Selective Functionalization of High-Resolution Cu$_2$O Nanopatterns via Galvanic Replacement for Highly Enhanced Gas Sensing Performance

Ju Ye Kim $^{1,2,†}$, Soo-Yeon Cho $^{1,2,†}$ and Hee-Tae Jung $^{1,2,*}$

$^1$ Department of Chemical and Biomolecular Engineering (BK-21 Plus), Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Korea; juyekim@kaist.ac.kr (J.Y.K.); chosooyeon@kaist.ac.kr (S.-Y.C.)

$^2$ Korea Advanced Institute of Science and Technology (KAIST) Institute for NanoCentury, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Korea

* Correspondence: heetae@kaist.ac.kr; Tel.: +82-042-350-3931

† These authors contributed equally to this work.

Received: 21 November 2018; Accepted: 13 December 2018; Published: 15 December 2018

Abstract: Recently, high-resolution patterned metal oxide semiconductors (MOS) have gained considerable attention for enhanced gas sensing performance due to their polycrystalline nature, ultrasmall grain size (~5 nm), patternable properties, and high surface-to-volume ratio. Herein, we significantly enhanced the sensing performance of that patterned MOS by galvanic replacement, which allows for selective functionalization on ultrathin Cu$_2$O nanopatterns. Based on the reduction potential energy difference between the base channel material (Cu$_2$O) and the decorated metal ion (Pt$^{2+}$), Pt could be selectively and precisely decorated onto the desired area of the Cu$_2$O nanochannel array. Overall, the Pt-decorated Cu$_2$O exhibited 11-fold higher NO$_2$ (100 ppm) sensing sensitivity as compared to the non-decorated sensing channel, the while the channel device with excessive Pt doping showed complete loss of sensing properties.

Keywords: gas sensor; nanopattern; chemical sensitization; galvanic replacement; p-type metal oxide; high-resolution

1. Introduction

Metal oxide semiconductors (MOSs) (e.g., n-type [1–5] and p-type [6–12]) are widely used as gas sensing materials due to their high sensitivity, large specific surface area, applicability to various gases (NO$_2$, CO$_2$, H$_2$, volatile organic compounds (VOCs), etc.), high electron mobility, and good chemical/thermal stability at high operating temperature [13–20]. Many approaches have been adopted to enhance the gas sensing performance of the MOS, including grain size refinement, increasing the surface area, reducing the interface area between the substrate and the device, and introduction of dopants and defects [1,18–22]. Doping with noble metals such as Pt [21,22], Pd [23], and Ag [2] has been widely used to enhance the sensing performance of the MOS by tuning the gas adsorption or diffusion properties. As sensitizers on the MOS surface, noble metals can induce electronic or chemical sensitization pathways [1,21]. Electronic sensitization occurs due to the electronic interaction between the semiconductor and the doped metal. When metal dopants undergo partial oxidation in air, their oxidation state of the metal additive can be changed into metallic state depending on the environment. This increases the depth of the electron-depleted charge layer due to electron extraction from the metal oxide, thereby changing the electronic state change of the MOS. The chemical sensitization represents a spill-over effect by activating target gas adsorption on the semiconductor surface [24]. The doped promoter facilitates target gas as active state, leading to
increases gas concentration on the channel surface. During the sensing process, the concentration of the adsorbed target gas is effectively increased by the promoter.

Recently, a patterned p-type polycrystalline MOS with an ultrathin and a high aspect ratio showed 5-fold enhanced gas sensing performance due to its ultra-small grains (~5 nm) and large surface-to-volume ratio [6,25]. One of the promising ways to improve the sensing properties is noble metal decoration on the MOS sensing channel. The conventional methods for metal functionalization include sputtering [2,23], thermal evaporation [3], electrospinning [21], and wet impregnation [22] in an aqueous solution. Since the evaporation technique does not allow for selective functionalization of the MOS channel with noble metals, undesired decoration of noble metals on the electrode and substrate can hinder effective control of the doping concentration and cause non-uniform deposition. Moreover, non-directional decoration can produce another dopant-connected channel that reduces the sensitivity of the MOS channel and causes malfunction of the sensing device. Thus, for reduced channel dimensions and higher resolution, more selective and direct functionalization is required [26].

