Electronic Supplementary Material (ESI) for ChemComm.

Supporting information:

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

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Section 1

1. Electrodeposition of Ag nanoparticles

Nanoparticles were electrodeposited on a plane carbon rod or vertically oriented graphene electrode. The scheme for the sample preparation of the carbon rod and graphene electrode is shown in Fig 1.

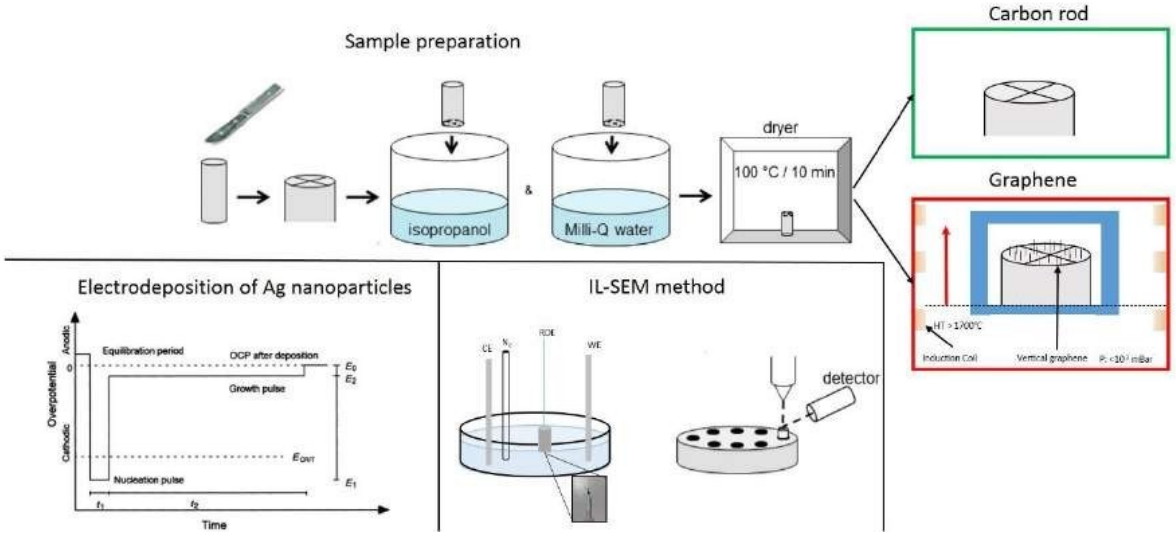

Figure 1: Sample preparation scheme

Before each deposition the plane carbon was intensively polished to prior extend followed by ultrasonic rinsing in isopropanol and ultra-pure water (18.2 MΩcm). The carbon rod and graphene electrode were placed in an electrolyte solution of Acetonitrile (J.T. Baker, HPLC gradient) containing tetrabutylammonium perchlorate (TBAP, Sigma Aldrich, 99%) and a metal salt. To obtain monometallic Ag nanoparticles $AgNO_3$ (Sigma Aldrich, >99%) was used as metal salt. Before each deposition the electrolyte was deaerated with N_2 to prevent oxide formation. Electrodeposition was carried out with a Nordic electrochemistry potentiostat ECI-200 from a classical three electrode electrochemical cell with a carbon rod/ graphene working electrode, Pt counter electrode and an Ag/AgCl reference electrode. Unless stated otherwise all mentioned potentials are reported vs. Ag/AgCl. The nucleation and growth parameters for the electrodeposition of nanoparticles was chosen based on the cyclic voltammogram (CV) recorded at $50mV.s^{-1}$ (Figure 2) of the respectfully metal salt in the electrolyte solution.

