

Supplementary Information

Fabrication of MoS₂ Thin Film Transistors via Novel Solution Processed Selective Area Deposition

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3D AFM topography of the deposited film

Figure S1 shows the 3D AFM line-profile of the MoS₂ channel between two Au electrodes. The thickness of the deposited MoS₂ film drastically changes at the edge of Au electrode and slowly decreases towards the center of the TFT channel.

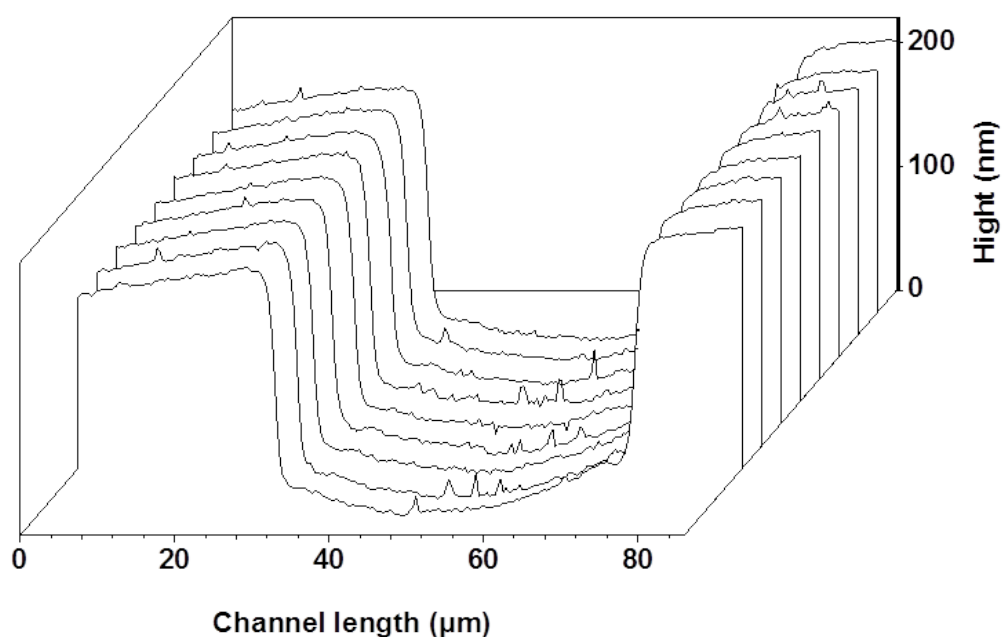


Figure S1 3D AFM line-profile of the MoS₂ TFT channel between the two Au electrodes.

SE (secondary electron) image and the EDS (energy-dispersive X-ray) mapping

The Si K peak map in Figure S2 (B) shows a relatively stronger signal in the channel compared to the signal under the Au electrodes. This is because the Au electrodes do not cover the channel. The Au M peak in Figure S2 (C) confirms the position of the two Au electrodes. Figure S2 (D) and (E) confirm that MoS₂ covers both the electrodes and the channel. Also the contrast between the electrode area and the channel area proves that MoS₂ on the electrodes is thicker compare to MoS₂ on the channel. The non-uniform oxygen K peak map, with similar contrast distribution to Si, shows that the oxygen K peak mainly originates from SiO₂ substrate rather than MoO₃.

