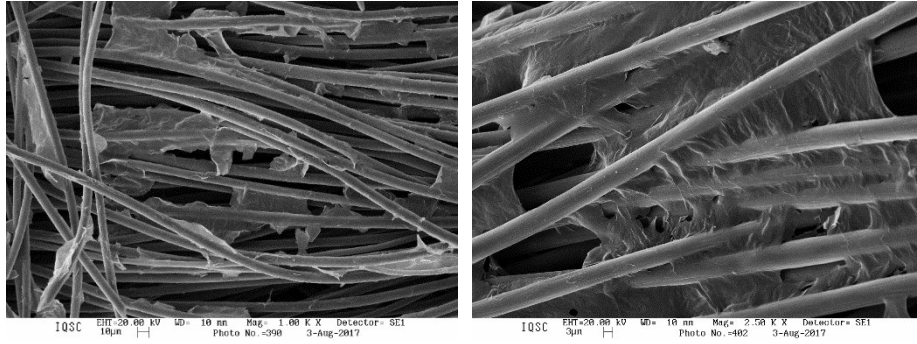


Fig. S5 SEM images of pristine rGO on carbon fabric.

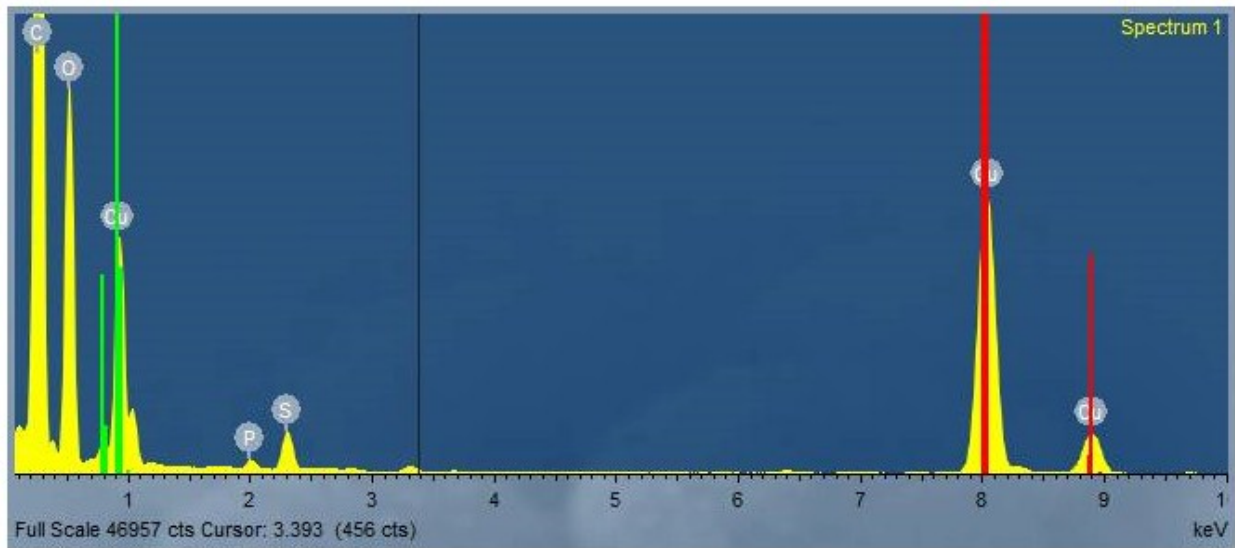


Fig. S6 EDX spectra of PS-rGO.