In this study, we selectively functionalized a high-resolution p-type Cu$_2$O sensing channel with Pt nanoparticles by galvanic replacement in order to significantly enhance the gas sensing performance. High-resolution (10 nm scale) and high-aspect-ratio (~25) Cu$_2$O nanopatterns are fabricated via a unique lithographic technique with low-energy plasma bombardments. The unique morphological characteristics (resolution, aspect ratio, grain composition, fully exposed structure) of the Cu$_2$O nanopattern and the possibility of large-area fabrication make it the optimum nanostructure for the sensing channel of gas sensors. Galvanic replacement was employed to further enhance the gas sensing performance of the high-resolution Cu$_2$O nanopattern. This facile decoration process involves a chemical reaction between two materials with different reduction potentials [27–30]. Hence, selective functionalization on the target site is possible, and the size and the amount of the state of Cu$_2$O and Pt on the surface. Decorated dopants can be controlled by adjusting the precursor concentration and reaction conditions. The optimally functionalized nanochannel array (Cu$_2$O/Pt) shows 11-fold higher sensitivity as compared to the pristine Cu$_2$O array upon exposure to 100 ppm NO$_2$ gas (300 °C), because of electronic and chemical sensitization effects of the decorated Pt nanoparticles.

2. Materials and Methods

2.1. Cu$_2$O Nanopattern Fabrication

A polydimethylsiloxane (PDMS) mold was obtained by using a Si pre-patterned mask after curing a silicone elastomer mixture (Sylgard 184, 10:1 weight ratio of base to curing agent; Dow Corning, Midland, MI, USA). Polystyrene (18000 g/mol) solution in toluene was spin-coated (3000 rpm, 45 s) onto a SiO$_2$-coated (200 nm) Si wafer to obtain a thin polystyrene (PS) film. The PS pre-pattern (500 nm width, 350 nm height) was created using capillary forces between PS and PDMS upon heating above the T$_g$ (glass transition temperature, ~135 °C) in a vacuum oven. Then, the target metal (Cu, 25 nm thick) was uniformly deposited onto the PS pre-pattern by electron beam evaporation. By Ar ion bombardment at low energy (500 eV) with a wide angle distribution, the Cu thin layer was etched and emitted into the PS pre-patterned side wall to obtain a polycrystalline feature. After the PS residue was removed by oxygen reactive ion etching (RIE) under a low vacuum and O$_2$ (100 standard cubic centimeters per minute (sccm)) plasma environment, thermal oxidation was performed in a tubular furnace at 450 °C for 3 h to obtain a Cu$_2$O line channel.

2.2. Galvanic Reaction

To decorate Pt nanoparticles selectively onto the Cu$_2$O line pattern, 1 mL of 1 mM potassium tetrachloroplatinate (K$_2$PtCl$_6$, Sigma Aldrich, Burlington, MA, USA), 1 mL of 1 mM hydrochloric acid (HCl, Sigma Aldrich), 5 mL of 20 mM sodium hydroxide powder (NaOH, Daejung), and 5 mL of 10 mM ascorbic acid (AA, Sigma Aldrich) were added to the Cu$_2$O line pattern substrate. This reaction
was performed at room temperature (RT) to control the reaction pace preventing over-loaded Pt. Then, the sample and solutions were injected into a 30 mL vial and agitated on a SK-300 benchtop shaker (90 rpm, Lab Companion, Daejeon, Korea). After each reaction, the substrate was cleaned with ethanol and DI water, and then dried under N₂.

2.3. Characterization

The surface morphology of the fabricated Cu₂O polycrystalline array and Pt-decorated line pattern was characterized by field-emission scanning electron microscopy (Magellan 400, Nova 230, ThermoFisher, Hillsboro, OR, USA) and energy-dispersive X-ray (EDS) spectroscopy (cmodel, manufacturer, city, xsttae abbrev if USA, country). The electron beam energy was 5 kV and 10 kV for the EDS analysis. For the line depth and width profiling of the metal oxide pattern array, atomic force microscopy (AFM; XE-100, Park Systems, Suwon, Korea) was used. X-ray photoelectron spectroscopy (XPS, K-alpha, ThermoFisher, Hillsboro, OR, USA) analysis was conducted to verify the oxidation state of Cu₂O and to confirm the existence of Pt on the surface.

