Supporting Information

Studies of surface of metal nanoparticles in a flowing liquid with XPS

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Supplementary note on thickness of the graphene membrane and how high the pressure of such membrane can hold under UHV

In graphite, the interlayer distance is 3.35 Å. Thus, the distance could be similar to 3.35 Å. Thus, we consider the thickness of the graphene membrane is about 6-7 Å after the thickness of carbon atoms of two graphene layers were accounted.

Graphene itself can survive at high pressure at least a few bars. How high the pressure of this membrane can hold under UHV is determined by the tightness of the joint between graphene and Si_3N4 membrane other than the mechanic strength of itself. As the graphene membrane was tested for flowing air of 1 bar and liquid of 3 bar, definitely our cell can hold gas or liquid for 3 bar or even higher.

Supplementary note on the inhomogeneous distribution of O1s in Figure 4c

O 1s was contributed from oxygen atoms of (1) the solvent molecules, tripropylene glycol methyl ether and phenol in the region near to graphene, (2) the poly(methyl methacrylate) (PMMA) left on graphene since PMMA was used in the preparation of graphene membrane, and (3) –COOH, or –OH groups, potentially introduced during preparation of graphene layer. The inhomogeneous intensity of O 1s in Figure 4a suggests that the distribution of solvent molecules could be heterogeneous. As solvent molecules are typically homogeneously distributed in the liquid, their contribution to the inhomogeneous contrast of O1s in Figure 4b can be excluded. Thus, the left PMMA and functional groups left on defects of graphene likely contributed to the inhomogeneity of O1s in Figure 4c.

Supplementary note on the mechanical stability of the two-layer graphene membrane

Based on our experiments of studying air of 1 bar pressure, the graphene membrane survived at a pressure of a bar at least. In the experiments of studying a flowing liquid, the pressure applied by the syringe pump to liquid was about 3 bar. The graphene membranes used in our XPS studies of liquids remained intact after an experiment of 1-2 hours. Thus, it is assumed the current graphene membrane cell can survive about 3 bar or above.

Supplementary note on the resolution of observed spectra

The energy resolution of a XPS spectrum is determined by resolution of X-ray, the resolution of energy analyser, the intrinsic resolution of photoemission which is determined by the core-hole life time, and the homogeneity of sample. The first two factors are determined by the instrument. Their overall resolution is called instrumental factor in some cases. The resolution determined by instrumental factors is about 0.8 eV when an Ag foil is used. The instrumental resolution is often much better than the energy resolution of spectrum since heterogeneity of chemical components of sample surface can largely extend the FWHM of collected spectrum, and different core-level photoemissions have different core-hole life time.

