Electronic Supplementary Information (6 pages)

Room temperature photo-induced deposition of platinum mirrors and nano-layers from simple Pt(II) precursor complexes in water-methanol solutions†

Liang Xian,[a] Leon Engelbrecht,[b] Shani Barkhuysen,[b] and Klaus R. Koch,[b,*]

[a.]On leave from Chemical Engineering Institute, Northwest University for Nationalities, Lanzhou 730030, China.
[b.]Department of Chemistry and Polymer Science. Stellenbosch University, P Bag X1, Matieland, 7602, South Africa. *Corresponding author E-mail: krk@sun.ac.za, Tel: 002721 8083020, Fax: 002721 808 2342.

EXPERIMENTAL SECTION

All chemicals were of reagent grade quality and used without further purification. Potassium tetrachloroplatinate(II) (99.9+%, K_2PtCl_4) and fluorine doped tin oxide (FTO) coated glass (7Ω/sq) was obtained from Sigma-Aldrich. HPLC-grade methanol was used throughout. A conventional 5 W (4000K) intense visible polychromatic LED light source was used for irradiation of solutions. Copper grids for TEM were supplied by SMM Instruments (Pty) Limited. Strips 1 x 10 cm of 2 mm thick FTO glass were cut from a sheet supplied form Sigma-Aldrich and cleaned in an ultrasonic bath using separately acetone, ethanol and distilled water for 20 min and dried in air. Cleaning pre-treatment of 2.5×7.5 cm regular microscope glass slide (soda glass) and other substrates used was similar above.

Photo-deposition of Pt-mirrors onto FTO glass and other substrates.

A freshly made 25.00 ml solution consisting of a mixture of distilled water and methanol (in a range of 1:1 to 1:0.8 ratio by *wt.*) containing 10.4 mg K_2PtCl_4 (giving ~ 1 mM $[PtCl_4]^{2-}$) was prepared at room temperature (20 ± 3 ^oC) in a darkened room. (Although 1 mM $[PtCl_4]^{2-}$ concentration is ideal for reproducible mirror formation, we find that concentration up to 5 mM give satisfactory results). Mirror deposition is achieved by immersing a previously marked end of a pre-cleaned strip of FTO glass vertically into a freshly made sample of pre-cursor solution using an apparatus constructed illustrated schematically in Figure 1. A polychromatic light source (4000 K) 5W LED is placed into position above the vertically secured 2 mm thick strip of FTO glass, so to allow as much light as possible to pass down the strip of FTO glass immersed into the precursor solution without stirring. In is important to use a light screen to prevent as much as possible of stray light from affecting the precursor solution. Ideally only light cascading down the FTO glass strip should irradiate the precursor solution in contact with the glass strip. Continuous illumination by this means for 15 ± 4 h, results in the photo-induced deposition of a good quality Pt mirror onto FTO glass surface. No significant temperature increase of the precursor solution is noticed over this time in the well ventilated dark room. The Pt-mirror was thoroughly washed with distilled water and allowed to dry in air prior to further analysis and characterization. The Pt-mirror can readily be removes from the FTO glass using a transparent adhesive strip or mechanically under a microscope. In this way this Pt foil can be produced kept under water. By a modification of this methodology a Pt-mirror mirror may be deposited onto other substrates as shown in Figure 2.

Examination and characterization of the Pt-mirror

Scanning Electron Microscopy (SEM) images as well as EDS elemental analysis were taken using a field emission microscope (FEI, Nova NanoSEM 230) operated at an accelerating voltage of 20 kV. EDS analysis and elemental mapping was collected using an Oxford X-Max detector and INCA software. XRD were recorded using a PANalytical X'Pert PRO Diffractometer (PANalytical, The Netherlands). Several samples of clean and dry Pt-mirror with mass between 4 to 8 mg were subjected to Thermo-gravimetric analysis (TGA) recorded with TA-Q500 operating over the range of 25 to 600 ^oC, with a heating rate of 10 K/min under an inert $N_2(g)$ at flow rate of 60 ml/min. The static contact angle (SCA) was determined of 1 μL droplet of distilled water placed onto the matt-side of the dry Pt-mirror on FTO glass, using a conventional optical microscopy with a Nikon SMZ-2T microscope.