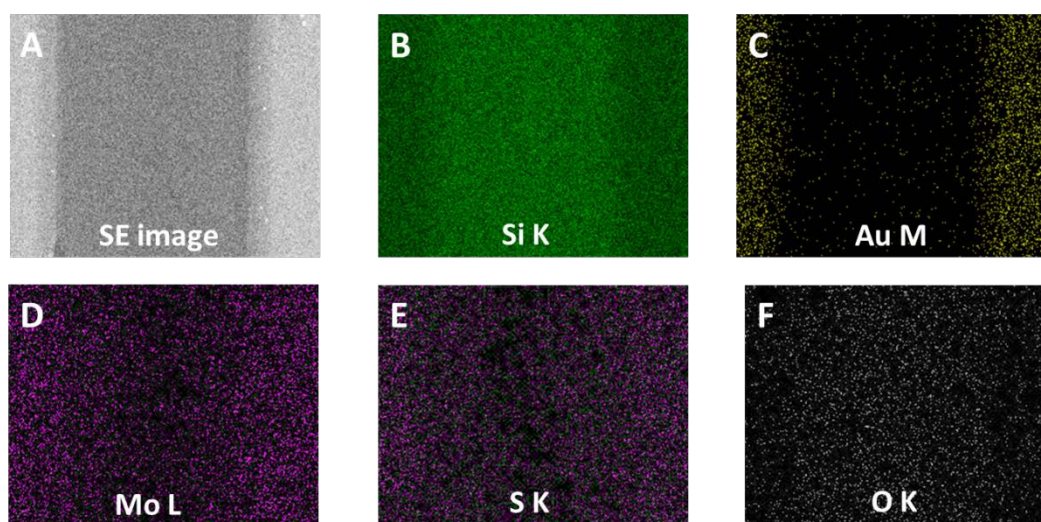


Figure S2 SE image and the EDS mapping of the MoS₂ TFT channel for Si, Au, Mo, S, and O elements, respectively.

Growth Mechanism

To show that Au surface functions as catalyst in the redox reaction, the following experiment was designed. Four substrates (See figure S3) were immersed in glass vials containing the same reaction solution. One control vial (no substrate) was used as reference. All samples were analyzed Raman microscope after 35 minutes and 180

minutes of reaction. All containers were located in the same water bath.

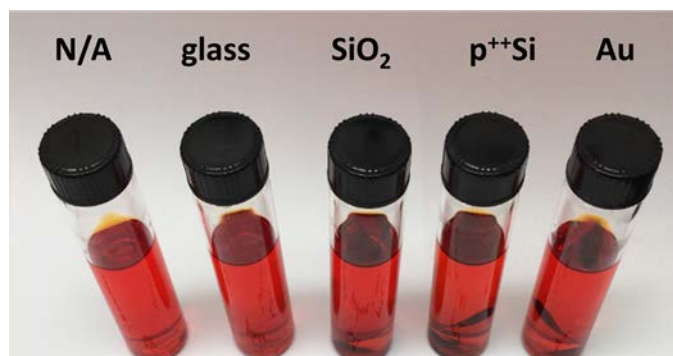


Figure S3 Five vials containing the same reaction solution with different substrates before merging into the water bath. After mixing the precursor and hydrazine the solution showed ruby transparent color. N/A indicates the vial with no substrate.

Three photos of the reaction containers group were taken at different times: before the reaction (Figure S3), after 35 min deposition time (Figure S4), and after 180 min deposition time (Figure S5). After each reaction time, 10 ml of each solution was collected and centrifuged for 5 minutes at 10,000 rpm. In addition, 20 μ l of each solution was collected from the bottom of the centrifuged solution and drop-casted onto a clean glass slide. Afterwards, all the substrates were air-dried for 10 minutes. Samples were examined with Raman microscope to check if MoS₂ was formed in the solution. At the same time, one substrate from each container was moved out and air-dried for 10 minutes for Raman characterization. Then, all the containers were placed back into the water bath for reaction to continue for additional 145 minutes for a total reaction time of 180 minutes.

