

Mercury vapor sensor enhancement by nanostructured gold deposited on nickel surfaces using galvanic replacement reactions

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Electronic Supplementary Information

Experimental details

Chemicals

Deionized water (resistivity of 18.2 MΩcm) was purified by use of a Milli-Q reagent deioniser (Millipore). H₂AuCl₄·3H₂O was prepared by dissolving gold (HGR Matthey, 99.999%) in aqua regia and evaporated to dryness. The solid was diluted with Milli-Q water until the desired concentration level (2×10^{-4} M) which was confirmed using a Perkin Elmer (Model 3110) Atomic Absorption Spectrometer. For mercury vapor sensing, Hg permeation tubes (VICI, TX, USA) were used to generate various concentrations of Hg vapor in a highly controllable manner. Hg vapor concentrations in the test stream were calibrated using acidic KMnO₄ (Sigma Aldrich, Australia) wet trapping method (similar to the Ontario Hydro method) and inductively coupled plasma mass spectroscopy (ICP-MS) analysis of the trapping solutions (D. Laudal, *Fres. J. Analy. chem.* 1997, **358**, 397-400). The NH₃ levels A1, A2 and A3 refer to 590, 1180 and 1770 mg/m³ respectively and are achieved by varying the flow of ammonia from the gas cylinder (3388 ppm or 2360 mg/m³, Coregas, Australia). The humidity generator was built in-house from Swagelok parts and custom made glassware specifically to fit with the rest of the Hg calibration system. The humidity generator was calibrated at three different flow rates, namely, 50, 100 and 150 sccm producing humidity concentrations of 4.2, 7.6 and 10.4 g/m³ (± 0.2 g/m³) using the humidity sensor (DP-CALC, Kenetec).

Preparation of e-beam evaporated substrates

The specially prepared QCM for this work were fabricated by evaporating thin titanium and nickel layers of 10 and 300 nm thick by BalzersTM electron beam evaporator onto AT-cut quartz (7.5 mm diameter, 10 MHz resonant frequency, Hy-Q Crystals, Australia) substrates. A separate unmodified Au control QCM was prepared by evaporating thin titanium and gold layers of 10 and 150 nm onto AT-cut quartz substrates using the same deposition method. The purpose of the Ti layer was to assist with the adhesion of the Ni layer to the substrate surface. The 2 sided Quartz crystal microbalance with 10 nm Ti adhesion layer and 300nm Ni film on each side (0.32 cm² total surface area) was placed in a dialysis bag (12 kDa cut-off) containing 10 mL of deionized water (Milli Q, Elix 3) and dialysed against 100 mL of H₂AuCl₄ (2×10^{-4} M) under constant stirring at room temperature for various time intervals (0.5 h, 1 h, 2 h, 4 h, and

8 h). The nickel films obtained after galvanic replacement reactions were thoroughly washed with Milli-Q water and dried under dry nitrogen. The confinement of nickel thin film in the dialysis bag assisted in the controlled inward movement of Au^{3+} ions to react slowly with the nickel film, as well as simultaneous outward movement of leached Ni^{2+} ions.

Materials Characterisation

Scanning electron microscope (SEM) measurements were performed on a FEI Nova SEM instrument with an AMETEK energy dispersive X-ray (EDX) system (Nova 200) operated at an accelerating voltage of 30 kV. Prior to SEM imaging, samples were thoroughly rinsed with Milli-Q water and dried under a flow of nitrogen. X-ray diffraction (XRD) data were obtained with a Bruker AX 8: Discover with General Area Detector Diffraction System (GADDS) operating at a voltage of 40 kV and a current of 40 mA with $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) measurements of the surfaces were carried out on a VG MicroTech ESCA 310F instrument at a pressure better than 1×10^{-9} Torr. The general scan and C 1s, Au 4f, Pb 4f and Ni 2P core level spectra for the respective samples were recorded with un-monochromatized Mg K α radiation (photon energy = 1253.6 eV) at a pass energy of 20 eV and electron takeoff angle of 90° . The core level binding energies (BEs) were aligned with the adventitious carbon binding energy of 285 eV. Atomic force microscopy (AFM) tapping mode measurements were performed on the relevant films using a NanoScope IIIa Multimode AFM (Veeco, USA) under air-ambient conditions (20 °C and 40 %RH). MikroMasch Ultrasharp (NSC15/Al BS) silicon etched SPM probes with a backside reflective Al coating, a spring constant of 40 N m $^{-1}$, a radius of curvature of tip <10 nm, a resonant frequency of approximately 325 kHz, and cantilever dimensions of 125 μm x 35 μm x 4 μm were used. Minor scan line errors were removed using AFM software. More than 5 AFM scans were carried out on different locations for each sample, and the results presented within this manuscript are typical examples. The AFM scan analysis software was provided by Veeco Co. (USA) with the AFM instrument and was used for surface analysis. Several days after the controlled Hg vapor exposure, secondary ion mass spectroscopy (SIMS) (Cameca IMS 5f) depth profiles were performed using a Cs^+ primary ion beam of 3 keV net impact energy, 1.5 nA beam current and a raster area of 500 μm x 500 μm .