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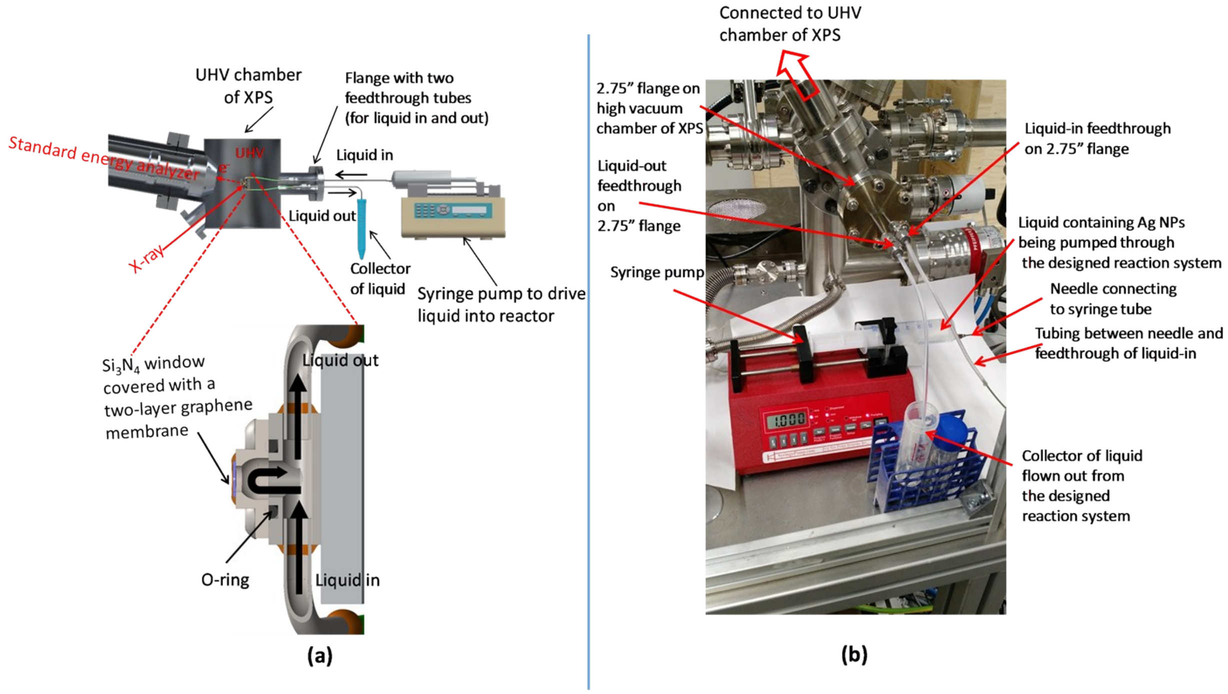
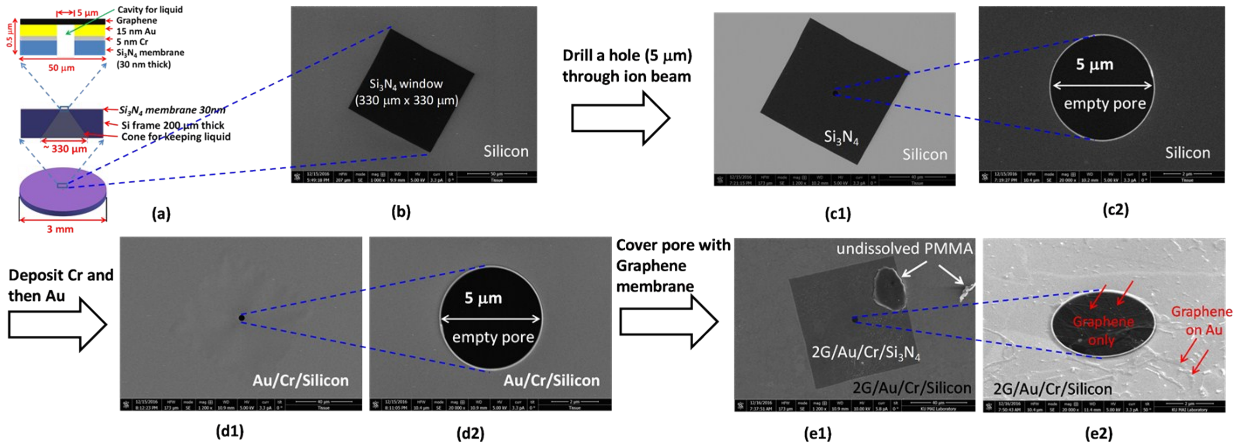
Supplementary note on time for collecting spectrum and the stability of flowing system

Each Ag 3d spectrum took about 15-20 minutes under the current concentration of Ag nanoparticles. It is expected the time to collect Ag 3d spectrum is determined by the requirement of signal to noise ratio and the concentration of the Ag nanoparticles. The flowing system used in this work was stable since the graphene membrane remained intact in the time scale of one days or longer.



Supplementary Figure S1. The reaction system of a flowing liquid containing catalyst nanoparticles for study by using XPS. (a) Schematic showing how a reactor system of flowing liquid containing catalyst nanoparticles was integrated into a high vacuum chamber of XPS equipped with a standard energy analyser; (b) Photo of parts in ambient of the designed reaction system.



Supplementary Figure S2. Processes of making a Si_3N_4 window covered with a two-layer graphene membrane. (a) Schematic of a Si_3N_4 window covered with a two-layer graphene membrane. (b) A Si_3N_4 membrane with thickness of 30 nm (the dark square) commercially fabricated on a miniature silica wafer with a thickness of 200 µm (the gray area). (c1 and c2) A Si_3N_4 membrane containing a pore made by authors with Ga ion beam milling of SEM. (d) Cr and Au thin films were deposited to the bored Si_3N_4 membrane. (e1 and e2) A 2G/Au/Cr/Si_3N_4 with a window covered with a two-layer graphene membrane. More details can be found in Nguyen et al, Langmuir 2018, DOI:10.1021/acs.langmuir.8b00806.

Notes related to Supplementary Figure S2

The structure of an empty cell was shown in Figures 2a, 2b and 2c in the main text. To make a liquid cell to separate liquid environment from UHV of XPS chamber, the first step is to make a pore of about 4.5 µm on Si_3N_4 membrane (20 nm thick). Commercial Si_3N_4 membrane was used in this study (Norcada, Part# NT005X). The micro opening (about 4.5 µm in diameter) was made on the Si_3N_4 membrane (30 nm in thickness) by milling a square Si_3N_4 window with Ga ion beam of SEM (FEI Versa 3D Dual Beam) in vacuum of 10^{-5} Torr. Then, Cr thin film with thickness of about 50 nm followed by 100 nm of Au were deposited on both sides of the Si_3N_4 membrane using a sputter coater (Quorum Q150T ES). The purpose of depositing Cr and Au layers on one side of the pore is to increase the adhesion of the unpored area of Si_3N_4 membrane to the graphene layer. The Au film on the other side of the pore was deposited for preventing sample surface charging during XPS experiments.

