

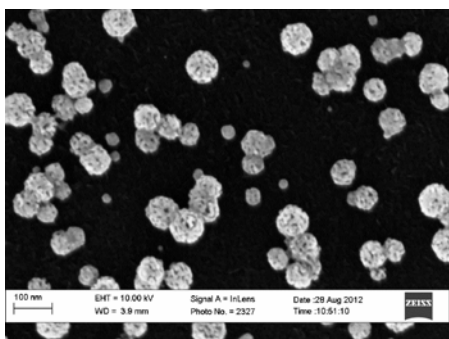
## Electrodeposition of Continuous Ultrathin Layers of Functionalized Nanoporous Catalyst on Glassy Carbon Electrodes

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Many catalytic processes utilize nanoscale materials in order to catalyze reactions such as methanol oxidation, formic acid oxidation, and oxygen reduction etc. However, the development of cost-effective synthetic routines requires such catalysts to be supported on inexpensive, usually C-based substrates. Among those, glassy carbon (GC) is a viable candidate due to its high conductivity, inertness in electrolytic solutions, and low cost. Currently, GC is a popular support for nanoparticle<sup>1</sup> (NP) catalysts in research grade experiments. The NPs immobilization is performed either by application of already synthesized catalyst or by in-situ deposition in the course of catalyst's preparation onto GC itself.<sup>2,3</sup>

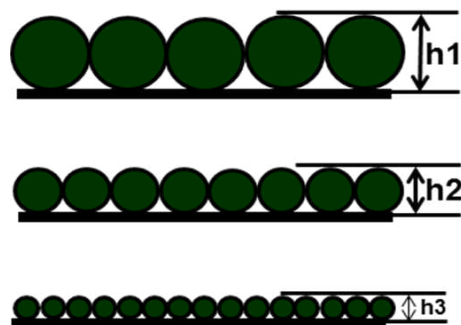
Nanoporous gold (NPG) is a material with unique structure and high surface area-to-volume ratio with applications in sensing and catalysis.<sup>4</sup> Recently, thin continuous films of Pt-NPG have been synthesized by Ag-Au alloy deposition followed by de-alloying and catalytically proven efficient for HCOOH oxidation after platinization.<sup>5</sup> However, when processed on inexpensive substrates like GC, these catalysts grow in large isolated clusters instead of uniform and continuous films (Figure 1). Key challenges with such scattered large-size cluster



**Figure 1.** NPG clusters fabricated on untreated GC.

coverage are associated with poor mechanical stability and limited accessibility of the catalytically active surface. Addressing these challenges, an effort has been made in this work to electrodeposit on GC surfaces ultrathin and continuous alloy films structurally resembling layers deposited on metal. The entertained experimental approach relies on exploring strategies for densification of the deposited alloy precursor on the GC surface. Among those, key emphasis has been placed on seeding of the GC with a dense ensemble of metal clusters and on control of the oxygen content in the deposition solution. The ultimate goal has been to facilitate the growth of a high-density alloy cluster network that is prone to uniform coalescence at very low thickness of the deposited layer (Figure 2).

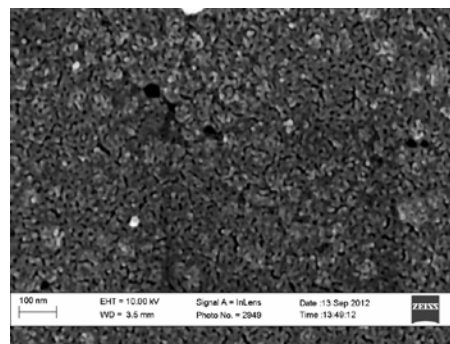
The seeding has been performed using electroless and electrodeposition approaches for metallization. In parallel with the seeding, different steps of the synthetic process have been studied in naturally aerated and de-oxygenated solutions and with different supporting electrolytes. The outcome of the densification process has been assessed



**Figure 2.** Thickness at coalescence as a function of cluster size.

electrochemically throughout the synthesis and by scanning electron microscopy (SEM) after completing the routine producing NPG structures. Focus of the assessment has been the surface coverage, thickness, and overall surface area of the NPG layer. The compositional homogeneity of the deposited alloy has been examined by de-alloying polarization curves. The overall surface area evolution of the NPG structure has been studied by Pb UPD following a protocol described in our earlier work.<sup>6</sup> The surface area has been also cross-examined by H UPD measurements<sup>7</sup> performed after platinization of developed accordingly NPG structures.

The talk summarizes steps of the optimization effort towards achievement of continuity. The optimum set of conditions associated with oxygen content, seeding approach and supporting electrolyte are demonstrated and critically discussed vis-a-vis the entire set of characterization results. Figure 3 clearly demonstrates the NPG layer continuity on GC when the optimized strategy



**Figure 3.** Continuous NPG layer fabricated on modified GC.

proposed in this report is applied. Comparison is made with other approaches for fabrication of a continuous metal layers on GC. Analysis of the cost-effectiveness of the proposed approach in a variety of applications is also presented. Possibilities for further optimization of these routines are discussed at the end of the presentation from the stand-point of achieving enhanced catalyst adhesion to the GC substrate.

- Xu, D.; Bliznakov, S.; Liu, Z.; Fang, J.; Dimitrov, N., *Angew Chem Int Ed Engl* **2010**, *49*, 1282-5.
- Domínguez-Domínguez, S.; Arias-Pardilla, J.; Berenguer-Murcia, Á.; Morallón, E.; Cazorla-Amorós, D., *Journal of Applied Electrochemistry* **2007**, *38*, 259-268.
- Savouchkina, A.; Foelske-Schmitz, A.; Scherer, G. G.; Wokaun, A.; Kötz, R., *Journal of The Electrochemical Society* **2011**, *158*, D420.
- Seker, E.; Reed, M. L.; Begley, M. R., *Materials* **2009**, *2*, 2188-2215.
- McCurry, D. A.; Kamundi, M.; Fayette, M.; Wafula, F.; Dimitrov, N., *Acs Appl Mater Inter* **2011**, *3*, 4459-4468.
- Liu, Y.; Bliznakov, S.; Dimitrov, N., *J Phys Chem C* **2009**, *113*, 12362-12372.
- Mayrhofer, K. J. J.; Strmcnik, D.; Blizanac, B. B.; Stamenkovic, V.; Arenz, M.; Markovic, N. M., *Electrochim Acta* **2008**, *53*, 3181-3188.