128.8 MHz ^{195}Pt NMR Spectroscopy.

^{195}Pt NMR spectra were recorded at 298 K using a Varian Unity *Inova* 600 NMR spectrometer equipped with a 5 mm broad-band probe, operating at 128.8 MHz. ^{195}Pt NMR spectra are referenced externally to $[PtCl_6]^{2-}$ (δ^{195}Pt = 0 ppm) in 500 mg/cm^3 H_2PtCl_6 in 30% v/v D_2O/1 M HCl, in a 1 mm coaxial capillary tube inserted into the conventional 5 mm outer diameter sample tube. ^{195}Pt NMR acquisition parameters were as follows: pulse duration 8.2 μs (corresponding to a *ca.* 45° pulse), data acquisition time 0.869 s, followed by a delay period of 1 s; 50 000 scans were accumulated over a total acquisition period of *ca.* 24 hours. The ^{195}Pt NMR data was processed with a 20 Hz exponential line broadening function to improve the signal-to-noise ratio.

FIGURES

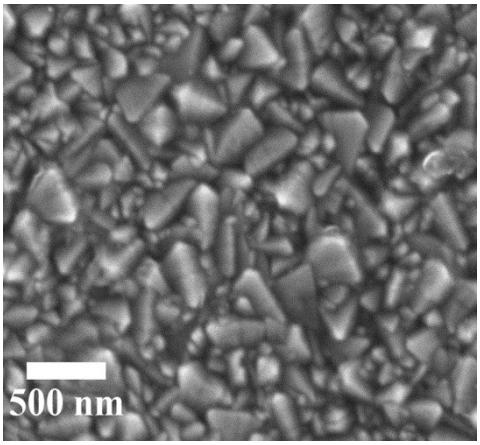

FIGURE S1. A SEM image, showing the micromorphology of the tin-oxide surface on a blank strip of clean FTO glass.

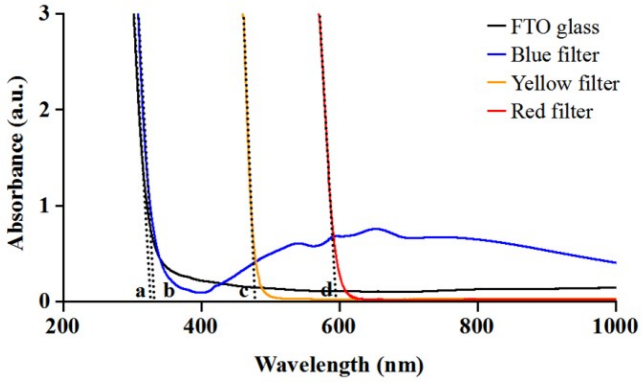

FIGURE S2. Wavelength cut-off characteristics of optical photographic filters used to generate blue, yellow and red light from the polychromatic white LED source. a = 324 nm, b = 329 nm, c = 475 nm, d = 595 nm

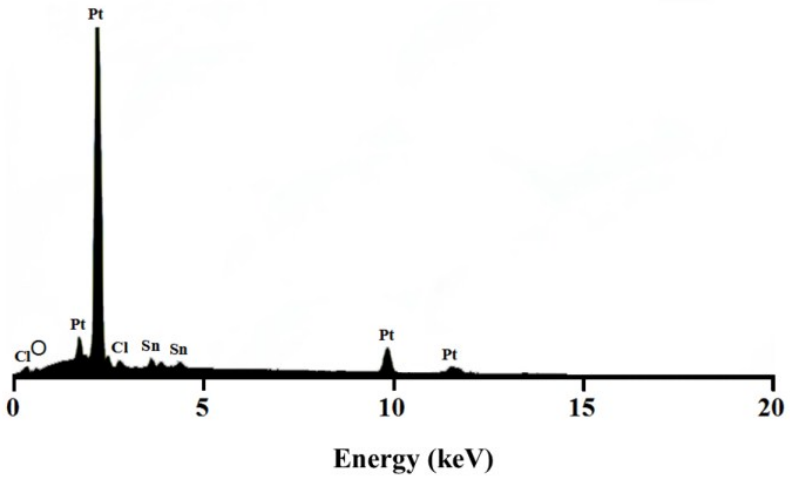

FIGURE S3. EDS analysis of the surface of a portion of Pt-mirror during SEM, confirming that surface purity of the Pt-mirror.