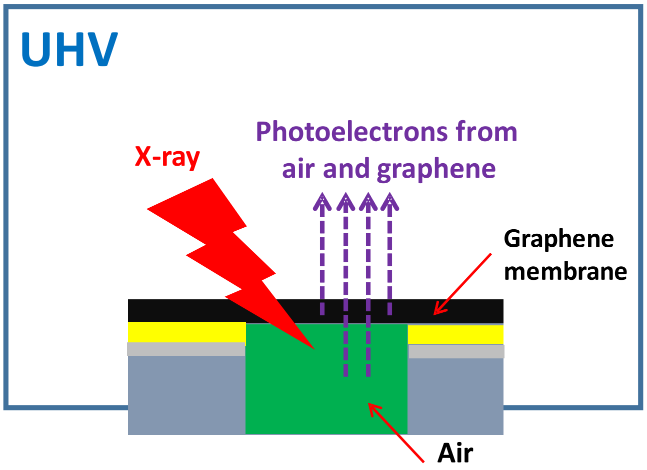
The second step is to introduce graphene membrane to the Cr-Au of the Si_3N_4 window. The actual practice to prepare a graphene layer without holes is not trivial and the successful rate increases along the accumulation of experience. A monolayer of graphene was grown on each side of a Cu foil with a thickness of 25 µm. The most challenging part is the transportation of graphene layer from its substrate to the bored Si_3N_4 membrane. To protect the graphene layer from being damaged during the transferring process, we coated PMMA on one side of the Cu foil/graphene with thickness of about 100 nm by spin coating using a solution of 4wt% PMMA/Toluene at a spin rate of 4000 rpm. Then, Cu was dissolved by gently dropping a piece of graphene/Cu/PMMA

(PMMA side face up) foil to an aqueous solution of $(NH_4)_2S_2O_8$ (0.22 M) at a temperature of 45°C with gentle stirring at 60 rpm. It took approximately 0.5 hour for dissolving the Cu foil. To completely dissolve the Cu foil, it was remained in solution for an additional half an hour. It was washed through refreshing the solution with fresh DI water for several times.

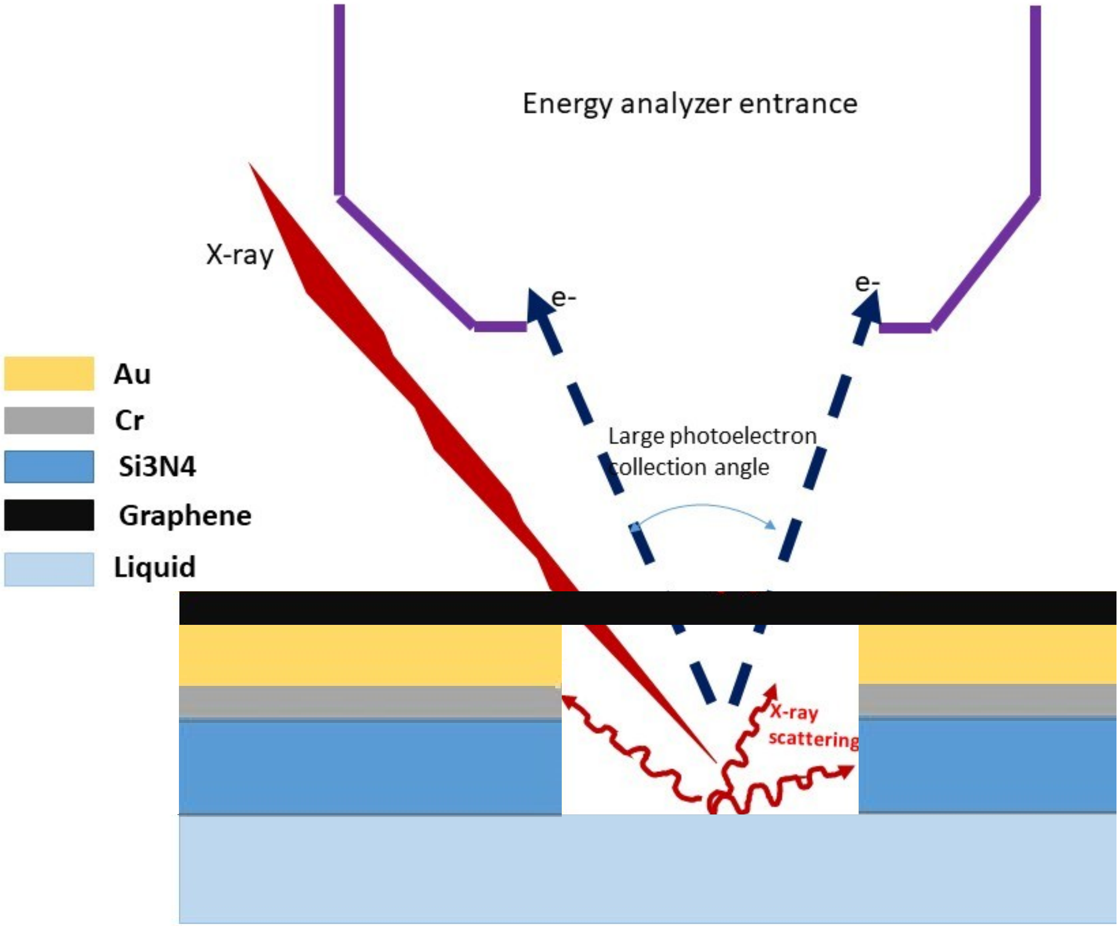
Once the single layer of graphene was prepared, we then transferred it onto another graphene/Cu foil to produce a two-layer graphene membrane (PMMA/2G/Cu). First, a new piece of graphene/Cu foil was positioned in water exactly underneath the floating graphene/PMMA film. The graphene/Cu foil was then gently pulled up to the surface of the water (edge first) along with lifting the prepared PMMA/G film. This step formed the PMMA/G film covering the G/Cu foil, producing PMMA/2G/Cu structure. Water was often trapped underneath the film but this can be removed by the following drying process.

