Supplementary Information

Nanostructured Systems Obtention Using LbL Self-Assembly or the Cysteine-Assisted Adsorption Method and their Application as a Water Splitting Single Catalyst

Rhauane A. Galvão, [#,a,b] *Paloma B. Barreto,* [a,c] *Thiago A. S. Soares,* [a,c]
Letícia B. V. Sales, [a,c] *Jeice M. dos Santos,* [a,c] *Larissa A. de Santa-Cruz,* [a,c] *Tassia S. Seeger,* [d]
Fabio A. Duarte, [d] *Germana M. M. Silva* [a] *and Giovanna Machado* [*,a]

[a]*Laboratório de Nanomateriais, Centro de Tecnologias Estratégicas do Nordeste (CETENE), 50740-545 Recife-PE, Brazil*

[b]*Departamento de Engenharia Mecânica, Centro de Tecnologia e Geociências (CTG), Universidade Federal de Pernambuco (UFPE), 50740-550 Recife-PE, Brazil*

[c]*Programa de Pós-graduação em Ciência de Materiais (PGMtr), Centro de Ciências Exatas e da Natureza (CCEN), Universidade Federal de Pernambuco (UFPE), 50740-560 Recife-PE, Brazil*

[d]*Departamento de Química, Universidade Federal de Santa Maria (UFSM), 97105-900 Santa Maria-RS, Brazil*

_____

*e-mail: giovanna.machado@cetene.gov.br
[#]Present address: Programa de Pós-graduação em Ciência de Materiais (PGMtr), Centro de Ciências Exatas e da Natureza (CCEN), Universidade Federal de Pernambuco (UFPE), 50740-560 Recife-PE, Brazil

Transmission electron microscopy (TEM) images for the mainly systems are presented on Figure S1. On these images it is possible to see the nanotubes length and their attached nanoparticles, whose appearance significantly varies from one system to the others. As discussed in the manuscript, both bind agent and pH-dependence influence directly on surface gold size and distribution. In addition, for cysteine 2.3 thiol group nucleophile feature appears to remain, promoting the nucleation and growth of nanoparticles in a more controllable path.
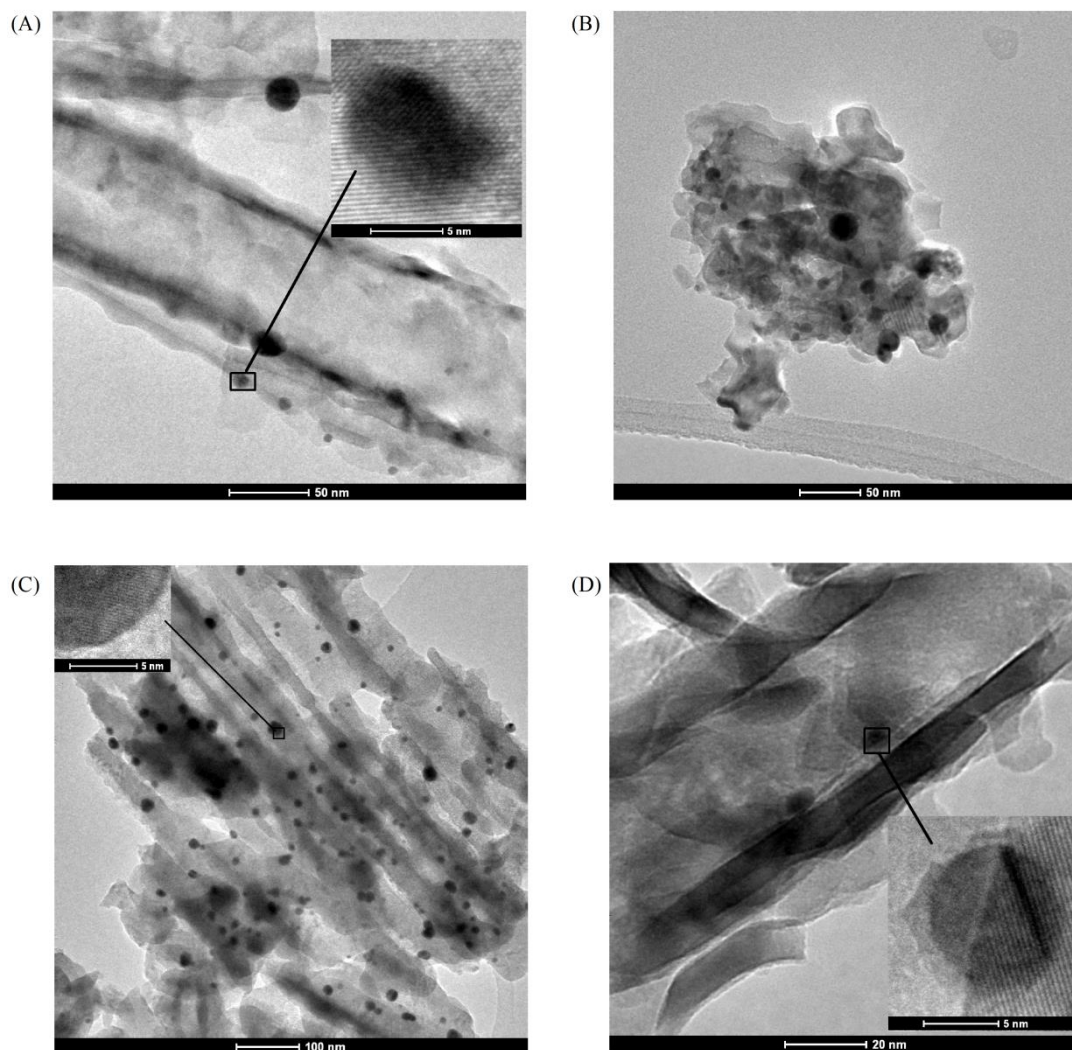