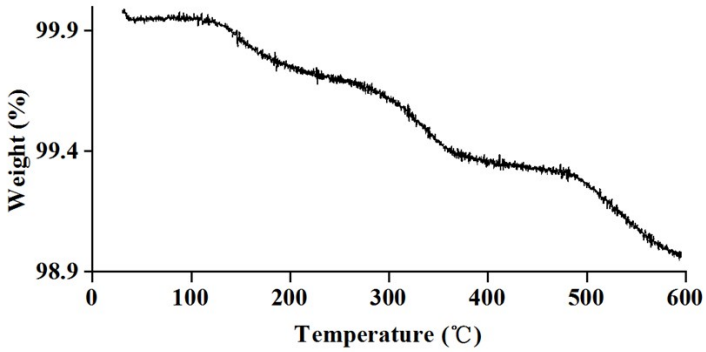

FIGURE S4. Thermogavimetric analysis (TGA) of a fragment of Pt-mirror (rinsed with distilled water and dried at room temperature) showing an overall ~ 1.0% mass loss over the temperature range from room temperature to 600°C under nitrogen. The mass loss profile suggests a slight degree of porosity of the Pt-mirror, with absorbed moisture and/or other molecules as well as traces of precursor salts not completely removed by washing.

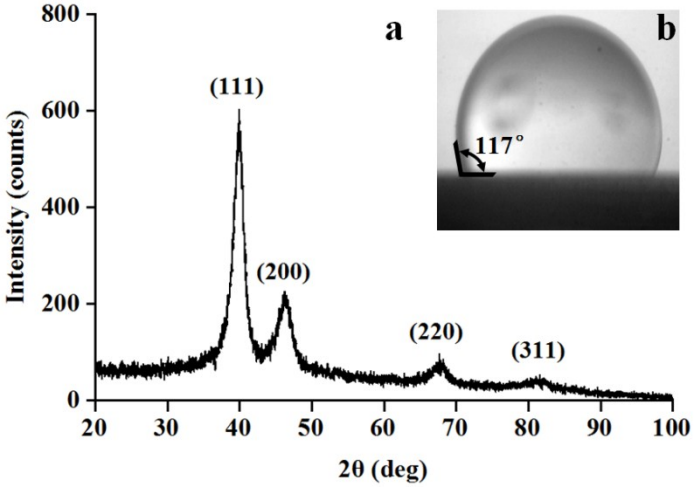

FIGURE S5. (a) A XRD pattern of a portion of a Pt-mirror, confirming that it essentially consists of pure Pt showing Pt(111) and Pt(200) reflections characteristic of an *fcc* packing habit; (b) A static contact-angle (SCA) measurement of 117° with 1μL water droplet on the matt side of a sample of a sample of Pt-mirror.