2.4. Sensor Fabrication and Measurement

To measure the resistance signal of the channel, 70-nm-thick Au electrodes with a predeposited 5-nm-thick Ti adhesion layer, as well as 100 µm spacing and width, were deposited on the Cu₂O-Pt line pattern by e-beam evaporation using a customized SERS mask [31]. For saturation of oxygen gas on the substrate, air (400 sccm) was injected over 3 h at 260 °C into the sealed gas reaction chamber where the prepared metal oxide channel device was located. The external sources are used to heat sensing substrate. Heater module is right below the chamber plate. The size of the sealed gas sensing chamber was approximately 10 cm (width) × 5 cm (height) × 8 mm (depth). The resistance signals were displayed directly on a computer via a customized data acquisition module (34970A, Agilent, Santa Clara, CA, USA) to verify the gas sensitivity. NO₂ gas (100 ppm) was delivered into the sensing chamber every 10 min by a mass flow controller (MFC, 5850E, Brooks, Seattle, WA, USA). Air was used for observing the desorption properties.

3. Results and Discussion

3.1. Fabrication of Pt Decorated High-Resolution Cu₂O Nanochannel

The overall fabrication of the Pt-functionalized Cu₂O sensing channel (Cu₂O/Pt) is illustrated in Figure 1. First, a PS prepattern with 500 nm width and 350 nm height was formed on a Si wafer substrate on which SiO₂ was deposited via thermal pattern transfer using a PDMS mold (Figure 1a). By e-beam evaporation, a 25-nm-thick Cu nanofilm was uniformly deposited on the prepatterns (Figure 1b). The Cu layers were then etched such that they covered the side surfaces of the prepattern by using wide-angle distribution by a lower-energy plasma (500 eV, Ar⁺) bombardment process using ion-milling instruments. Bombardment of the Cu precursor layers with low-energy Ar⁺ plasma ruptures the Cu nanofilms to form 5-nm high-resolution grains that are sputtered over a wide area [32,33]. This leads to the formation of a polycrystalline Cu nanopattern with a high aspect ratio as a result of the attachment of the 5-nm Cu grains to the side wall of the PS prepatterns. After removing the polymer residue by oxygen RIE, ultra-high-resolution of the Cu line nanochannel remained (Figure 1d). To oxidize Cu into Cu₂O, the fabricated nanopattern was subjected to thermal annealing in a tubular furnace at 450 °C for 3 h in air and then cooled to RT (Figure 1e).

Since the galvanic reaction occurs only between target materials that have different reduction energy potentials, selective doping on the Cu₂O device channel can be possible without undesired deposition (e.g., on the substrate). Functionalized Pt can enhance the sensing performance of the Cu₂O channel due to the spill-over effect, i.e., easy dissociation of the adsorbed gas on the metal surface and subsequent migration into the metal oxide surface. Therefore, interparticle doping via galvanic replacement not only leads to an accessible contact distance so that gases can easily adsorbed...
and desorbed, but also prevents the target gas from being captured by stray particles, which may hinder gas detection. Pt functionalization by the galvanic reaction was performed after synthesizing the Cu$_2$O nanopattern (Figure 1f). Since galvanic replacement generally results in a porous interior morphology [34], changing the exterior surface of the original material using another precursor in a strongly acidic environment induces fast reduction, and the reaction pathway can be controlled by precise adjustment of the solution pH [35]. To control the reaction time slowly and prevent collapse of the nanopattern structure by reducing the power of galvanic reaction moderate, a certain amount of sodium hydroxide (NaOH) solution was added. Under harsh acidic conditions, the synthesized Cu$_2$O channels were destroyed, resulting in rapid dissolution of Cu$_2$O. Generally, reduction by a galvanic reaction will lead to the formation of a hollow structure via oxidation of the inner metal [34]. When the Cu$_2$O sensing array is dispersed in an aqueous mixture solution which are Pt$^{4+}$ precursor for functionalizing, H$^+$ to initiate the galvanic reaction and NaOH salt for limiting the chemical reaction slowly maintaining the pH value around 5, electrons transfer from Cu$_2$O to Pt$^{4+}$ and reduction of Pt$^{4+}$ itself on Cu$_2$O surface occur at the same time. Since Pt has a higher reduction potential energy than does Cu$_2$O, Pt is preferentially reduced, so that Cu$_2$O is replaced with Pt on the surface [36]. It is well known that when the pH of the reaction solution increases, the reducing power of AA is enhanced [35].

