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Reference:

Vanrenterghem Bart, Hodnik Nejc, Bele Marjan, Sala Martin, Amelinckx Giovanni, Neukermans Sander, Zaplotnik Rok, Primc Gregor, Mozetic Miran, Breugelmans Tom.- Increase of electrodeposited catalyst stability via plasma grown vertically oriented graphene nanoparticle movement restriction
ChemComm / Royal Society of Chemistry [London] - ISSN 1359-7345 - 53:67(2017), p. 9340-9343
Full text (Publisher's DOI): <https://doi.org/10.1039/C7CC05828D>
To cite this reference: <http://hdl.handle.net/10067/1457000151162165141>

ChemComm

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This article can be cited before page numbers have been issued, to do this please use: B. Vanrenterghem, N. Hodnik, M. Bele, M. Šala, G. Amelinckx, S. Neukermans, R. Zaplotnik, G. Primc, M. Mozetic and T. Breugelmans, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC05828D.



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Chemical Communications

COMMUNICATION

Increase of Electrodeposited Catalyst Stability via Plasma Grown Vertically Oriented Graphene Nanoparticles Movement Restriction

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Beside activity, electrocatalyst stability is gaining in importance. The most common degradation mechanism is the loss of active surface area due to nanoparticle growth via coalescence/agglomeration. We propose a particle confinement strategy via vertically oriented graphene deposition to overcome degradation of the nanoparticles.

Electrocatalysis possesses a manifold of advantages compared to the traditional heterogeneous catalysis approach for many synthetic and conversion reactions^{1,2}. Industrial attractiveness is promising by exceptional selectivity³, better control over reactions rates⁴, the ease with which many electrochemical reactions can be scaled up⁵, as well as the intrinsic "greenness" of the reactions; the electron being a cheap, clean and energy efficient reagent⁶. In organic electrochemistry a selective introduction and removal of electrons from organic molecules is an ideal tool to activate functional groups^{6,7}. Besides this many current grand challenges like carbon dioxide induced global warming, sustainable energy conversion and storage are being directly addressed by the usage of electrocatalysts in electrochemical reactors^{8,9}. There is a strong need for the development of efficient, durable electrocatalyst that enables the synthesis of added value products. Many electrocatalysts suffer from stability issues usually related to loss of electrochemical active surface area (EASA). Degradation mechanisms range from particle coalescence/agglomeration, Ostwald ripening, corrosion of the support, particle detachment, dissolution, reshaping and deactivation¹⁰⁻¹². Generally degradation mechanisms can be divided in two groups depending at which potentials they occur. At oxidative potentials corrosion and dissolution are expected, whereas at reductive potentials coalescence/agglomeration is assumed to be the dominant

mechanism.

This paper investigates the stability issue on the reductive cleavage of organic halides (RX) as a model reaction and more specific benzylbromide reduction for which the electrocatalyst plays an important role¹³. The electrocatalytic reduction of RX compounds proceeds through an attenuated radical intermediates involving R, X and M. It has been shown that the molecular structure (R)¹⁴, the nature of the halogen atom (X)¹⁵, cathode material (M)¹⁶ and electrode surface morphology¹⁷ play a decisive role. Research indicates that Ag based nanoparticles are the catalyst of choice for good catalytic properties towards the halide reduction¹⁶. Electrodeposition is used as nanoparticle synthesis technique due to its versatility^{17,18} and ability to form nanoparticles directly in-situ on the electrode. Although lots of research has been devoted to the development of new active catalysts¹⁴, not much attention has been dedicated to the stability of the catalyst towards reductive cleavage of RX compounds. It is for instance known that nanoparticles like Ag and Cu have a strong tendency to coalescence/agglomeration at reductive potentials which results in a decrease of EASA^{2,19}. However, no mitigation strategy has been proposed to overcome this issue.

To improve the stability of electrodeposited Ag nanoparticles we propose to physically separate the Ag nanoparticles. This is achieved by, at first, growing vertically oriented graphene (VOG) with plasma on a plane carbon rod; electrode. Secondly nanoparticles are electro-deposited insight the thin film of VOG, which acts as barrier to protect the nanoparticles from migration and dissolution in to the bulk (confinement effect). In this work we will show the great possibilities of VOG in comparison to a planar carbon electrode as supporting material. This will be investigated on both the initial activity as well as the long term performance of Ag nanoparticles towards electrochemical C-X bond activation. Here the authors would like to add that a similar physical separation strategy of nanoparticles can also be used for other reaction such as CO₂- or oxygen reduction reactions. Fig. 1 shows a SEM image of electrodeposited Ag nanoparticles on a carbon rod electrode and Fig. 2A their polarisation curves in