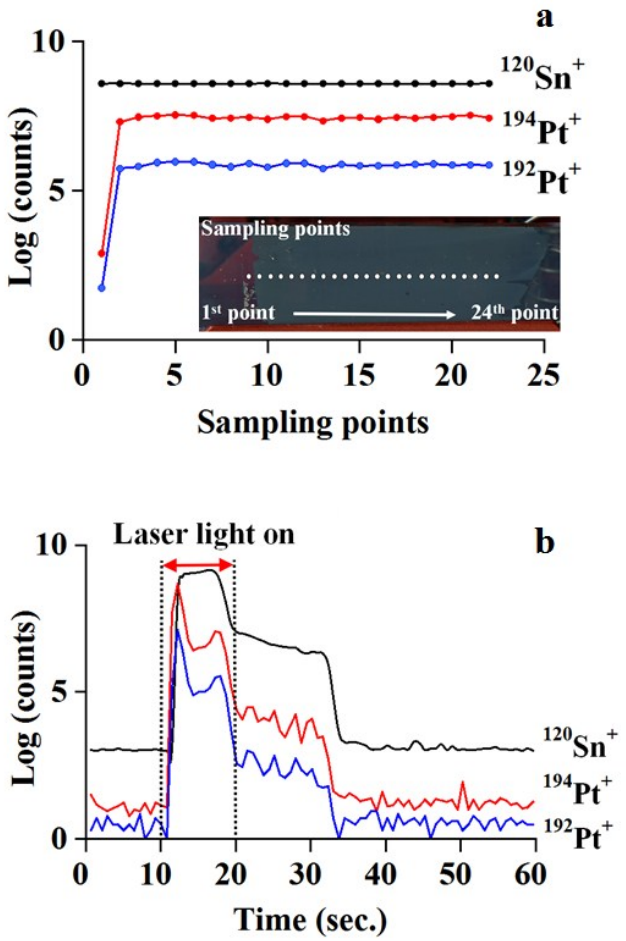

FIGURE S6. Definitive LA-ICP-MS analysis of the Pt-mirror performed a strip of platinized FTO glass confirming the relative purity of the Pt-mirror. (a) A plot of the $^{120}Sn^{+}$, $^{194}Pt^{+}$ and $^{192}Pt^{+}$ isotope ion-counts for 23 Pt-mirror sample ablation spots including the 1st 'blank' spot of FTO glass. These data indicate that the metal nano-layer is essentially pure Pt of uniform thickness along the length of the sample; (b) A typical time-dependent profile of ion-counts after a 10 s ablation by the 193 nm laser, followed by a 45 s "flush-out" time with Argon carrier gas. These profiles are highly reproducible for all ablation spots.

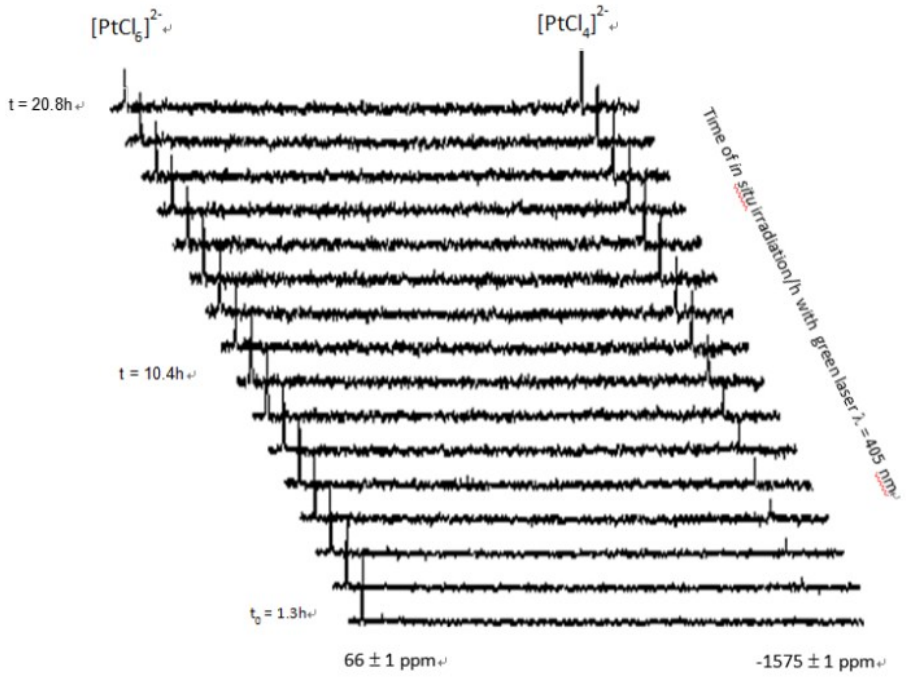

FIGURE S7. (a) ^{195}Pt NMR as a function of time and continuous *in situ* irradiation with a *ca* 50 mW green laser light (λ= 405 nm) of a 0.3mM solution of commercial dry "$H_2[PtCl_6].xH_2O$" in methanol. The first spectrum in the array recorded at 1.3h after making the solutions, shows only a signal of $[PtCl_6]^{2-}$ relative to an external reference of $[PtCl_6]^{2-}$ in D_2O 1MHCl at δ= 0.0 ppm at 25°C. The clean *photoinduced* reduction of the $[PtCl_6]^{2-}$ give only $[PtCl_4]^{2-}$ by methanol is clear. The release of 2 equivalents of Cl^- ions per two-electron reduction of Pt evidently stabilizes the $[PtCl_4]^{2-}$ anion to further reduction from methanol in these solutions for more than 31.2 h.