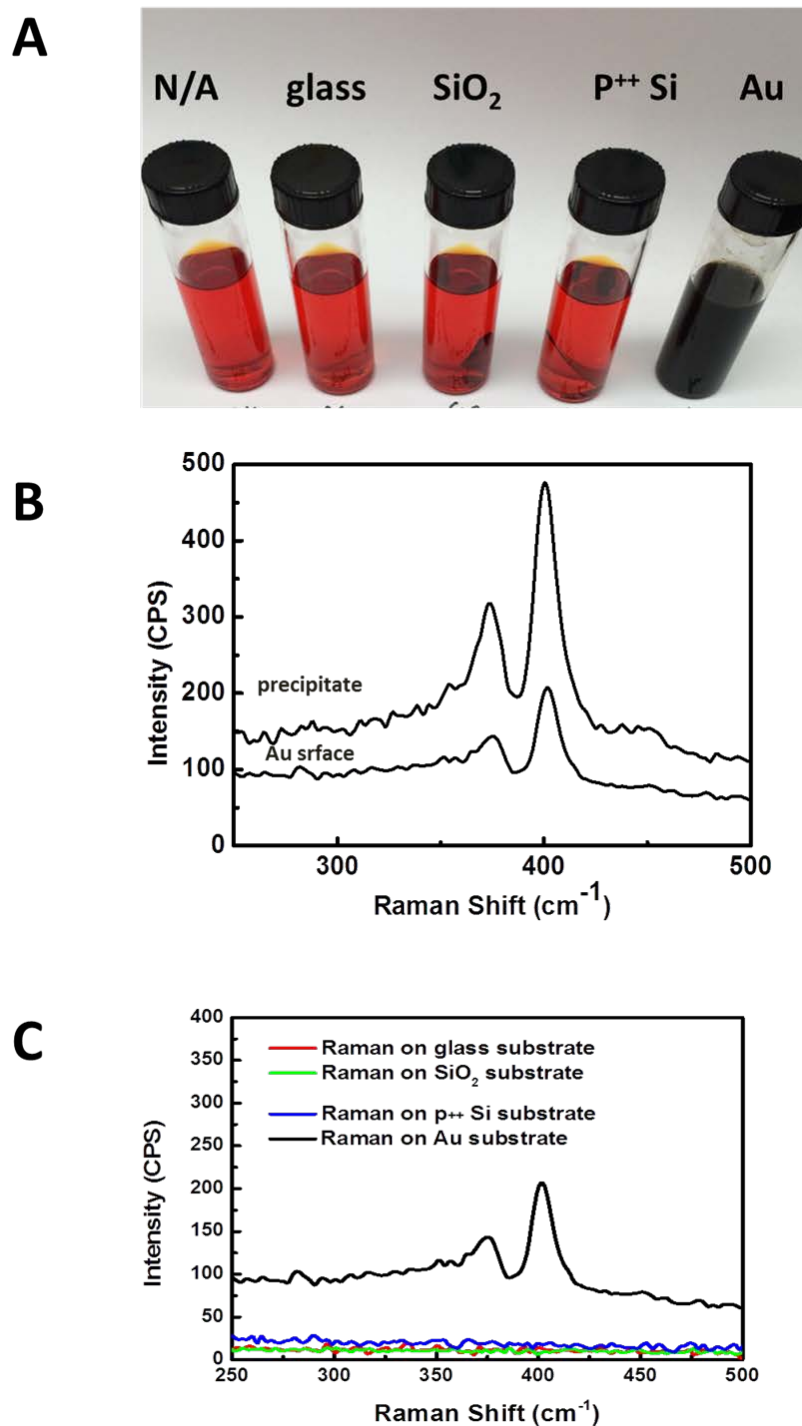


Figure S4 (A) shows the five vials after 35 minutes reaction. After centrifugation, only the vial with Au substrates showed precipitates from solution. As shown in (B) and (C) Raman spectra, MoS₂ was formed on the Au substrate. The formation of MoS₂ indicated that with Au, the reaction had already started at 35 minutes. By comparison of Raman results on different substrates, it was concluded that MoS₂ formed only on the Au substrate.