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

acetonitrile + benzylbromide (1 mM) as electrochemical active compound. The electrodeposited Ag nanoparticles are spherical with an average size of 125 nm in accordance with previous results¹⁷ and the activation of the C-Br proceeds at -0.97 V vs. Ag/AgCl^{17,20}. More information concerning the deposition procedure, the advanced electrochemical degradation protocol, identical location scanning electron microscopy (IL-SEM) and performance measurement approach with the same electrode can be found in the supplementary information (Supplementary Section 1). Fig. 2c shows the progressive loss of activity on Ag nanoparticles deposited on a planar carbon electrode with an increasing amount of degradation cycles (DC). To study the stability issue the kinetic current, obtained at a fixed potential by performing linear sweep voltammetry at constant rotation rate (459 RPM), is plotted vs. the number of performed cycles. After 15 000 DC the kinetic current has decreased to a quarter of the initial value. This clear drop in kinetic current is attributed to a loss of EASA as a result of particle growth via coalescence mechanism. The agglomeration of nanoparticles under electrochemical operation conditions is caused by particle surface migration and subsequent coalescence. The other particle growth mechanism would be Ostwald ripening that occurs due to atom migration from small crystals to larger ones, the driving force of this process being the minimization of the clusters

Gibbs free energy²¹. Continuous cycling of the Ag nanoparticles results in strong clustering whereas the average nanoparticle size increases from 125 nm until 604 nm. The plots regarding the change of particle distribution can be consulted in the supplementary information (Supplementary Section 1). In addition the analytical determination of the concentration of detached nanocatalyst is investigated with ICP-MS (Supplementary information Section 2). Investigation of the electrolyte after 15 000 DC shows that 14 m% of the catalyst is lost during electrochemical operation conditions, most likely due to particle detachment. In this study we confirm that the degradation occurs besides particle detachment due to the coalescence mechanism. Close inspection of the IL-SEM figures (Fig. 1a and 1d) reveals two unique features: (i) particles clearly move from their primary position and (ii) the degraded sample contains typical irregular and even anisotropic nanoparticle morphologies produced by consumption of primary small nanocrystals as "building blocks"²². Our unique IL-SEM technique enables the unambiguous conformation on particle movement, where in contrast to coalescence, Ostwald ripening predicts no particle movement and spherical shapes. We therefore conclude that coalescence is the primary mechanism for particle clustering. More IL-SEM with different magnifications can be found in Supporting information (Supplementary Section 1).