Figure S1. TEM images of selected samples (A) $[PAH_{7.5}/PAA_{3.5}]_5$ + $HAuCl_4$-2.3; (B) $[PAH_{7.5}/PAA_{3.5}]_{5.5}$ + $HAuCl_4$-2.3; (C) Cys + $HAuCl_4$-2.3 and (D) TiO_2 + $HAuCl_4$-2.3. Insets show high resolution images of the samples.

X-ray diffraction (XRD) analysis (Figure S2) allowed observing the crystal structure of the samples, where it was possible to identify the Bragg reflections regards to TiO_2 and Au. Crystalline anatase phase, with tetragonal structure, was confirmed by the peaks corresponding to the planes (101), (103), (004), (112), (200), (105), (211), (220), and (301), JCPDS card No. 21-1272, while gold adsorption, with cubic structure, is verified through the peaks due to the (111), (200), (220) and (311) planes, JCPDS card No. 4-784. These comportments were observed for all samples, except for the absence of gold (200) Bragg reflections on the samples without binds (TiO_2 + $HAuCl_4$-m), suggesting that is smaller gold adsorption when it is made directly on TiO_2 nanotubes (NTs) surface.

The presence of anatase phase, which is due to the temperature used on heat treatment, in detriment to rutile phase formation, is of great importance, once anatase is more photocatalytic active than rutile.[1] It is related to the increased recombination rate observed on rutile, which reduces the charge transfer, and consequently the system efficiency. Anatase phase has a higher surface area, a high density of active sites for adsorption, slowly recombination rates and bigger electronic mobilities.[2]
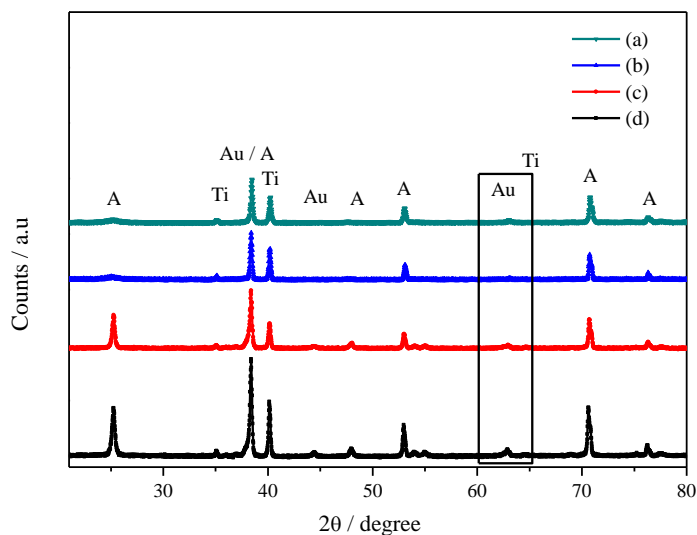

Figure S2. XRD analysis of selected samples (a) TiO_2 + $HAuCl_4$-2.3; (b) Cys + $HAuCl_4$-2.3; (c) $[PAH_{7.5}/PAA_{3.5}]_{5.5}$ + $HAuCl_4$-2.3 and (d) $[PAH_{7.5}/PAA_{3.5}]_5$ + $HAuCl_4$-2.3.