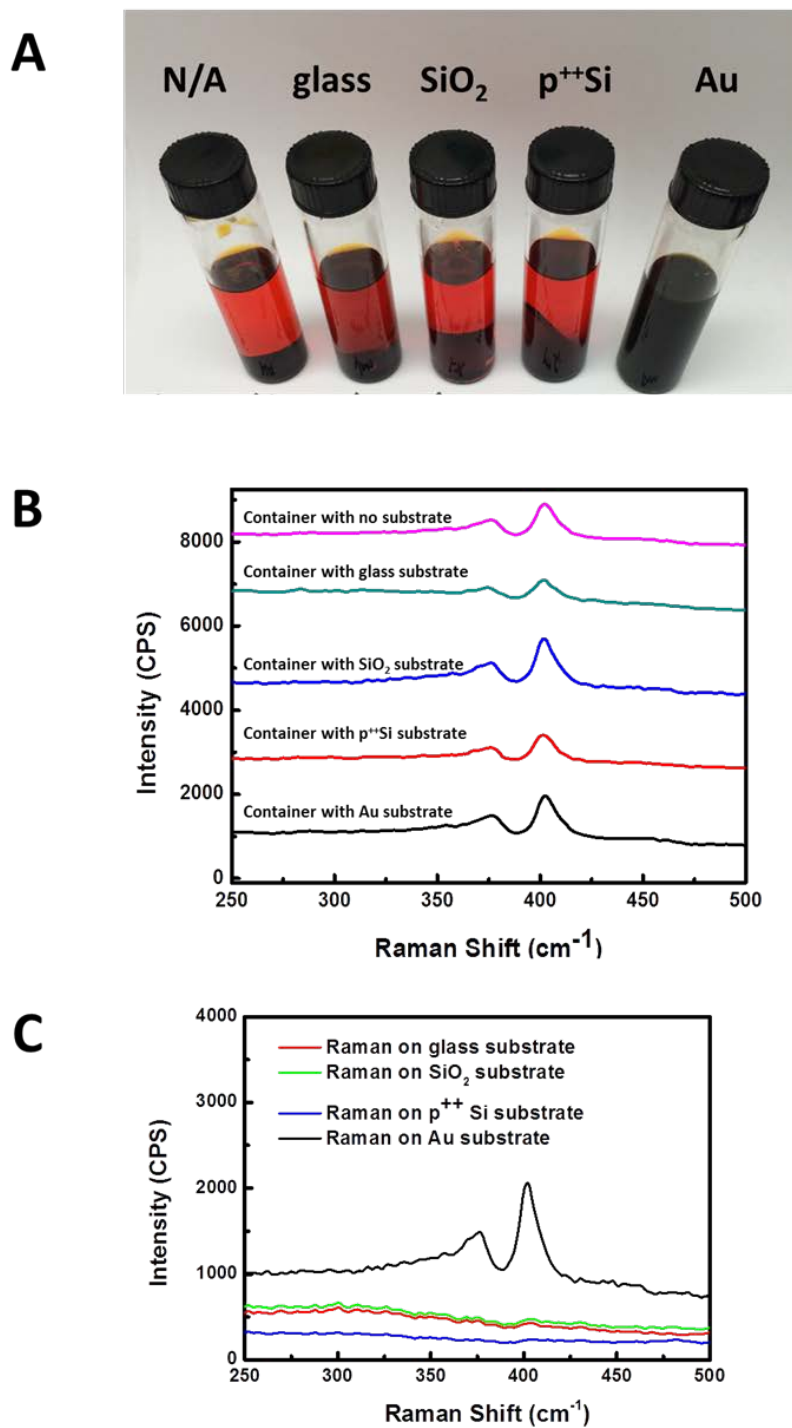


Figure S5 (A) The reaction vials after 180 min. (B) Raman spectra of precipitates in each container. (C) Raman spectra of the substrates.

In Figure S5 (A), all containers showed black precipitates, but the container with Au substrate had no obvious aggregated precipitate. Raman spectra shown in Figure S5 (B) show that precipitates collected from all the vials were MoS_2 . Raman spectra in (C) show that MoS_2 film forms only on the Au substrate, which confirms the 2nd step

in the proposed growth mechanism. The MoS₂ formation in container with no substrate indicates that the reaction may undergo without any catalyst, however, it takes longer time for the reaction to occur without the catalyst.