To eliminate potential edge effects, a combination of lens setting was used to restrict the secondary ion yield to a 100 μm diameter region within the centre of the rastered area. The SIMS measurements were conducted at the Australian Nuclear Science and Technology Organisation (ANSTO) facility in NSW, Australia through an Australian Institute of Nuclear Science and Engineering (AINSE) grants. Inductively coupled plasma mass spectroscopy (ICPMS) measurements were performed in order to calibrate the Hg vapor delivery system using a HP4500 series 300, ShieldTorch System ICPMS instrument. The solutions containing the trapped Hg were diluted such that the final solution for analysis contained no more than 5 ppb Hg and had a clear colour (no potassium permanganate's purple colour could be visible); in order to avoid detector memory effects and blockage of sampling tubes on the HP4500. All solutions were spiked with 100 ppb Tb as the internal standard and 100 ppb Au to keep Hg solution stable and draw all the Hg out of the sampling tubes on the HP4500. All solutions contained 5% HNO_3 with less than 0.02% of HCl for more accurate results. The sampling tubes of the ICPMS were washed with 5% HNO_3 solution as well as milli-Q water before each sample solution was analysed for better accuracy. The control software was set to analyse each sample three times before an average Hg concentration was displayed and recorded.

Mercury Monitoring Procedures

The galvanically replaced along with the unmodified QCMs were tested for their sensing capability towards a dynamic range of elemental mercury vapor concentrations (1.02, 1.87, 3.65, 5.70, and 10.55 mg/m^3). Prior to Hg testing, the unmodified and GR based sensors were tested for their mercury sorption capacity (MSC) at 28°C. In order to determine their MSC the GR, Ni control and Au control based QCMs were first exposed to Hg vapor at a concentration of 5.70 mg/m^3 for a period of 8 hours followed by exposure to dry nitrogen for a recovery period of 5 hours at an operating temperature of 28 °C. The sensors were then tested for their sensing capability towards elemental mercury vapor concentrations of 1.02, 1.87, 3.65, 5.70, and 10.55 mg/m^3 at 89 °C. Thereafter, the sensors were tested towards the different concentrations of Hg vapor in the presence of interferent gases. The experiments were performed in duplicates in a custom built gas cell, which housed 4 QCM sensors, and were exposed to a gas stream containing a mixture of dry N_2 and a known concentration of Hg vapor for 1 hour. Thereafter, the sensors were regenerated by N_2 flow alone for 1 hour while holding them at the same operating temperature. This

2 hour step is referred to as a single pulse. This process was performed for five different Hg concentrations in an order from lowest to highest concentration (1.02, 1.87, 3.65, 5.70, 10.55 mg/m³ ± 0.05 mg/m³) at an operating temperatures of 90 ± 1 °C in order to simulate industrial conditions (M. Levlin et al., *Fres. J. Analy. chem.* 1996, 355(1), 2.). Furthermore, the sensors were tested towards Hg vapor in the presence of ammonia and humidity at 90°C. This involved introducing either H₂O (4.2 g/m³) or NH₃ (1.18 g/m³) or both simultaneously during the Hg exposure part of a pulse. Throughout the experiments, the total gas flow rate (N₂ + Hg or N₂ alone) was kept constant at 200 sccm using a specially developed multi-channel gas delivery system employing mass flow controllers (MKS instruments, Inc. USA).

