Correlation of hierarchical porosity in nanoporous gold with the mass transport of electron transfer-coupled-chemical reactions

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Calculation of ECSA of NPG

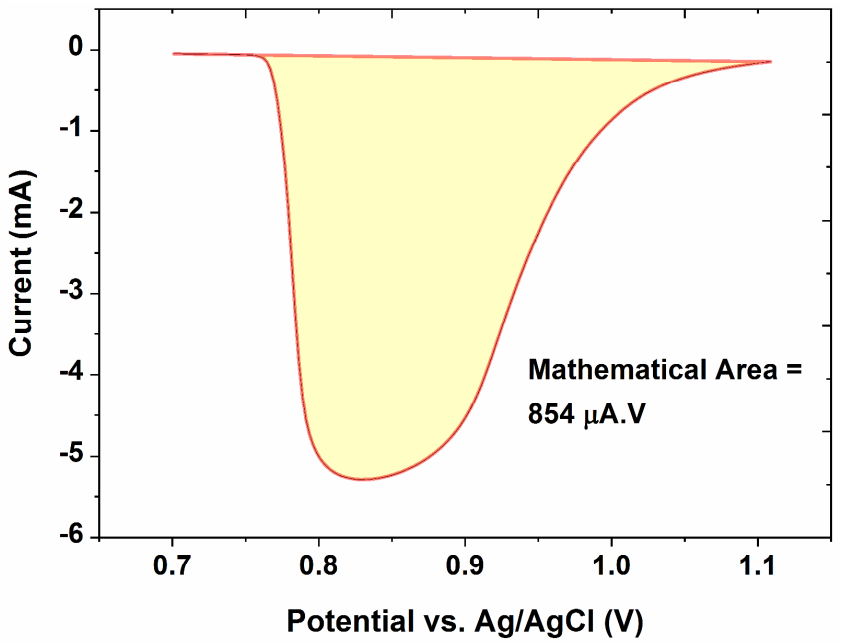

Figure S1: Mathematical area estimated by the integration of reduction peak of gold oxide into gold from the CV of NPG prepared at -4 V for 600 s in 0.5 M H_2SO_4 at scan rate 50 mV s^{-1} on 1.6 mm Au electrode

Charge (Q) = Peak area / Scan rate

= 854×10^{-6} (A.V)/ 0.05 ($V.s^{-1}$)

= 17080×10^{-6} A.s (equal to 17080 μC)

ESA = Q / 390μC cm^{-2}

= 17080 μC / 390μC cm^{-2}

= 43.79 cm^2

Note: *A value of 390 μC cm^{-2} was used for one monolayer charge of gold oxide reduction. Ref: Pure & Appl. Chem., 1991, 63, 711).*