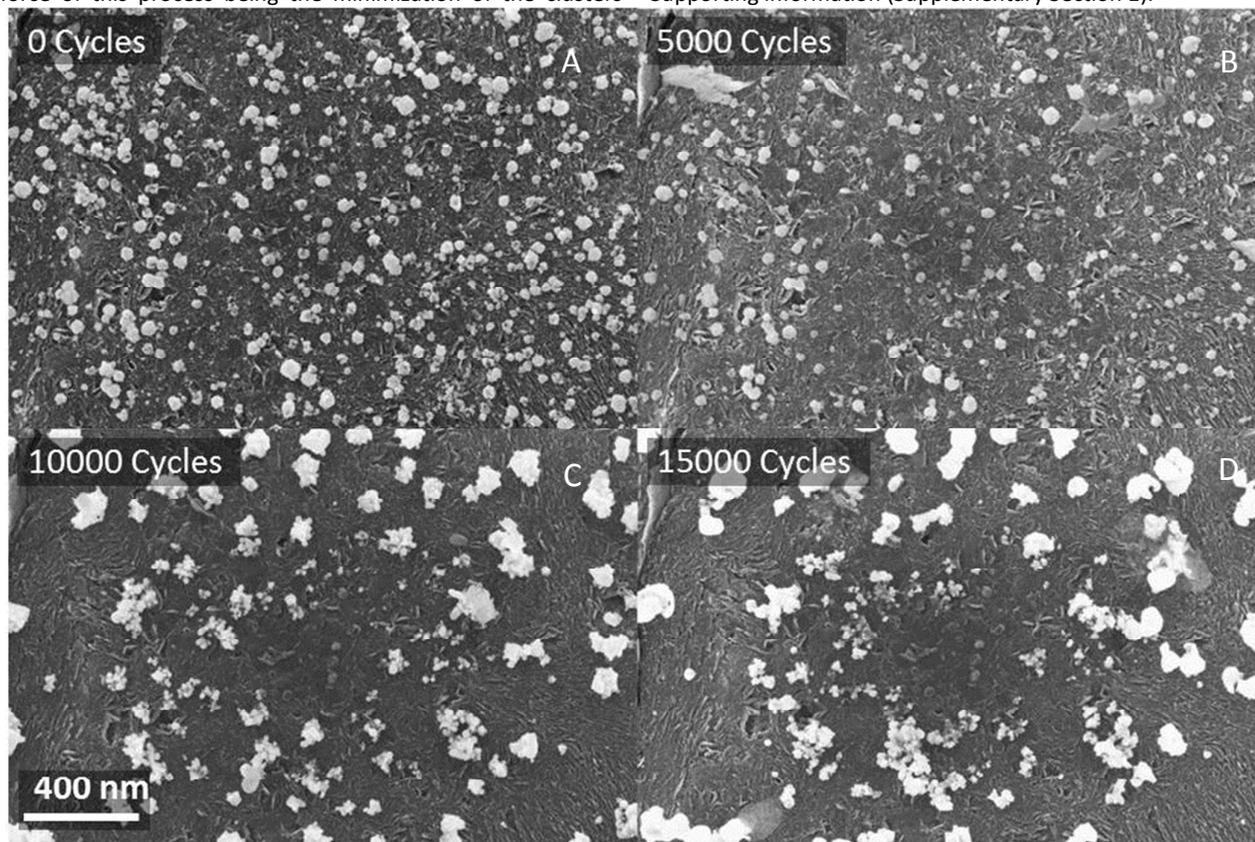


Figure 1: Degradation of electrodeposited Ag nanoparticles on a carbon rod, SEM images before (0 Cycles) and after 5000, 10000 and 15000 Cycles.

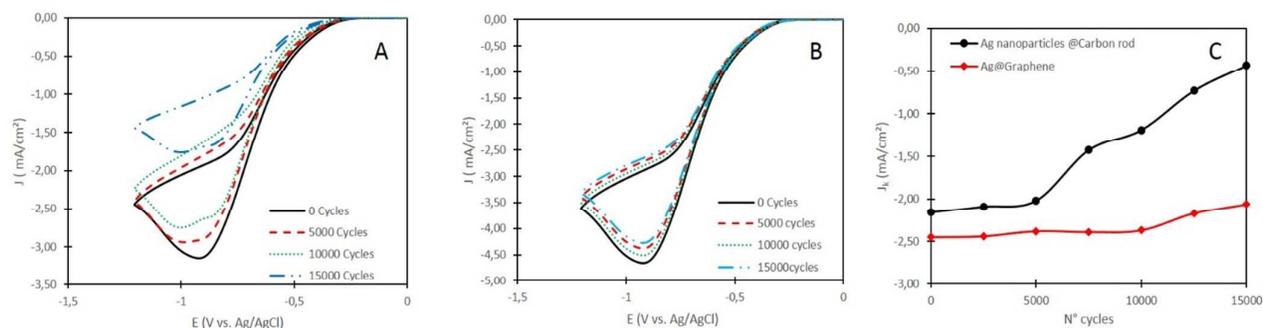


Figure 2: CV features of (A) Ag nanoparticles on a planar carbon electrode and (B) Ag nanoparticles on a VOG electrode recorded at $50 \text{ mV}\cdot\text{s}^{-1}$. (C) decrease of the kinetic current recorded with LSV at 459 RPM.

In order to prevent loss of metal particles and agglomeration of the nanocatalyst caused by detachment and migration on the support, we propose a particle confinement strategy by changing the morphology of the supporting material. Instead of a planar carbon electrode we choose to deposit Ag nanoparticles inside a plasma grown, VOG electrode under the assumption that this will physically restrict nanoparticles to move on the support and detach into the electrolyte. More information on plasma grown graphene can be found in previous research and supplementary information (Supplementary section 3). In contrast with a planar electrode the graphene electrode offers interesting structures due to its reduced dimensionality, open boundaries, sharp edges and its high surface-to-volume ratio. Raman spectra (supplementary information) shows a narrow full width half maximum for G and 2-D bands giving an I_G/I_D ratio of 1, which confirms the characteristics of highly crystallized few layered graphene. The columnar morphology, with well-separated columns allows crystal seed deposition to occur inside the confined, protective support. In Figure 3A-D one can see that no Ag particles are present on the outer surface edges of the graphene support (in-lens detector, Fig 3A-B) but all the Ag is encapsulated inside the graphene structure (secondary electron detector, Fig 3C-D). This statement is supported in Fig 3G-H where a cross section of graphene is shown and Ag can be seen inside the columnar graphene structure. The average particle size is 273 nm, which is double in comparison with a planar carbon rod surface for identical deposition parameters. It is assumed that the larger particle size arises from the porosity²³ of graphene where nuclei grow faster²⁴ and more favourable inside the cavities. Although a larger particle size is obtained, the particle size distribution (Supplementary section 4) is more narrow resulting uniform distribution. The authors believe that by optimising the size of the plasma grown graphene channels and most of all the deposition procedure smaller Ag nanoparticles could be obtained. Crucially, activity is shown to be unaffected by particle confinement the authors assume the pores inside the graphene structure remain of adequate size (ca. 100 nm) for mass transport to occur without limitations. The reduction peak for benzyl bromide is present at a similar potential in reference to the carbon rod sample (-0.98 V vs. Ag/AgCl). ICP-MS results show that 17 % less of Ag is being