Therefore, by controlling the pH of the reaction solution with NaOH, we can adjust the galvanic reaction slowly, thus allowing both replacement and reduction without destroying the line pattern structure. After several hours of galvanic reaction at room temperature on a shaker, Pt ions were reduced into Pt particles onto the Cu$_2$O array surface, resulting in a Pt-decorated Cu$_2$O nanopattern (Figure 1g). To induce complete replacement, the experiment was performed in the same manner except for the addition of NaOH in the case of Pt nanowire array fabrication (Figure 1h). Under strongly acidic conditions without the addition of NaOH, the galvanic reaction predominates, resulting in

**Figure 1.** Schematic illustration of fabrication of Pt-functionalized high-resolution Cu$_2$O nanopattern. (a) The PS prepattern was transferred from the PDMS mold. (b) The target metal (Cu) was deposited onto the prepattern. (c) By low-energy plasma bombardments, the deposited metal was widely sputtered onto the side wall of the prepattern, resulting in polycrystalline Cu walls. (d) The prepattern residue was removed by RIE and (e) the ultra-thin Cu line pattern was oxidized by thermal annealing. (f) To functionalize the Cu$_2$O surface with Pt, the prepared channel was immersed in a Pt precursor solution. (g) The electrons were transferred from Cu$_2$O to Pt ions, resulting in the Pt-decorated Cu$_2$O nanopattern. (h) In case of an excessive galvanic reaction, the Cu$_2$O baseline channel was completely converted into Pt.
complete replacement of Cu$_2$O with Pt. To understand the reaction mechanism, schematic illustrations and supporting experimental results are presented in Figures S1 and S2.

3.2. Morphology, Elements, and Dimension Characterizations

To verify that selective Pt functionalization occurred only on the desired spot, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM) were used (Figure 2). The pristine Cu$_2$O nanochannel with high resolution and high aspect ratio was well fabricated over a large area with a periodic spacing of 500 nm (Figure 2a). X-ray diffraction (XRD) shows that Cu nanopattern is successfully synthesized to Cu$_2$O nanopattern via thermal oxidation process (Figure S3). Photographs of the devices show that the Cu$_2$O nanopattern was fabricated over a large area (cm$^2$ scale) with excellent pattern fidelity (Figure S4). After 4 h of galvanic reaction, a part of the Cu$_2$O channel was successfully replaced with Pt nanoparticles without destruction or collapse of the high-aspect-ratio nanostructure. The yellow particles on the Cu$_2$O surface in Figure 2c were confirmed to be Pt via point EDS analysis by comparison that of the pristine Cu$_2$O. In addition, the overall distribution of the functionalized Pt was observed by TEM mapping analysis (Figure S5). Low-magnification SEM-EDS images clearly confirmed that the Pt nanoparticles existed only in the Cu$_2$O nanopatterns and there was no Pt in the substrate area between the Cu$_2$O channels (Figure 2c–f and Figure S6). These results revealed that the galvanic replacement selectively occurs at the target spots, i.e., the surface of the Cu$_2$O nanopatterns. With the reaction was carried out for a sufficient time under acidic conditions, replacement of Cu$_2$O with Pt was predominant, resulting in a pure Pt line pattern at the site of the Cu$_2$O pattern. To ensure complete reaction, the reaction was performed without the addition of NaOH (pH ~2). After a few hours, a Pt line pattern could be located at the original Cu$_2$O channel spots (Figure 2e), which supported the occurrence of the galvanic reaction, while EDS observations confirmed the presence of pure Pt wires (Figure 2f). AFM analysis revealed the feature dimensions of the Cu$_2$O nanopattern channel. The periodic Cu$_2$O lines were 15 nm in width and 320 nm in depth before the galvanic reaction; after Pt doping, the Cu$_2$O line nanopattern maintained its original features within the error range of the synthesis, thus indicating that the structure did not collapse during doping (Figure 1g–h). Overall, we fabricated high-resolution (15 nm) and high-aspect-ratio nanopatterns uniformly on a large area and achieved selective functionalization of Pt nanoparticles on the patterns. As discussed in a previous study [6], these nanopattern arrays have distinct advantages as a gas sensor: (1) polycrystalline feature with small grains; (2) low channel resistance caused by the large surface-to-volume ratio, which is derived from the ultrahigh resolution and high aspect ratio (~25). In addition, the noble metal acting as a sensitizer to enhance the gas sensing performance could be selectively decorated onto the surface of the ultrahigh-resolution nanopattern array by the galvanic replacement method.