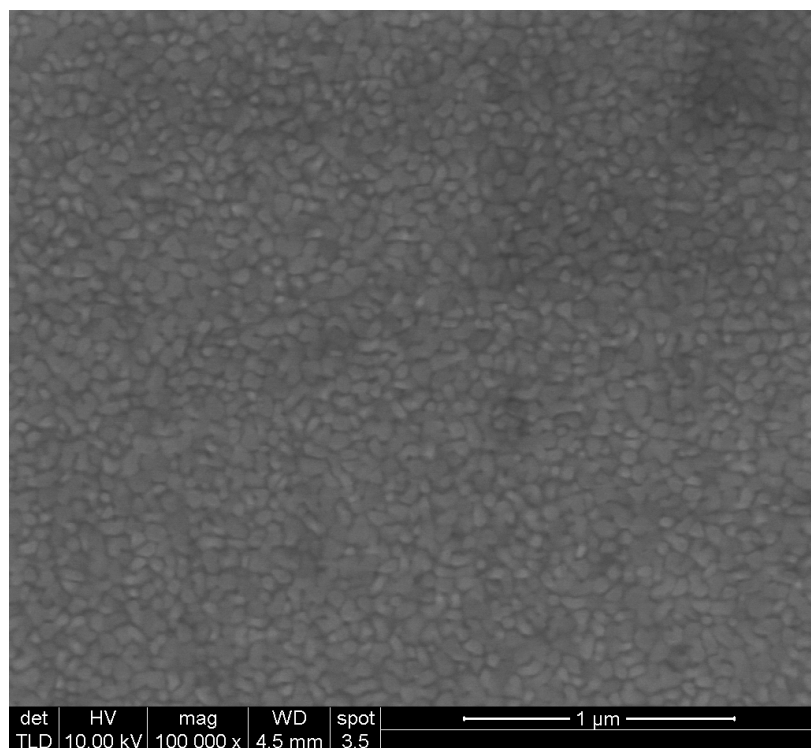


Figure S1: SEM image of Au-control film (200nm) on a quartz crystal substrate.

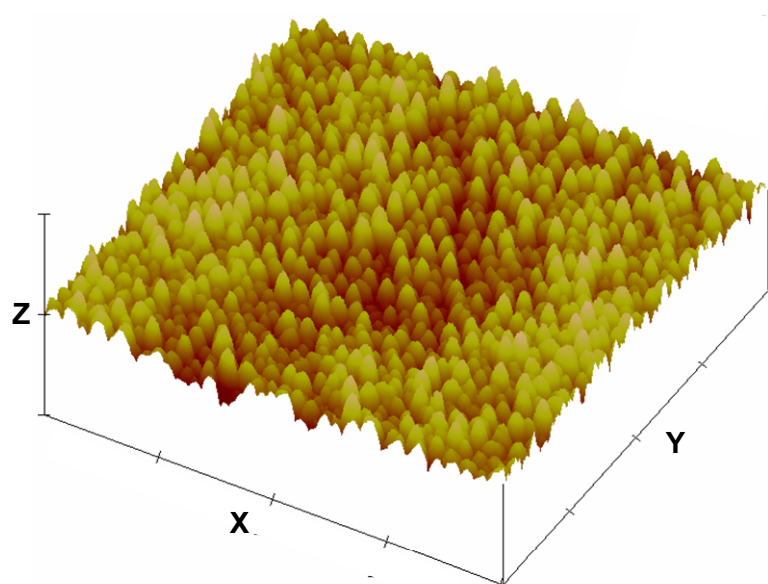
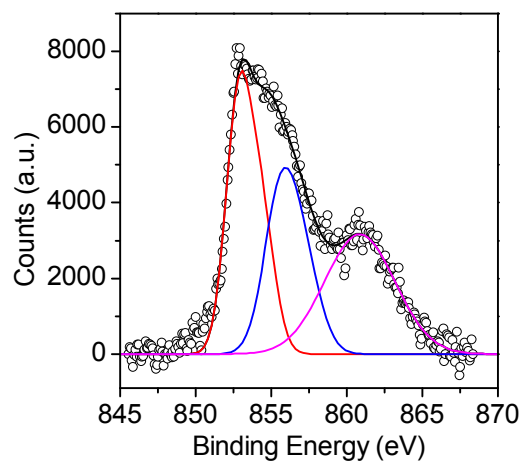
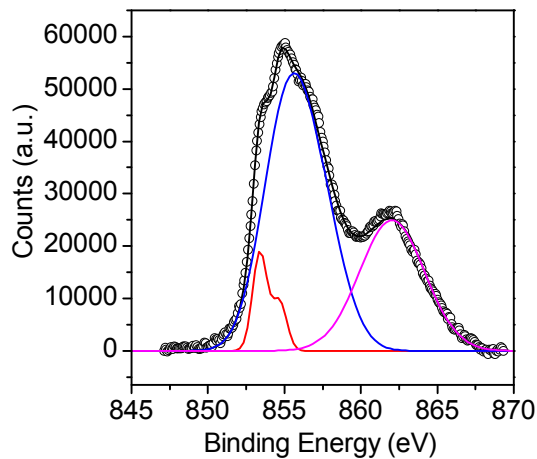