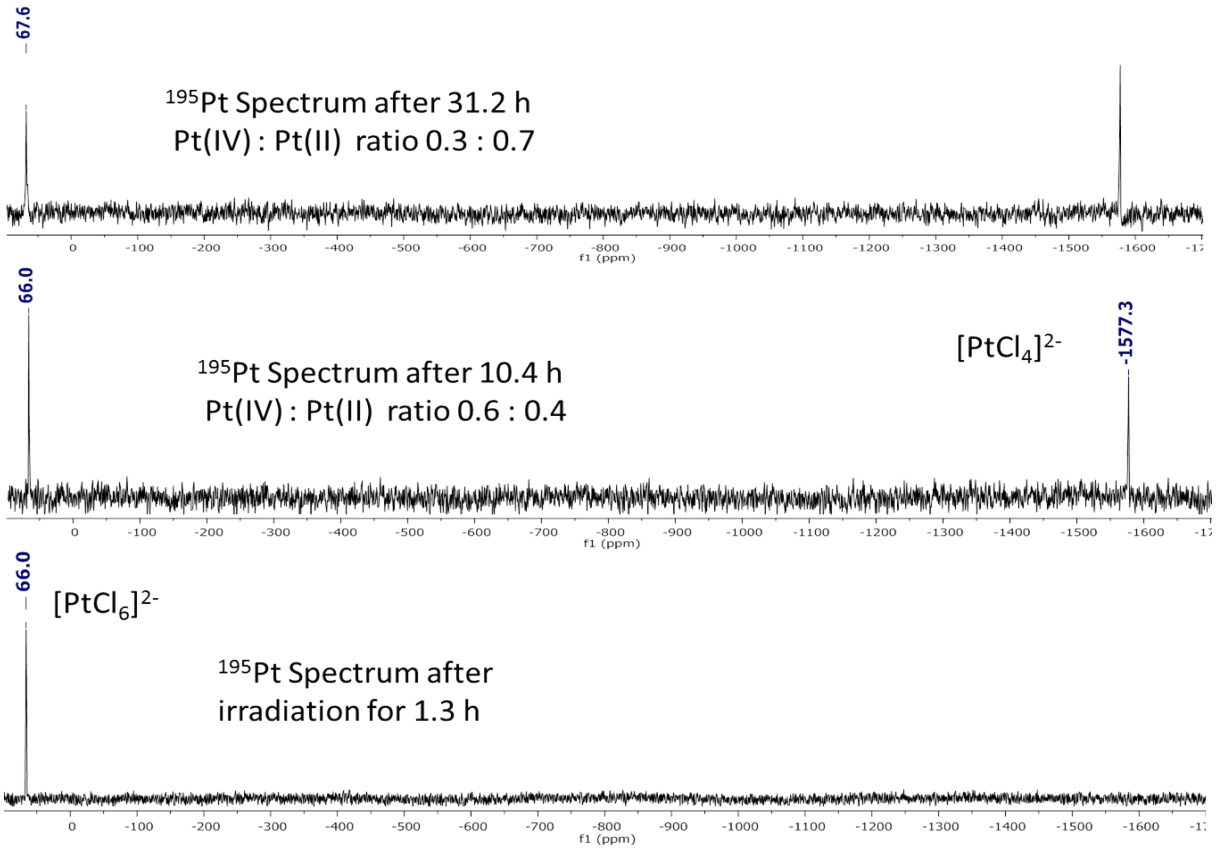

FIGURE S7. (b) The time dependent photoinduced reduction of $[PtCl_6]^{2-}$ to $[PtCl_4]^{2-}$ in methanol is relatively slow, as shown by the relative ratios of the ^{195}Pt NMR resonance integrals reflecting the relative concentrations of

Pt(IV):Pt(II) remaining in solution after 31.2h of continuous irradiation at 25 ^{o}C as described in Fig S7 (a). The small changes of the chemical shift of particularly the $[PtCl_6]^{2-}$ species is ascribed to slight temperature increases due to continuous irradiation, given the well-known[27] temperature sensitivity of ^{195}Pt shielding to temperature changes.