Morphologies characterizations of NPG surfaces

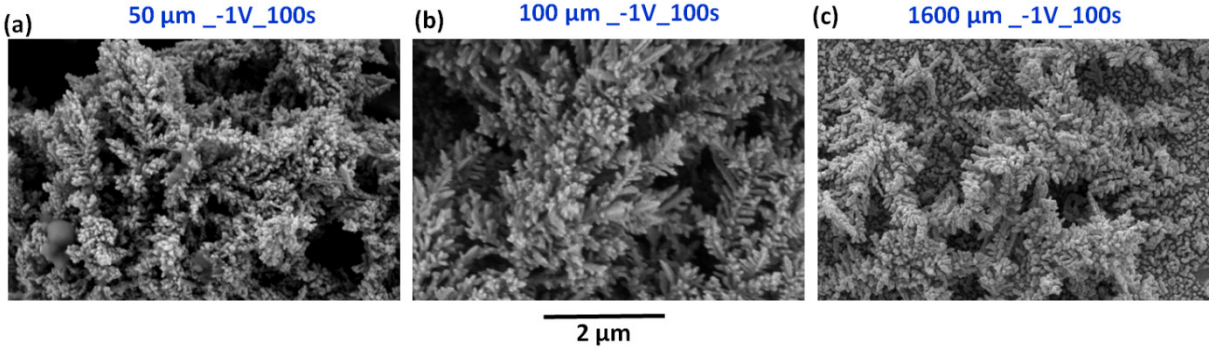

Figure S2: *SEM images of NPG films prepared at E_d = -1V and t_d = 100s.*

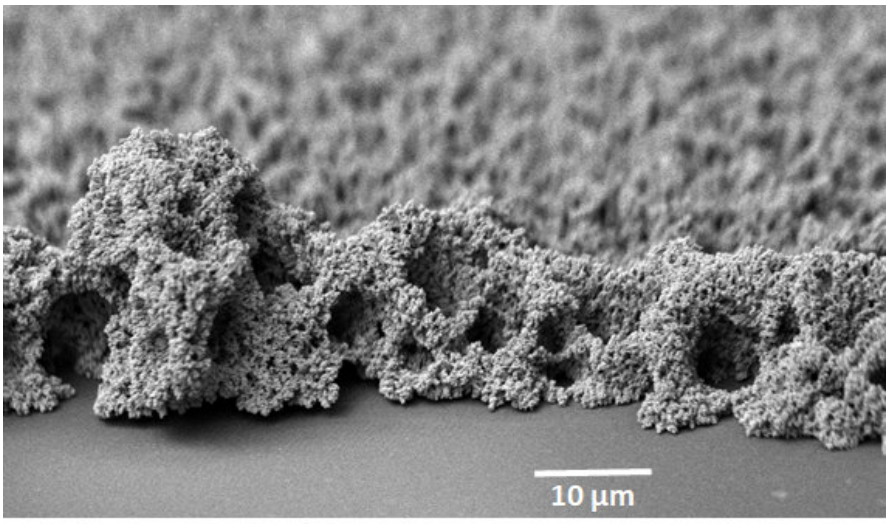

Figure S3: Cross section SEM image of NPG film deposited on 1.6 mm size Au electrode (*E_d = -4 V and t_d = 200 s)*.

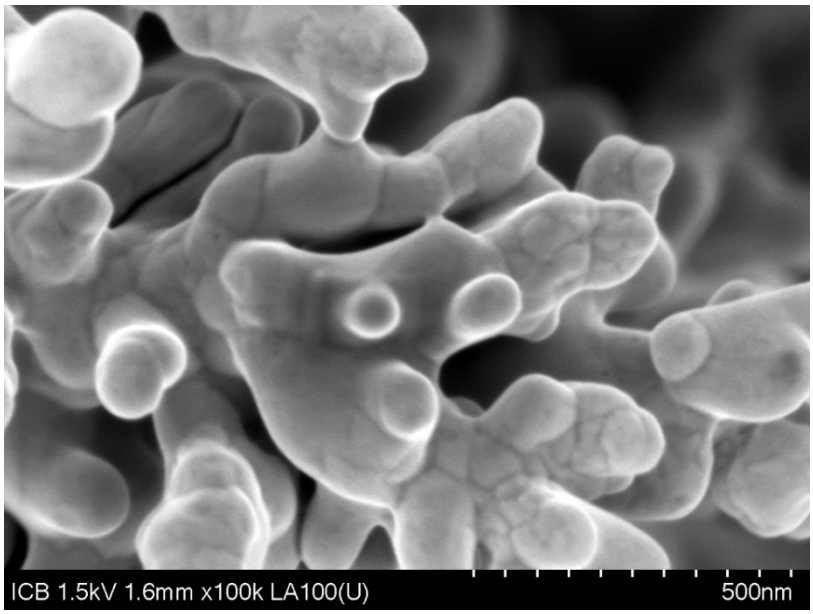

Figure S4: SEM image of NPG film deposited over Au electrode of diameter 1.6 mm (*E_d = -4 V and t_d = 200 s)*.