3.3. Chemical Binding States of Pt/Cu$_2$O Nanochannel

To confirm the chemical binding state and oxidation state of the nanopattern channel, detailed surface elemental analysis was carried out by X-ray photoelectron spectroscopy (XPS). The obtained binding energy was calibrated with that of the C-C peak, 284.7 eV. Overlapping peaks were deconvoluted and identified using the Avantage Software program (Thermo Scientific™). As shown in Figure 3a, the metallic Cu nanopattern was completely oxidized and converted to Cu$_2$O upon thermal annealing. For Cu 2p photoelectron analysis, the binding energy range from 925 to 965 eV was scanned. The binding energy of metallic Cu was not detected in the Cu 2p spectrum, confirming that the Cu channel was fully oxidized into Cu$_2$O under the mild oxidation conditions. The high-resolution Cu 2p spectrum showed two main peaks at 933.18 eV and 952.98 eV, which could be assigned to the Cu$^{2+}$ double peaks for Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ and three satellite peaks, respectively [37]. The two O 1s peaks represented the O$^2-$ state (529.18 eV) from Cu$_2$O and the OH$^-$ state (531.17 eV) from the adsorption of atmospheric oxygen on the surface [38]. The Cu 2p and O 1s peaks confirmed the formation of metal oxide (Cu$_2$O). Figure 3c shows the electron states of the Pt atoms in the nanopattern
channel. The doublet peaks at 74.24 eV and 71.19 eV corresponded to the binding energy of metallic Pt, and the binding energies at 78.2 eV and 75.3 eV were in agreement with Pt$^{4+}$ which came from the binding between metal oxide and doped Pt [39]. During galvanic replacement, the Pt$^{2+}$ ions penetrated the Cu$_2$O environment to form Cu$_2$O/Pt species, ascribed to Pt$^{4+}$ in the X-ray photoelectron spectrum. This Pt species binds to other Pt ions by accepting electrons from Cu$_2$O to form metallic Pt. From the Pt 4f spectral analysis, we can confirm that Pt$^{2+}$ in the galvanic reaction solution (PtCl$_4^{2-}$) is successfully reduced to Pt metal without remaining in the ionic state on the Cu$_2$O surface.

Figure 2. Characterization of fabricated Cu$_2$O, Pt/Cu$_2$O, and Pt sensing channel. SEM image of the fabricated pattern array for (a) pristine Cu$_2$O, (c) optimized Pt-doped Cu$_2$O, and (e) completely reacted Pt. (b–f) EDS point analysis of each channel. (g–h) AFM depth and width profiles show ultrathin line channel and no disruption of the pattern after Pt doping.