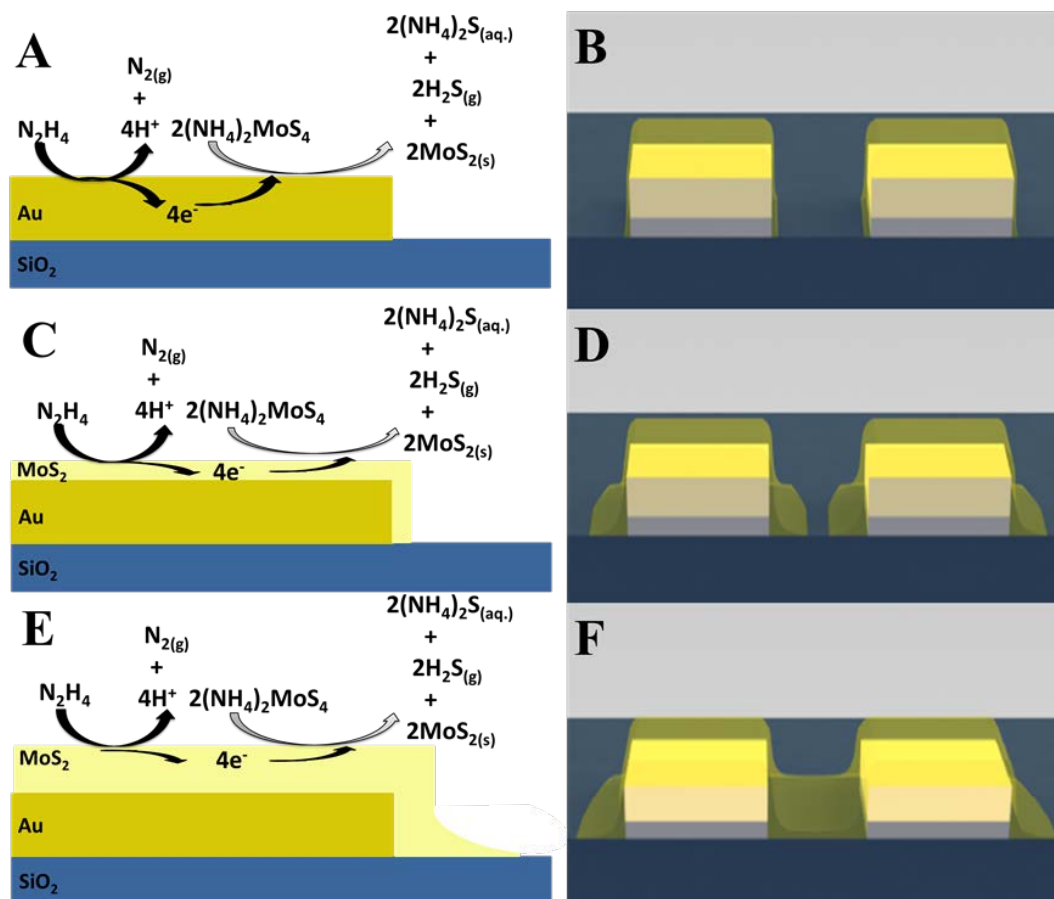


Figure S6 Schematic images of the steps during MoS₂ growth on top of the electrodes and between electrodes.

For this complex agent-free and surfactant-free solution process, MoS₂ is unlikely to be transported away from the Au surface where it is formed in the 1st step of reaction. Therefore, once the initial MoS₂ was formed on the Au surface as a consequence of the catalytic action of the hydrazine, as shown in Figure S6 (A) and (B), the newly formed MoS₂ is likely acting as a growth surface for the further reduction of the (NH₄)₂MoS₄ to Mo(IV) resulting in the growth of MoS₂ away from the Au surface, (as shown in Figure 6S C - F). This also explains the fact that thicker MoS₂ was formed on the top of the Au electrodes with the gradual thickness reduction away from the Au surface.

Figure S7 shows double-sweep for I_d - V_g curve. It indicates that the majority trapping type is interface trapping. The interface trapping comes from MoS₂ and SiO₂ interface. This could be alleviated annealing the TFT after the semiconductor deposition and is currently being investigated by our research group.

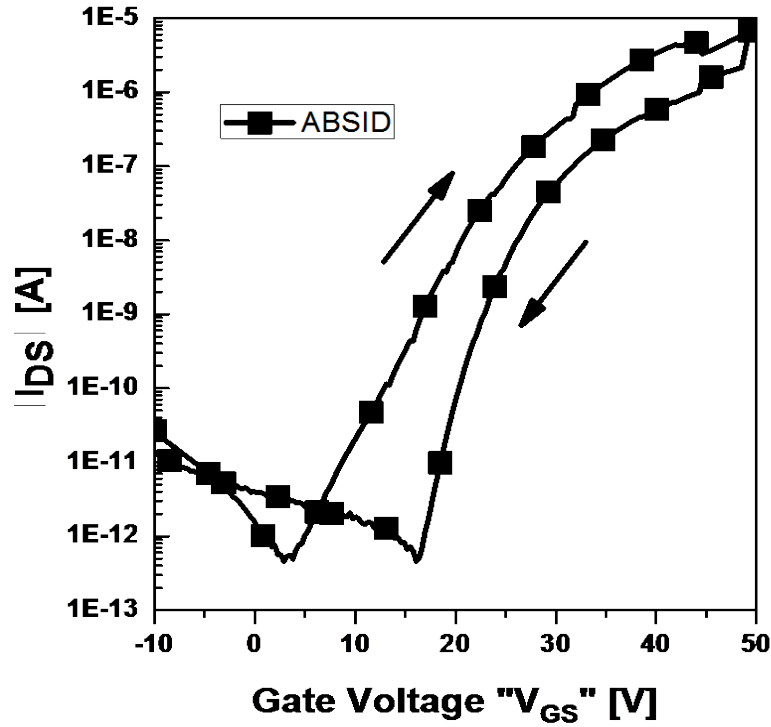


Fig. S7 Double-sweep for I_d - V_g curve.