Scanning electron microscopy (SEM) images proved TiO_2 NTs obtention from titanium foils. Figure S3 shows the surface morphology of the samples, with no significate alterations regards to the surface treatment or gold addition. An energy dispersive spectrometry (EDS) representative analysis is also presented, which confirms the gold incorporation to the samples. It was observed for all studied systems that addition of layer-by-layer (LbL), cysteine or none did not change the sample morphology, as well as gold incorporation was achieved using both the systems.
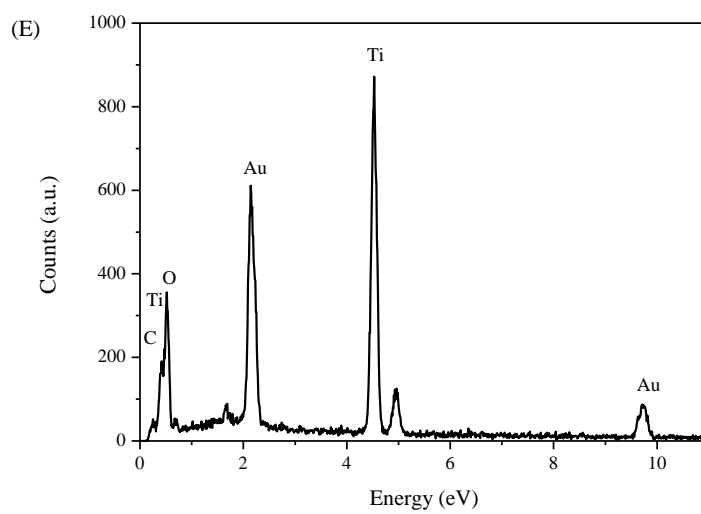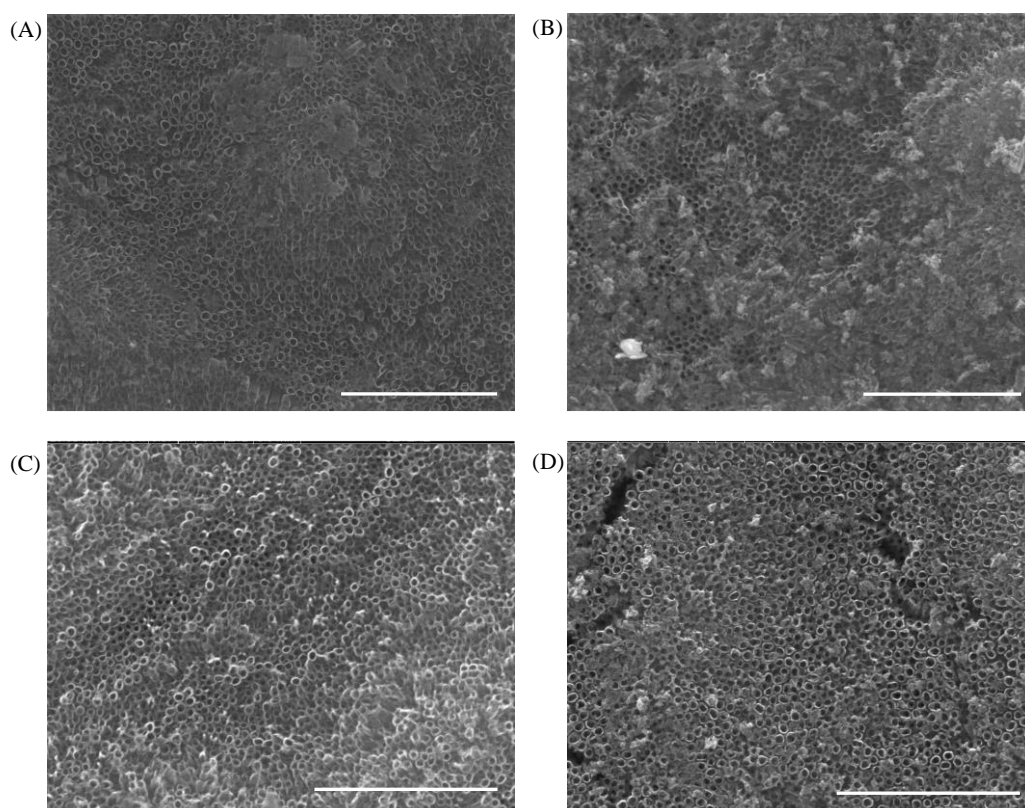
Figure S3. SEM images of selected samples (A) [PAH$_{7.5}$/PAA$_{3.5}$]$_5$ + HAuCl$_4$-2.3; (B) [PAH$_{7.5}$/PAA$_{3.5}$]$_{5.5}$ + HAuCl$_4$-2.3; (C) Cys + HAuCl$_4$-2.3 and (D) TiO$_2$ + HAuCl$_4$-2.3; an EDS representative analysis is shown in (E).

References

1.   Sreekantan, S.; Hazan, R.; Lockman, Z.; *Thin Solid Films* **2009**, *518*, 16.

2.   Luttrell, T.; Halpegamage, S.; Tao, J.; Kramer, A.; Sutter, E.; Batzill, M.; *Sci. Rep.* **2015**, *4*, 1.