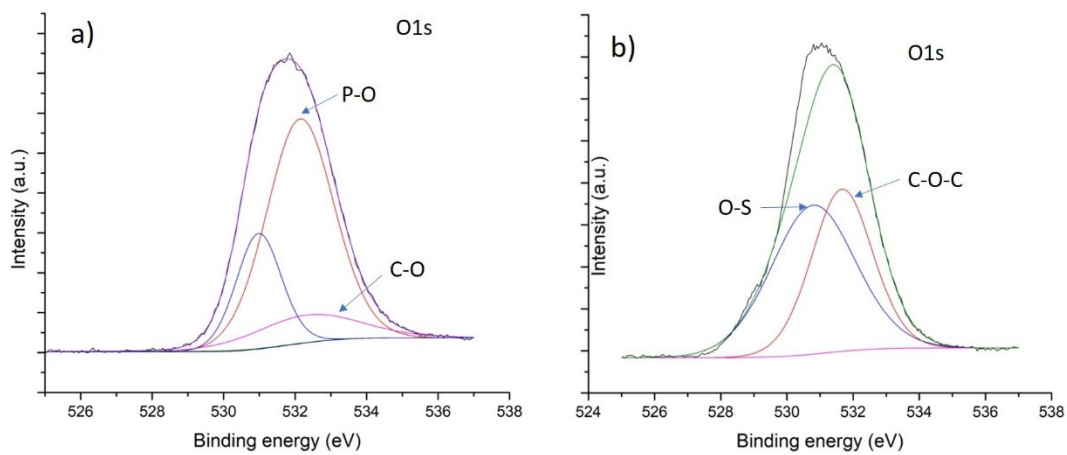


Fig. S7 a) High resolution O 1s spectra EDX spectra of P-rGO and b) High resolution O 1s spectra of S-rGO.

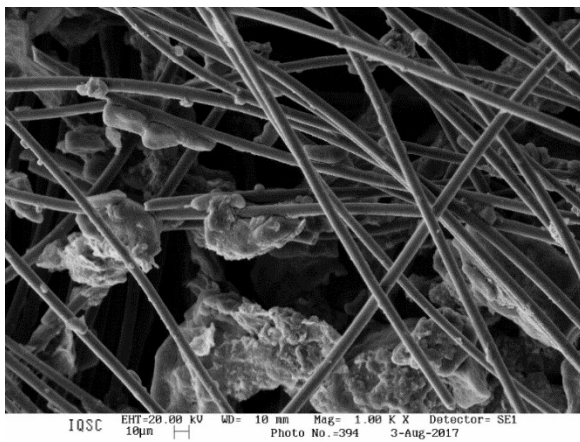


Fig. S8 SEM image of P-rGO (2:1) on carbon fabric.

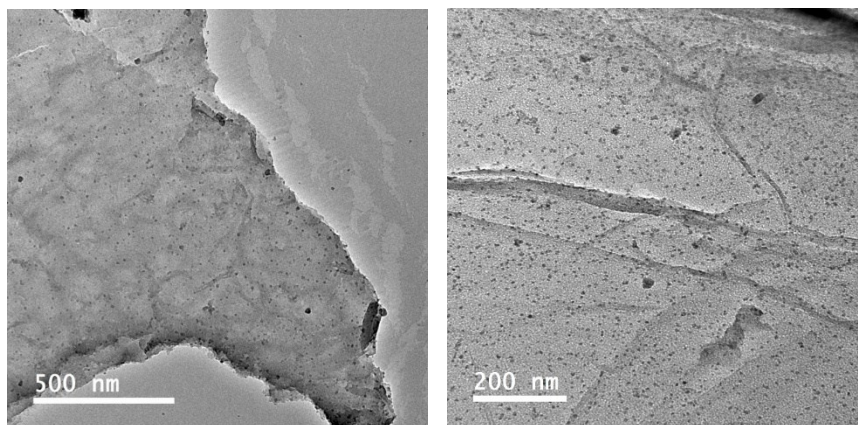


Fig. S9 TEM images of P-rGO after cycling.