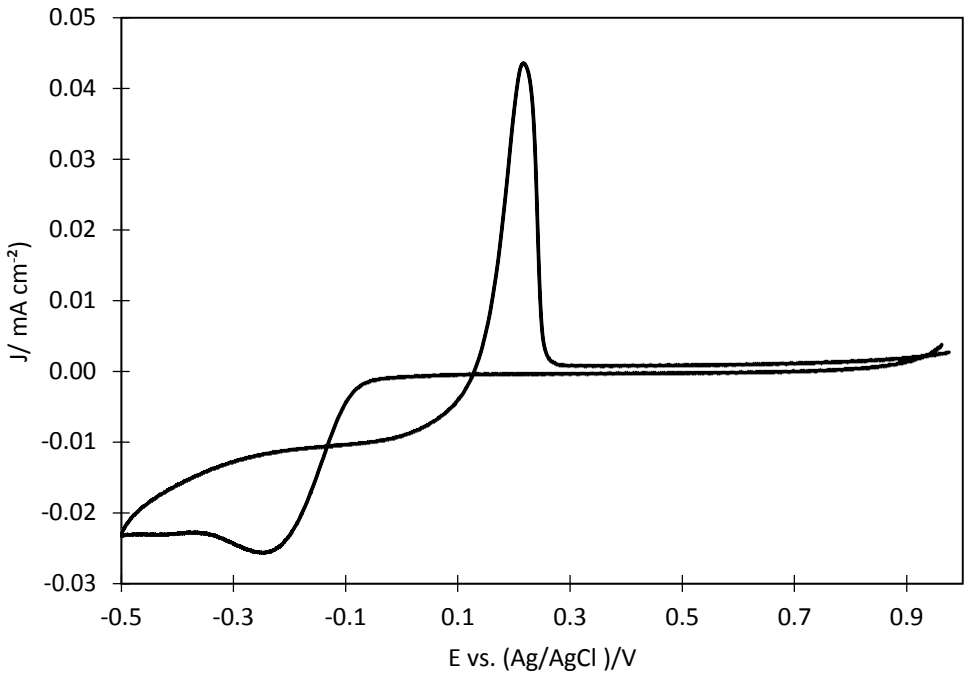

Figure 2: CV features at 50 mV s^{-1} of $AgNO_3$ in Acetonitrile.

Studying the CV features of Figure 2 one notices a system with clear reduction/oxidation peaks indicating a diffusion controlled electrodeposition and stripping. The same voltammetric response was obtained for a carbon rod and graphene electrode. The onset potential of the scan determines the critical deposition potential. To prevent progressive nucleation and deposit spontaneous crystal seeds on the surface a pulse in the mass transport region is chosen. The second pulse is applied for crystal growth and is set in the mixed kinetic region of the reduction peak. Based on these findings a nucleation potential of -0.8 V for a charge of 0.125 mC cm^{-2} is set. While afterwards a growth potential of -0.14 V with a charge of 1.8 mC cm^{-2} is applied. Extra information concerning the electrodeposition of Ag can be found in:

B. Geboes, B. Vanrenterghem, J. Ustarroz, and D. Pauwels, “Influence of the Morphology of Electrodeposited Nanoparticles on the Activity of Organic Halide Reduction,” *Chem. Eng. Trans.*, vol. 41, pp. 73–78, 2014.

M. Ueda, H. Dietz, A. Anders, H. Kneppe, A. Meixner, and W. Plieth, “Double-pulse technique as an electrochemical tool for controlling the preparation of metallic nanoparticles,” *Electrochim. Acta*, vol. 48, no. 4, pp. 377–386, Dec. 2002.

2. IL-SEM imaging

The electrodes were microscopically characterized with a field-emission SEM (Supra 35 VP Carl Zeiss, Germany and Quanta FEG 250). Imaging took place with an in-lens- and secondary electron detector. Before each SEM measurement the electrodes were dried to air overnight while imaging took place at an acceleration voltage of 7-15 keV. ImageJ SXM 192.1 was used to extract the average particle diameter from thresholded SEM images.

The morphological changes were investigated using an Identical Scanning Electron Microscopy (IL-SEM) approach. This method allows, as the name suggests, the observations of the same site (and thus same nanoparticles) before and after electrochemical treatment (polarization). For a complete and fully description we refer to the work of Hodnik et all. [12], [17].