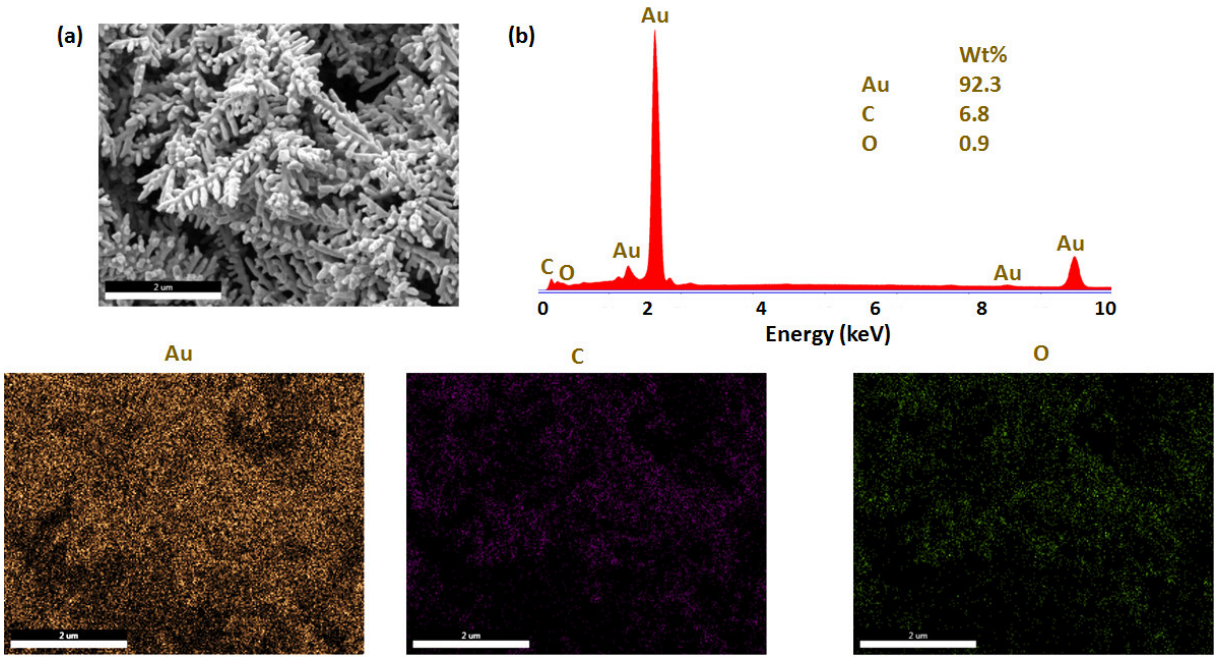

Figure S5: SEM image (a), EDS spectrum (b) and EDS mapping (lower image panels) of the NPG electrodeposited at E_d = -4 V and t_d = 200 s on 1.6 mm Au substrate.

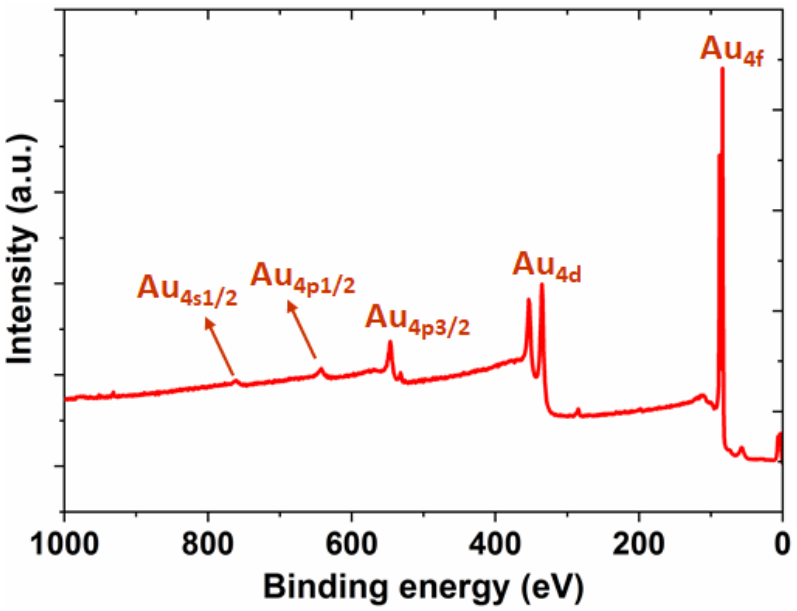

Figure S6: Survey XPS spectra of NPG thin film prepared at Ed= -4V and td = 200s.