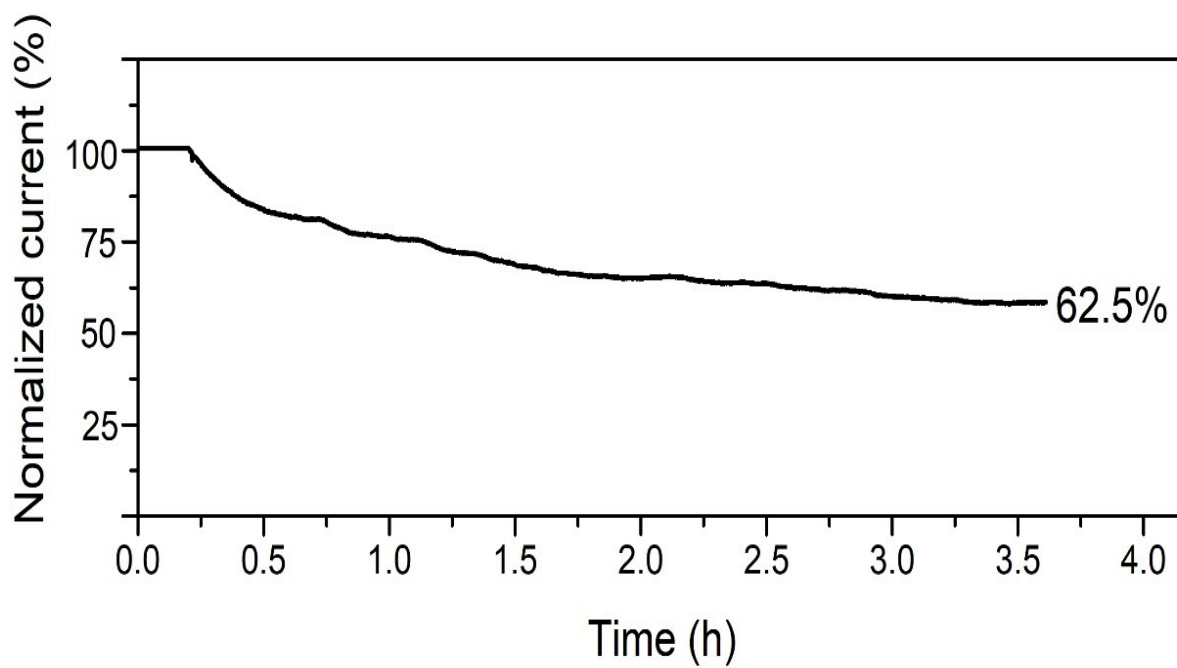


Fig. S10 Chronoamperometric response of Pt/C at -0.3 V.

Generally, under acidic conditions, hydrogen evolution undergoes a multistep reaction process for converting H^+ to H_2 , which can be described by two different mechanisms with three principle steps, commonly known as the Volmer, Heyrovsky, and Tafel reactions:



Theoretically, the Tafel slopes of Volmer, Heyrovsky, and Tafel reactions are calculated to be approximately 118, 39, and 29 mV decade⁻¹, respectively [1]. For our samples, the Tafel slopes of 47 mV decade⁻¹ for the P-rGO, 52 mV decade⁻¹ for PS-rGO, and 59 mV decade⁻¹ for S-rGO are indicating that Heyrovsky reaction was the rate-limiting step of HER.

The electrochemically active surface area (EASA) of samples were estimated according to literature [2]. To study the EASA of P-rGO, PS-rGO, and S-rGO, cyclic voltammetry was performed at various scan rates from 10 to 100 mV/s (Fig S8) in the potential region where there is mostly electrical-double layer capacitance (0.0 - 0.1 V). The EASA was calculated from the measured double-layer capacitance (C_{dl}), according to equation:

$$C_{dl} = \frac{Q}{U} = \frac{dQ/dt}{dU/dt} = \frac{j}{r}$$

Q is the charge per unit area,

U is the voltage,

j is the current density and

r is the scan rate

The C_{dl} of various samples can be determined from the slops of current density versus scan rate (Δj vs Δr). The average C_{dl} of P-rGO, PS-rGO, and S-rGO were measured to be 0.015 mF/cm², 0.012 mF/cm², and 0.010 mF/cm² respectively. Since the C_{dl} is proportional to the surface area of the electrode, the ratio of the C_{dl} can be regarded as the ratio of the specific capacitance of the electrode materials as:

$$EASA = \frac{C_{dl}}{C_s}$$

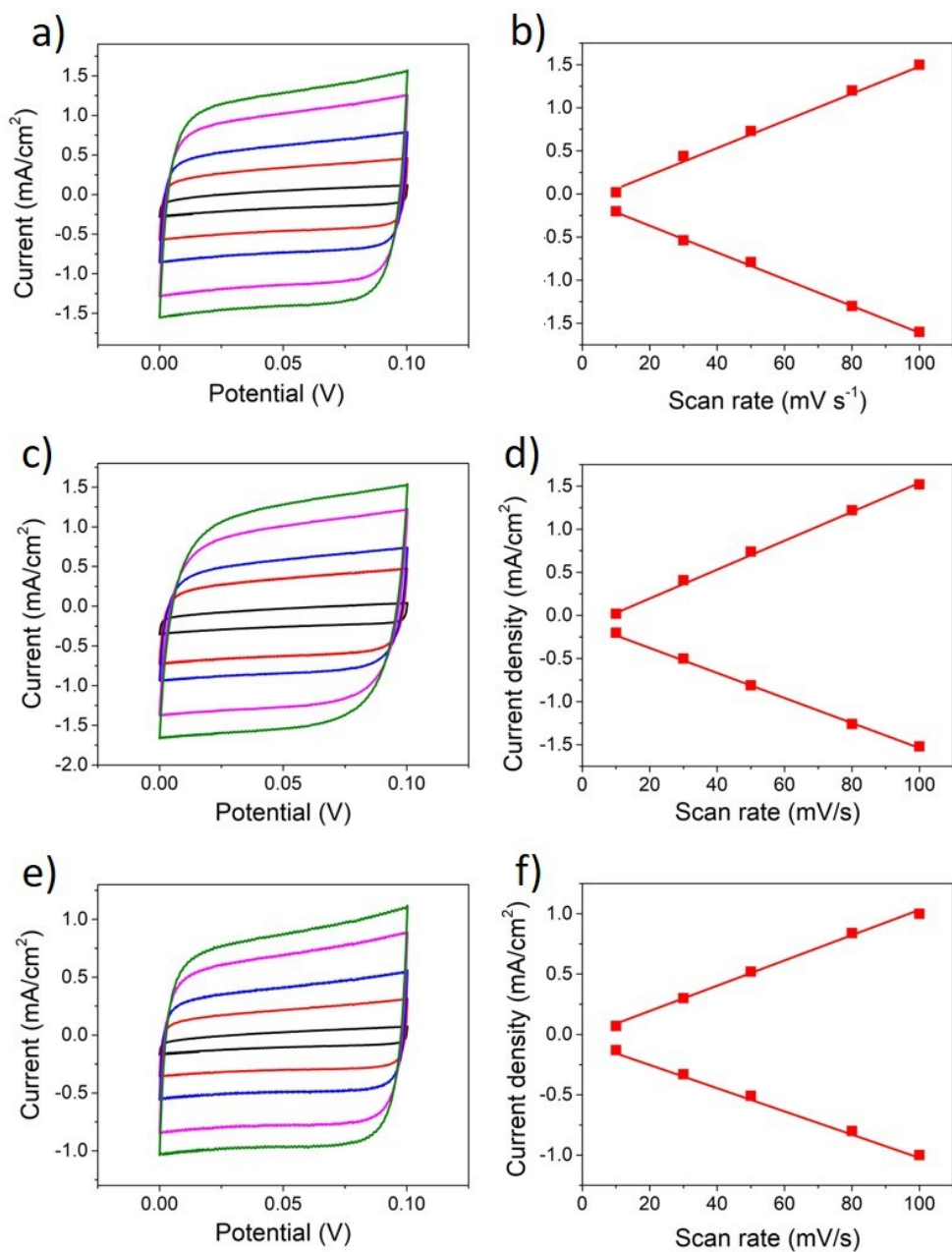


Fig. S11 a), c) & e) CV conducted at potential from 0.0 V to 0.1 V vs Ag/AgCl at scan rates of 10 mV/s, 30 mV/s, 50 mV/s, 80 mV/s, and 100 mV/s of P-rGO, PS-rGO, and S-rGO. b), d) & f) The current densities of anode and cathode measured at 0.05 V with different scan rates.

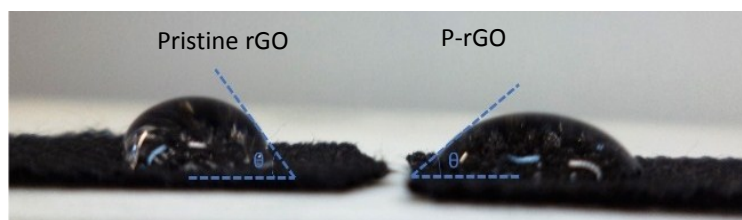


Fig. S12 water contact angle measurements for pristine rGO and P-rGO (digital photograph was taken after resting the water droplet on the surface of the electrodes for few seconds).

References

- 1 I. Danaee and S. Noori, *Int. J. Hydrogen Energy*, 2011, **36**, 12102- 12111.
- 2 M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li, S. Jin, *J. Am. Chem. Soc.* 2013, **135**, 10274-10277.