The PMMA/2G/Cu was dried in air at room temperature for half an hour. After that, it was remained on a hot plate and annealed in air at 200^{o}C for 2 hours. This annealing process helped dry the remaining water and allowed the PMMA/G film to be flexible and to adhere strongly onto surface of G/Cu. Notably, ramping rate of heating up to 200^{o}C and cooling down to 25^{o}C should be slow to prevent it from being damaged of the graphene layer during heating and cooling (< 3 – 4 °C/min). After annealing, this PMMA/2G/Cu foil was etched to remove Cu. After the etching of Cu foil, PMMA/2G was formed and was floating on fresh DI water. Then, the PMMA/2G was transferred to cover the bored Au-Cr-Si_3N_4 window using the same transfer procedure as before. This PMMA/2G/Au-Cr-Si_3N_4 was also dried in air and annealed at 200 °C for 2 hours. Lastly, the PMMA film of PMMA/2G/ Au-Cr-Si_3N was removed by dissolving it with warm acetone bath (70 °C) for 30 minutes for 2 cycles. So far a cell window which one face was covered with graphene membrane and the other face was left uncovered, was successfully made.

The body of the reactor of flowing liquid was made out of stainless steel with one port for liquid inlet and one for liquid outlet. Both ports have inter diameter (ID) of ~ 1.3 mm. The ports were attached to flexible PEEK tubing of the same size, which are connected to a 2.74″ CF flange liquid feedthrough. The use of flexible PEEK tubings allows the cell position to be adjusted freely during XPS experiment while it is being mounted on a piezo controlled sample stage.



Supplementary Figure S3. Schematic showing how the molecular O_2 and N_2 in air flew to the cell could be studied by XPS by irradiating the graphene membrane and air in the cell with X-ray and collecting photoelectrons from the high vacuum side of the cell.



Supplementary Figure S4. Schematic illustration on the detection of Si and Au signals on the wide band energy range XPS spectra in the graphene window region.

Notes related to Supplementary Figure S4

Figures 4d and 5e of the main text showed Si2p and Au4f signals even when the X-ray beam was focused to the region of window coved with the two-layer graphene membrane. The Si2p and Au4f signals was expected to come from Si_3N_4 and Au layers on the front surface of the window through residual X-ray scattering. The following two factors may cause small amount of Si 2p and Au 4f observed in the survey spectra (Figures 4d and 5e), (1) XPS setup used a regular UHV energy analyser with large photoelectron collection angle, which allowed for collection of more photoelectrons compare to the case of differentially pumped energy analyser which uses small front cone aperture, and (2) Some part of X-ray beam scattered off the sample region/graphene membrane and excited the surrounding Si_3N_4 and Au (There was always some small amount of X-ray scattering happens).