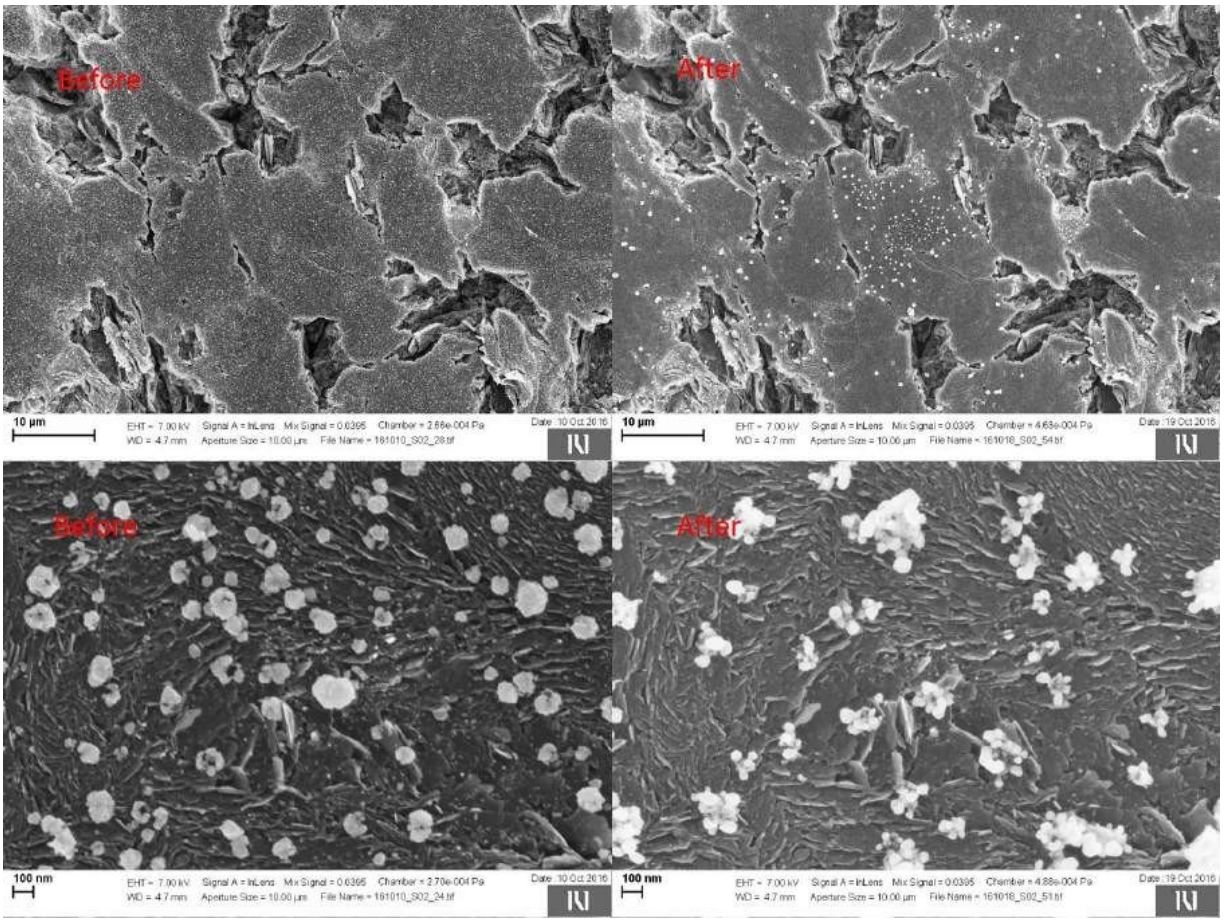

Figure 3: IL-SEM images of nanoparticles before and after cycling

3. Degradation protocol/ activity measurements

Degradation mechanism will be investigated using an accelerated-aging protocol at low-temperature conditions. During this protocol cycling is repeated between -2 V and 0 V at the rate of 1 cycle every few seconds. Repetitions of up until 15.000 cycles allows a durable evaluation of the stability of electrocatalysts. After respectfully 0; 5000 ; 10000 and 15000 cycles the activity of the catalyst is evaluated. This is done with linear sweep voltammetry in combination with a rotating disk electrode at a fixed rotation speeds of 459 rpm. The kinetic current recorded at -0.95 V vs. Ag/AgCl (reduction peak potential) is plotted vs. the number of performed cycles to investigate the electrochemical degradation of the catalyst.

Section 2

The analytical degradation of the catalyst was analysed using using mass spectrometry (MS) with inductive coupled plasma (ICP) after 1000 fold dilution. For sample dilution and preparation of standards, ultrapure (Milipore), ultrapure acids

(HNO_3), Merck, (Suprapur) and LC-MS grade Acetonitrile (Sigma-Aldrich) were used. Standards were prepared in-house by dilution of certified, traceable, inductively coupled plasma (ICP) grade single-element standards (Merck Certipur). An Agilent quadrupole ICP-MS instrument (Agilent 7900, Agilent Technologies, Santa Clara, CA), equipped with MicroMist glass concentric nebulizer and Pletier-cooled, Scott type spray chamber, was used for measurement.