Figure S8 (A) and (B) are SEM top view images from lower to higher magnifications at the center of TFT channel. (C) is AFM image that shows the topography of the TFT channel center. The SEM images and AFM topography image show a granular morphology with relatively uniform size and shape and no visible cracks or defects on the TFT channel surface.

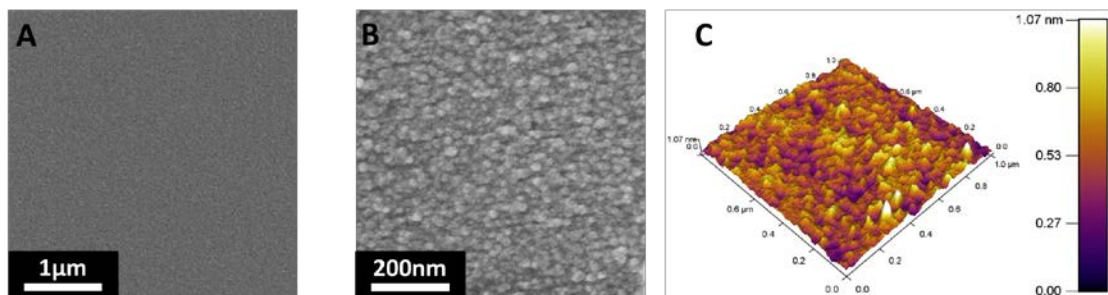


Fig. S8 Top-view SEM images (A) and (B), and AFM image (C) at MoS₂ channel center.

To avoid intense signal from the substrate and metal electrodes Grazing Incidence X-ray Diffraction (GIXRD) method was applied. The GIXRD scan was collected with a grazing incidence angle of 0.6°. It only shows sharp peaks of the Au as the contact metal. A broad peak around 20 comes from SiO₂ substrate. There is no peak for MoS₂, which indicates that the as deposited MoS₂ is amorphous.

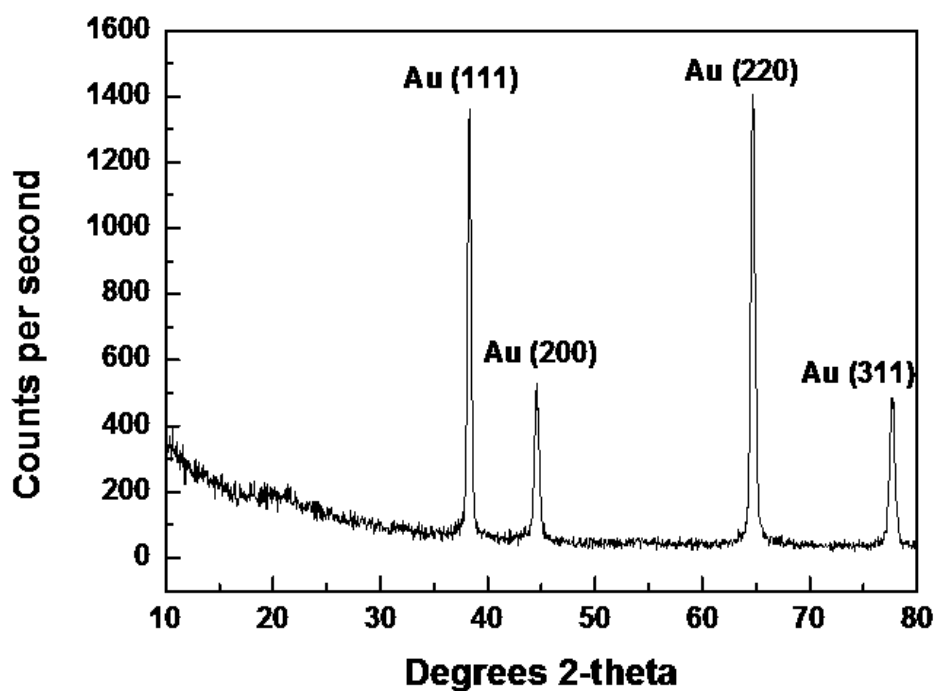


Fig. S9 XRD of the as fabricated MoS₂ TFTs wafer.