deposited in the case of VOG electrode. Despite the slightly lower mass of electrodeposited Ag, results (Fig 2C) recorded at identical rotation rate (459 RPM), exhibit a higher kinetic current meaning that the mass based activity is larger for the graphene based electrode. The authors speculate that this could be due to better accessibility of reaction sites (where the resistance of the channels is being neglected due to the adequate size) caused by the structured channels of the graphene and/or beneficial interaction of the graphene with Ag nanocrystals. We note that pure graphene does not exhibit any activity (Supporting Section 4) but previous research²⁵ regarding catalyst-support interaction has already shown the beneficial aspects of graphene-supported electrocatalysts.

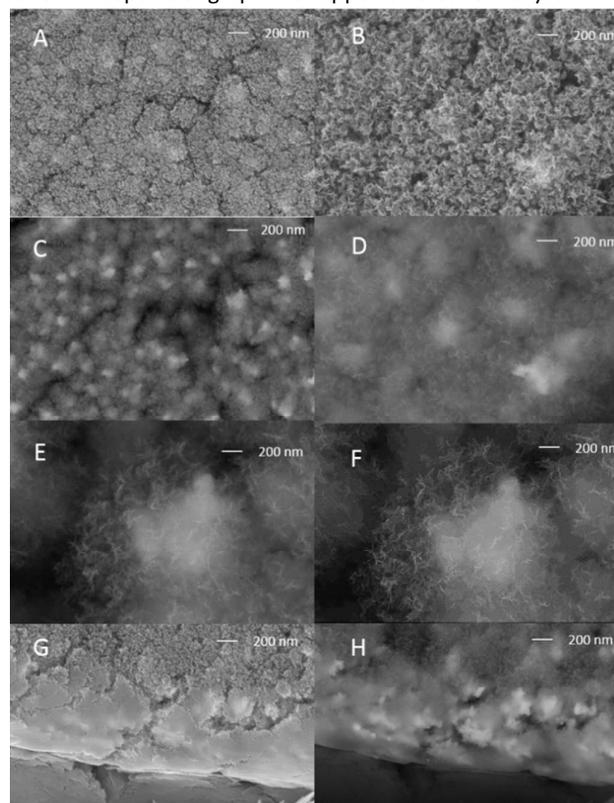


Figure 3: SEM images of Ag nanoparticles on VOG electrode, (A-B) in-lens detector (C-D) secondary detector, (E) IL-SEM before and (F) IL-SEM after

However, more importantly, much greater stability was obtained compared to the non-modified electrode. As indicated in Fig 2C the limiting current for the benzyl bromide reduction reaction stays almost constant under electrochemical operation conditions until 15 000 DC. IL-SEM images before and after DC (Fig 3E before–3F after Supplementary information Section 5) confirm superior stability of the VOG protected Ag nanocatalyst exhibiting no agglomeration or coalescence. The graphene structure acts as a barrier for particle migration and cluster formation. In addition ICP-MS of the electrolyte after degradation verifies that only 2.3 m% of the catalyst is lost due to Ag detachment. The superior stability of the nanoparticles is also confirmed for Cu and Au nanoparticles (supplementary information).

Conclusion

We conclude that by physically separating the Ag nanoparticles with VOG inter particle surface migration and subsequent coalescence together with particle detachment during electrochemical operation conditions can be effectively prevented. This strategy can be considered as a general way to prevent coalescence/agglomeration of metallic nanoparticles for any electrochemical reaction and other applications beside electrocatalysis and thus increase the nanoparticles long term stability.

Acknowledgment

This study was supported by the Slovenian Research Agency for the research programme P2-0152, P2-0082, P2-0393 and project Z2-8161. Bart Vanreenterghem acknowledges financial support from the FWO (travel grant 145992 FB V4.335.16N).

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