Table 1: Loss of Ag nanoparticles in m% at a carbon rod (left) and graphene (right) electrode after electrochemical degradation

N° Cycles	Loss of catalyst (m%)	N° Cycles	Loss of catalyst (m%)
0	0	0	0
2500	0,3	2500	0,3
5000	3,1	5000	0,9
7500	4,5	7500	1,3
10000	8,4	10000	1,5
12500	11	12500	1,6
15000	14	15000	2,3

Section 3

Vertically oriented graphene sheets have been deposited onto a carbon rod by Plasma-Enhanced Chemical Vapour Deposition (PECVD). Carbon-containing gaseous precursor was introduced into a vacuum chamber where the rod was mounted. After evacuation to the ultimate pressure the precursors were introduced through a needle valve so that the pressure in the system was about 30 Pa. Weakly ionized plasma was created inside the chamber using radiofrequency (RF) discharge. The RF generator operated at the standard industrial frequency of 13.56 MHz and nominal power of 1000 W. The deposition was accomplished in 300 s.

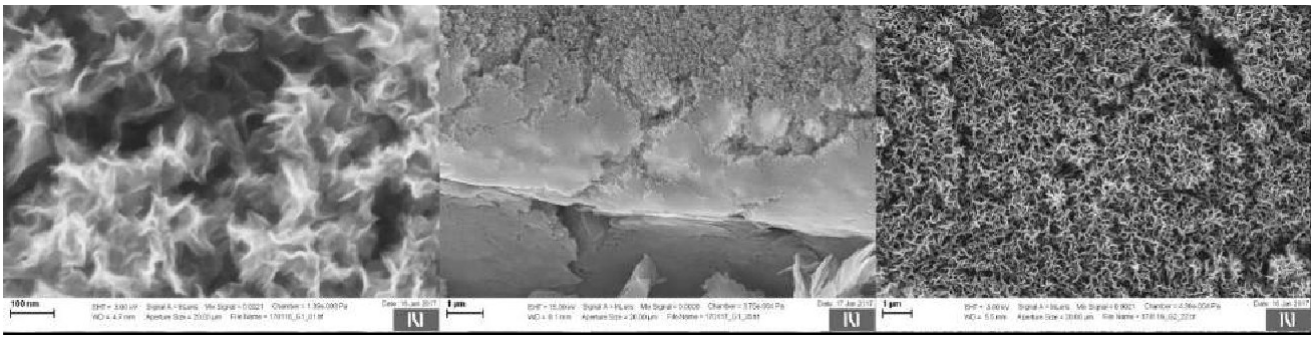

Figure 4: SEM images of vertically aligned graphene prepared on a carbon rod

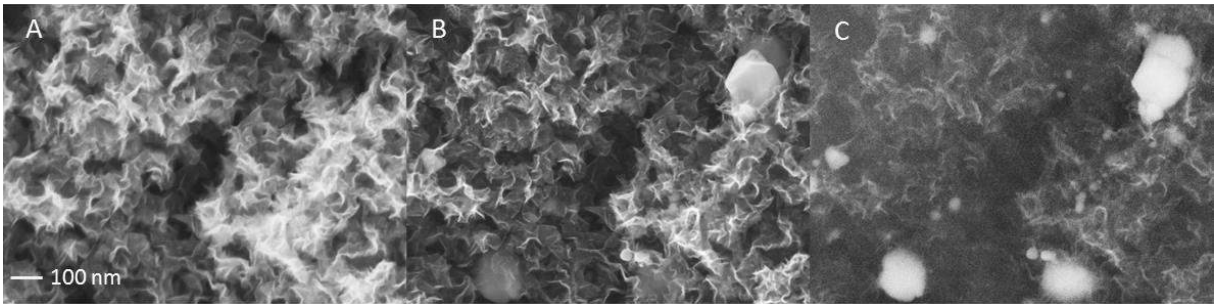

Figure 5: SEM images of Ag nanoparticles growing on top (B) and inside (C) graphene

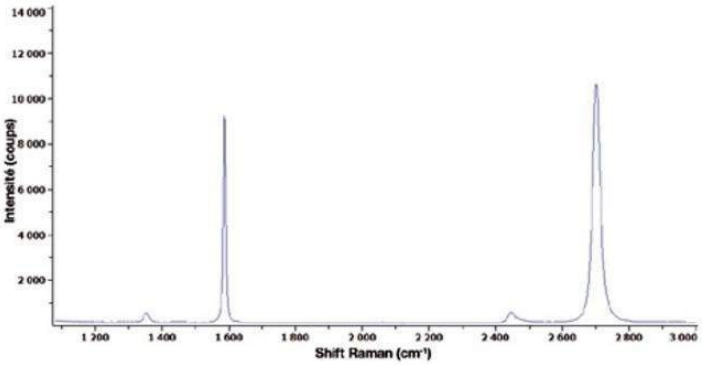

Figure 6: Raman spectra of graphene modified electrode.