Figure S10 shows an optical microscope image containing a group TFTs. The channel length of these TFTs varies from 25 μm to 175 μm . The smallest channel length ($L = 25 \mu\text{m}$) was defined by the shadow mask design used. We believe that scaling to smaller L will be possible since uniform MoS_2 films for channels of up to 25 μm can be easily achieved. However, to control the MoS_2 thickness for narrower L , changes in the deposition time and possible concentration of the reactants will be likely required. For example, for devices with $L = 25 \mu\text{m}$ the minimum deposition time is 23 minutes, but for narrower L the deposition time might be shorter.



Fig. S10 A group TFTs were fabricated with different channel length from 25 μm to 175 μm .

To verify whether the Au catalyst is unique, different metals deposited on SiO₂ substrates were evaluated. Substrate preparation was as follows: First, the substrate (p⁺⁺ Si) was cleaned with isopropanol (IPA), acetone and de-ionized water, and subsequently dried in nitrogen (N₂) flow. Next, 350 nm SiO₂ was thermally grown on the p⁺⁺ Si wafer via thermal oxidation. After this step, a shadow mask was used to define five different metals as source and drain: Cr/Ge (10/100 nm), Cr/Ru (10/100 nm), Cr/Al (10/100 nm), Cr/Pt (10/100 nm) and Cr/Au (10/100 nm). After this, all samples were kept with nitrogen to prevent oxidation. Another Cr/Ru (10/100 nm) sample was prepared and left in atmospheric condition to form RuO₂ on top of Ru. After source and drain definition, the MoS₂ thin film was deposited on the different metals using the same method reported in the manuscript. After deposition, the films were ultrasonically cleaned in distilled water, dried with nitrogen and subsequently annealed at N₂ ambient for 1 h at 350°C.

Figure S11 shows Raman data collected on these different metal substrates after deposition of MoS₂ for 27 min. The results show that inert metals, which have no oxide layer on the surface during the reaction, function as catalyst. However, although Ge, may partially oxidize before deposition, the fact that GeO₂ is water-soluble allows this metal to also grow MoS₂. The results show that the oxygen-free surface is the key for the catalytic effect of this solution-processed reaction. In addition, we tried Al₂O₃ and HfO₂ to deposit onto p⁺⁺ Si wafer. However, since hydrazine is very reactive, the Al₂O₃ and HfO₂ films were removed during deposition and prevented proper device

fabrication.

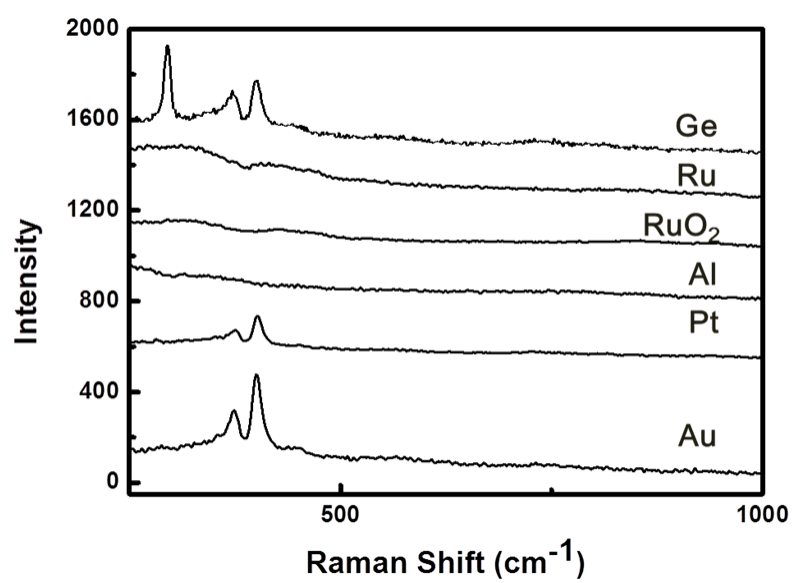


Fig. S11 Raman spectra on various substrates.