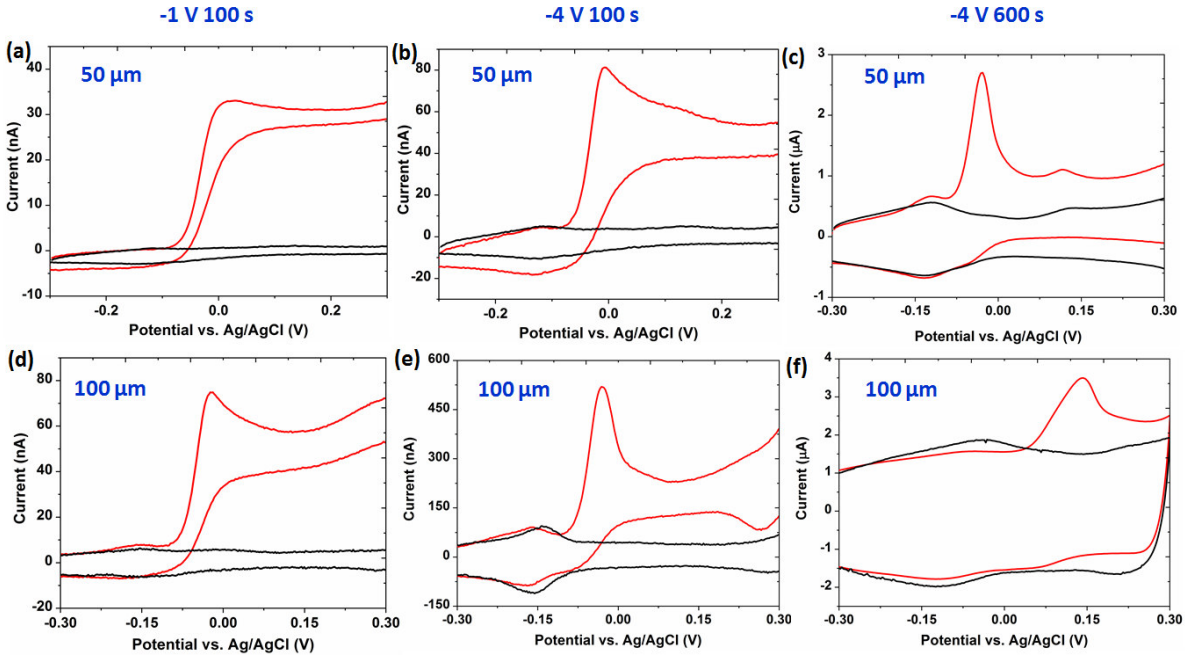

Figure S7: Comparison of cyclic voltammograms recorded in 0.6 mM AA + 0.1 M PBS and in 0.1 M PBS solutions of NPG prepared at E_d = -1 V and t_d = 100 s (a and d), E_d = -4 V and t_d = 100 s (b and e) and E_d = -4 V and t_d = 600 s (c and f) on 50 µm and 100 µm diameter Au electrodes. Scan rate: 10 mV s^{-1}.

Table S1: Summarizing deposition parameters such as t_d, E_d, the size of the electrode and their corresponding peak current, nature of the AA oxidation and dominant diffusion behavior.

Au electrode size (μm)	t_d (sec)	E_d (V)	Peak current	Nature of AA oxidation wave	dominant diffusion behavior
25	100	−1	13 nA	Sigmoidal	Bulk diffusion
	100	−4	41 nA	Sigmoidal	Bulk diffusion
	600	−4	132 nA	Non-symmetric peak	Bulk diffusion
50	100	−1	34 nA	Sigmoidal	Bulk diffusion
	100	−4	82 nA	Non-symmetric peak	Bulk diffusion
	600	−4	2.75 μA	Symmetric peak	Thin layer diffusion
100	100	−1	75 nA	Non-symmetric peak	Bulk diffusion
	100	−4	525 nA	Symmetric peak	Thin layer diffusion
	600	−4	3.51 μA	Symmetric peak	Thin layer diffusion
1600	100	−1	2.82 μA	Non-symmetric peak	Bulk diffusion
	100	−4	4.25 μA	Non-symmetric peak	Bulk diffusion
	600	−4	60 μA	Symmetric peak	Thin layer diffusion