Section 4

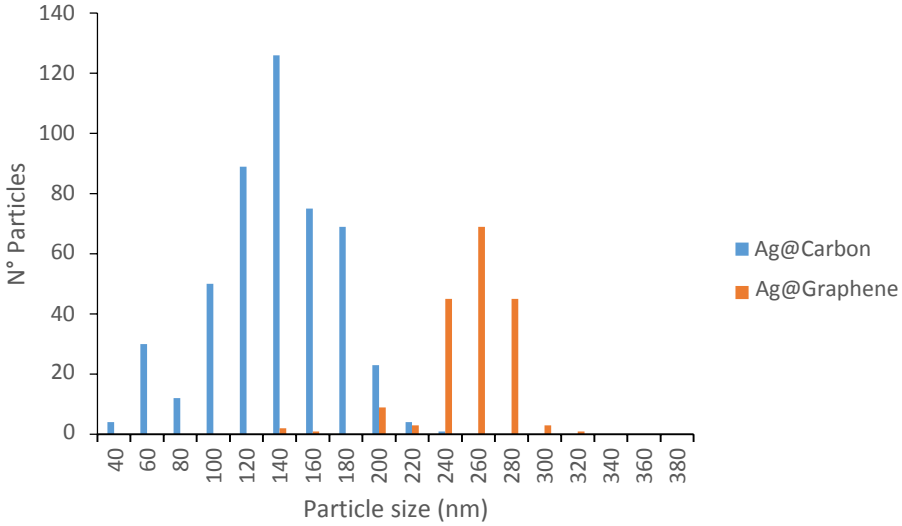

Figure 7: Particle distribution of Ag at VOG (graphene) or planar carbon electrode