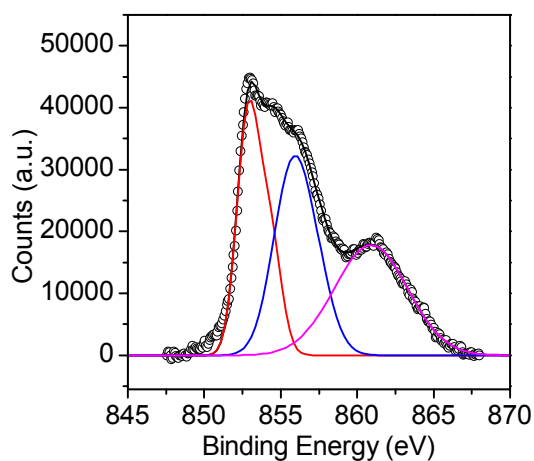
Figure S2: AFM images showing the Au-control film on a quartz crystal microbalance. Scale for x, y and z axis are 2000, 2000 and 20 nm, respectively. The average roughness (R_a) and the root-mean-square roughness (R_q) are observed to be 1.38 and 1.73 nm, respectively.



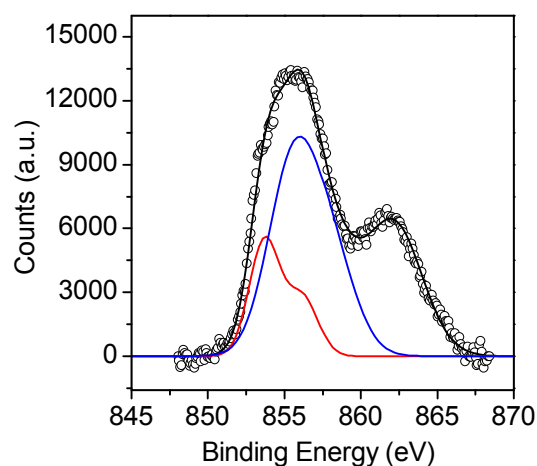
a) Ni



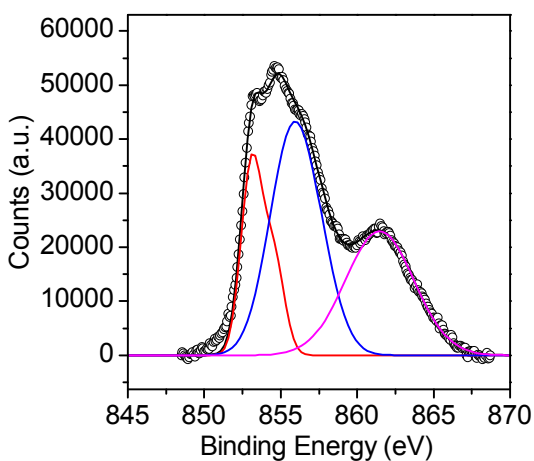
d) 2 h GR



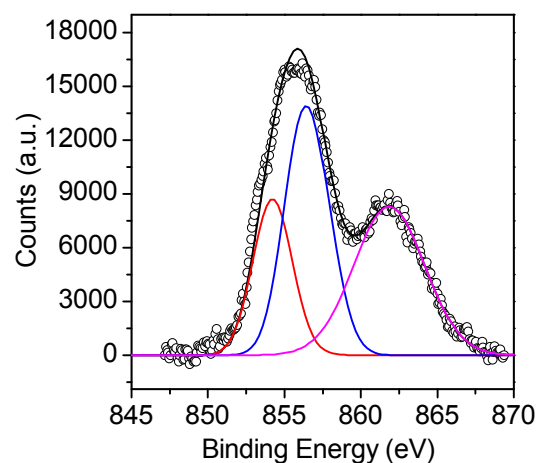
b) 0.5 h GR



e) 4 h GR



c) 1 h GR



f) 8 h GR

Figure S3: XPS spectra (Ni 2p core level region) for the Ni-Au GR QCM electrodes. The deconvoluted peak areas were used to estimate the NiO to Ni ratio and presented in Figure 6.6b. In each image, the left, middle and right curves refer to Ni, NiO and satellite peaks, respectively.