The synthesized ultrathin Pt/Cu$_2$O nanopattern exhibited 11-fold higher sensitivity than did the pristine Cu$_2$O nanopattern. To determine the feasibility of using the Cu$_2$O/Pt nanopattern as an electronic sensing channel, the baseline resistances and noise level of the channel were measured during 300 °C operation (Figure 4a). The channel resistance of the pristine Cu$_2$O sensor was 24 MΩ, which increased, and approaching ~45 MΩ upon Pt nanoparticle decoration; a resistance level of tens of MΩ is within the optimal range for MOS-based gas sensors. The increase in the channel resistance was due to the formation of a depletion layer on the Cu$_2$O channel because of electron transfer from the decorated Pt nanoparticles. In addition, the noise from the Cu$_2$O/Pt channel increased from 0.88% to 4.59% of the baseline resistance. However, the Pt nanopattern obtained by the excessive galvanic reaction showed a significantly low resistance (tens of Ω) with an ultra-low noise level due to
the metallic conductivity of the Pt nanopattern channel. To investigate the effects of Pt nanoparticle decoration on the sensing characteristics of the Cu$_2$O nanopattern, a sensing device was fabricated with integration of a nanopattern channel (Cu$_2$O, Cu$_2$O/Pt, Pt) and two-terminal resistor type electrodes. A constant bias from 0.5 to 1.5 V was automatically applied to the two-probe electrode, and the electrical resistance of each channel was recorded as a sensing signal by a data acquisition module (Agilent 34970A). The sensing devices were simultaneously loaded on a home-made gas sensing chamber, and the sensing signals from each device were measured with multi-channel sensing systems.

![Figure 3](image)

**Figure 3.** X-ray photoelectron spectra of Cu$_2$O/Pt nanopattern. High-resolution elemental spectra of (a) Cu 2p, (b) O 1s, and (c) Pt 4f.

### 3.4. NO$_2$ Sensing Performances and Mechanism

Details of the in-house fabricates gas delivery system are provided in the Supporting Information (Figure S7) [40]. Figure 4b shows the responses of the Cu$_2$O, Cu$_2$O/Pt, and Pt nanopatterns toward 100 ppm NO$_2$ at 300 °C. Gas response is defined as $R_a/R_g$, where $R_a$ and $R_g$ are the resistances of the sensor in air and in the target gas, respectively. The Cu$_2$O/Pt nanopattern exhibited a markedly higher sensitivity upon exposure to NO$_2$ ($R_a/R_g = 11$) than did the pristine Cu$_2$O nanopattern ($R_a/R_g = 1$), which was attributed to the effect of the noble metal (Pt) nanoparticle decoration. For the Pt nanopattern obtained by the excessive galvanic replacement reaction, NO$_2$ detection was not observed due to the perfect metallic properties of the nanopattern. To further investigate the high sensitivity of the Cu$_2$O/Pt nanopattern sensor, real-time sensing response to single ppm of NO$_2$ (1 to 4 ppm) is measured (Figure 4c). It is clearly seen that Cu$_2$O/Pt nanopattern sensors show significant responses to single ppm NO$_2$ with distinguishable signal resolutions. Figure 4d further demonstrates that the Cu$_2$O/Pt nanopattern sensors show linear response variations to single ppm NO$_2$ (1–4 ppm) with significant repose amplitudes ($\Delta R/R_g$) which was comparable value with other previous works (Table S1). Here, $R_g$ and $\Delta R$ represent the baseline resistance of the sensor exposed to dry air and the change in resistance after exposure to NO$_2$, respectively. Thus, selective functionalization of the Cu$_2$O channel by galvanic replacement had a significant impact on the enhancement of the gas sensing performance. The response/recovery time (r90%, time taken to reach the 90% of the minimum resistance level) of the sensors for NO$_2$ is shown in Figure S8. Moreover, functionalized Cu$_2$O/Pt doesn’t change the selectivity characterization comparing that of Cu$_2$O (see the Figure S9 which shows similar response selectivity comparing that of Cu$_2$O [6] among various gases). In addition, long-term stability test of the Cu$_2$O/Pt nanopattern sensor was conducted showing high-stability of synthesized catalyst (Figure S10). The highly enhanced gas sensing performance of Cu$_2$O with the Pt galvanic reaction could be explained via two mechanisms: electronic sensitization (ES) [24,41,42] and chemical sensitization (CS) [24,43,44]. The detailed enhancement mechanisms are shown in Figure 4e–g. First, the decorated Pt nanoparticles played an ES role during the sensing process. When exposed to air, each Pt nanoparticle consisting of Pt and Pt$^{4+}$ forms a redox electrode Pt$^{4+}$/Pt$^0$. To achieve electronic equilibrium with the Pt nanoparticles, the Fermi level of Cu$_2$O will be shifted and pinned at the Pt$^{4+}$/Pt$^0$ electrode potential, which produces an electron-depleted space charge region and decreases the charge (hole) accumulation layer (HAL) (Figure 4e). This eventually leads to an increase in the resistance of the
pristine Cu$_2$O/Pt in air. Second, the functionalized Pt nanoparticles also play an important role via the CS mechanism because of the spillover effect. For the pristine Cu$_2$O nanopattern, the adsorbed oxygen ions (O$^-$, O$_2^-$) localize the electrons, which leads to an increase in the concentration of holes in the surface layers. Upon exposure to NO$_2$, the adsorbed NO$_2$ ions (NO$_2^-$) further localize the electrons of Cu$_2$O, thus increasing the HAL thickness and decreasing the resistance of the sensors (Figure 4f–g). In the case of Cu$_2$O/Pt, significantly larger amounts of NO$_2$ can be adsorbed onto Cu$_2$O via the spill-over effect [43,44] due to the high catalytic activity of the Pt nanoparticles (Figure 4f). Thus, the high-resolution Cu$_2$O nanopattern is selectively functionalized with Pt nanoparticles via the galvanic replacement reaction, and the gas sensing performance is significantly improved via both the ES and CS mechanisms.