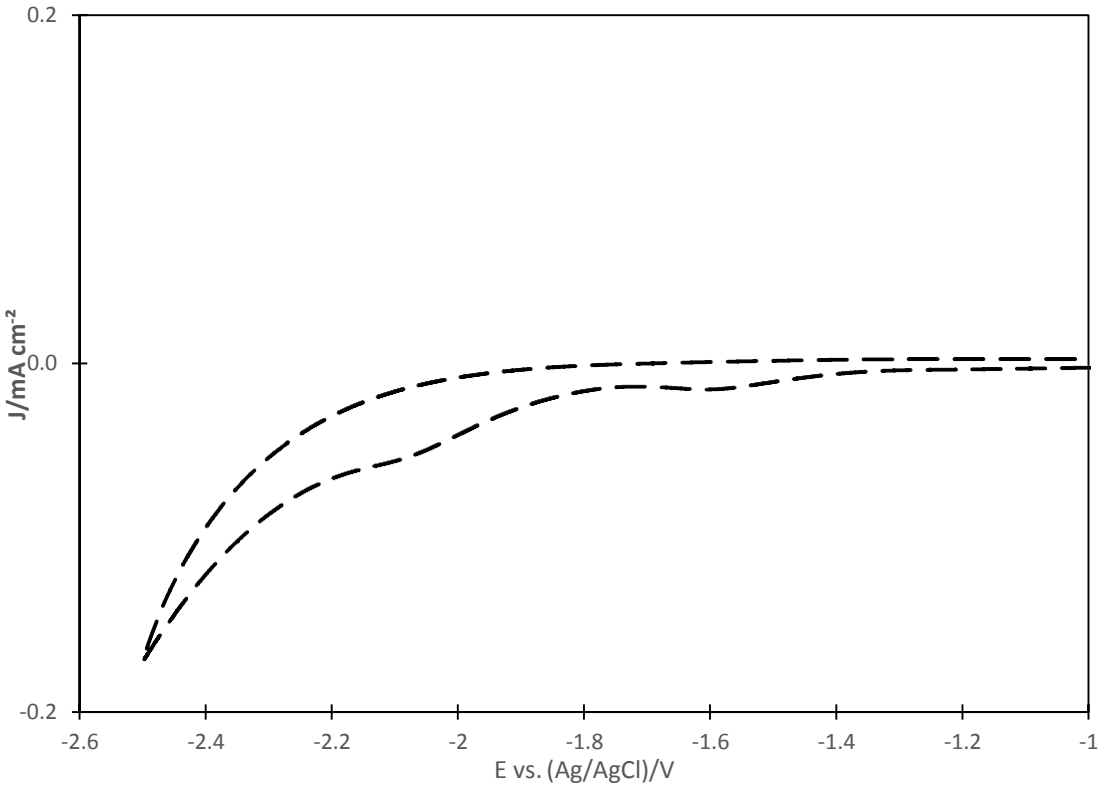

Figure 8: CV features for 1mM benzylbromide + 0.1 M tetrabutyl ammonium perchlorate + Acetonitrile recorded on a graphene electrode (without nanoparticles) at 50 mV.s^{-1}

Section 5

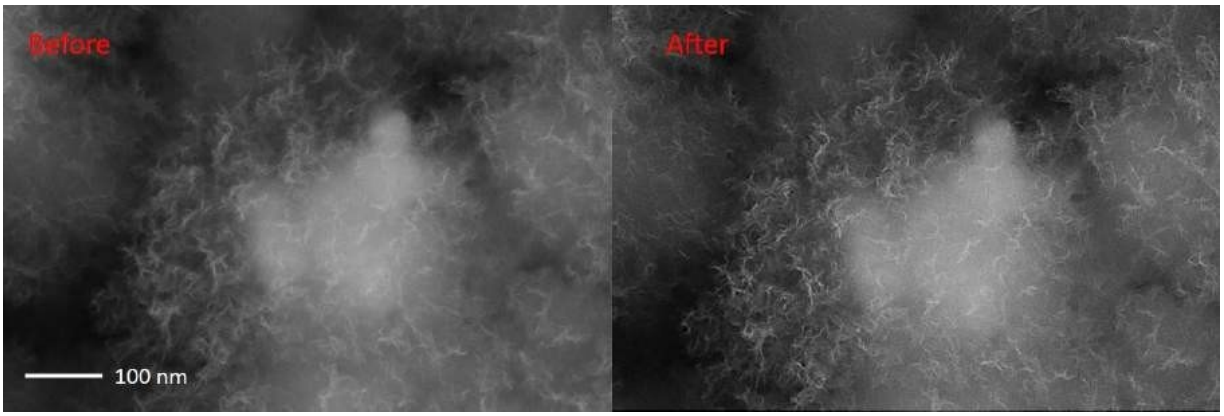

Figure 9: Identical SEM image of Ag nanoparticles in vertically aligned graphene before (cycles) and after (15000 cycles) degradation protocol

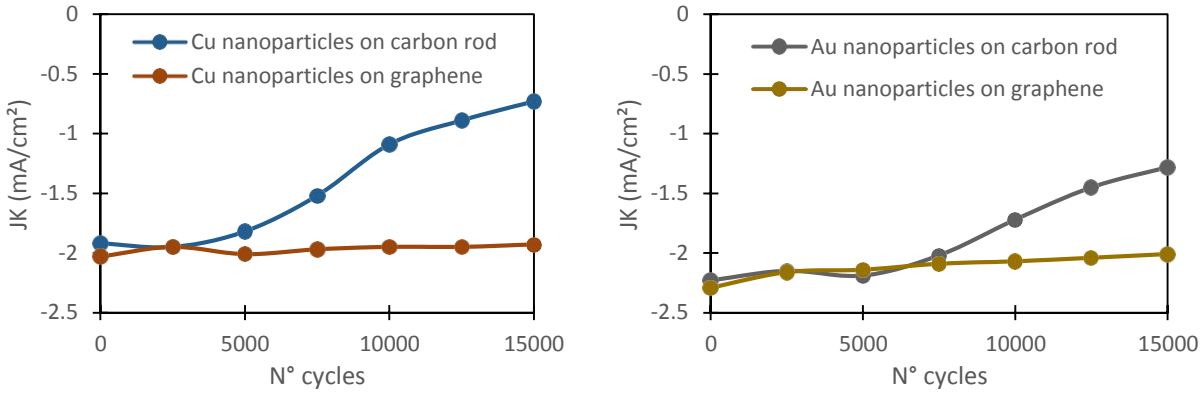

Figure 9: Stability of Cu and Au nanoparticles