Figure 4. Device characteristics and gas sensing performance of the Cu$_2$O, Cu$_2$O/Pt, and Pt nanopattern sensors. (a) Baseline resistance and noise of the Cu$_2$O, Cu$_2$O/Pt, and Pt nanopattern. (b) Real-time NO$_2$ (100 ppm) sensing performance of the Cu$_2$O, Cu$_2$O/Pt, and Pt nanopattern sensors. (c) Real-time response behavior of the Cu$_2$O/Pt nanopattern sensor to low concentration NO$_2$ (1 to 4 ppm). (d) Maximum response amplitudes of the Cu$_2$O/Pt nanopattern sensor (three sensors) to low concentration NO$_2$. (e) Band diagram scheme of Cu$_2$O/Pt to elucidate electronic sensitization (ES). Schematic illustrations of chemical sensing mechanism of (f) Cu$_2$O and (g) Cu$_2$O/Pt nanopattern with chemical sensitization (CS) of spill-over effect by Pt nanoparticles.

4. Conclusions

In conclusion, an ultrahigh resolution array, i.e., a thin, polycrystalline, and high-aspect-ratio p-type sensing channel array (Cu$_2$O) was selectively functionalized with Pt via galvanic replacement. Herein, by using a galvanic reaction which involves a chemical reaction between two materials, we achieved selective doping of Pt onto the surface of the ultrahigh-resolution nanopattern array.
We successfully fabricated an ultrathin nanopattern array with a high surface-to-volume ratio over a large area by our unique lithography technique (low-energy plasma bombardment [23]) and showed enhancement of the sensing performance after selective Pt functionalization through the galvanic replacement reaction. The sensor with Pt-functionalized Cu$_2$O showed a 11-fold increase in the gas response ($R_0/R_g$) to the bare Cu$_2$O channel when exposed on 100 ppm NO$_2$. The role of the functionalized Pt particles was suggested in terms of both ES and CS mechanisms. Using the selectively Pt-decorated high-resolution Cu$_2$O array obtained via galvanic replacement, we could achieve significant enhancement of the NO$_2$ sensing performance.

Supplementary Materials: The following are available online at http://www.mdpi.com/1424-8220/18/12/4438/s1, Figure S1: schematic illustrations of expected galvanic reaction process, Figure S2: scanning electron microscope (SEM) observations depending on various reaction condition, Figure S3: XRD spectrum of the Cu$_2$O nanopattern before and after thermal oxidation, Figure S4: photo and SEM image of the Cu$_2$O nanopattern sensors, Figure S5: elemental distribution analysis by transmission electron microscopy (TEM) - energy dispersive X-ray spectroscopy (EDS), Figure S6: the composition analysis of over-galvanic reacted sample to confirm a selective decoration property of galvanic reaction, Figure S7: schematic of the overall gas delivery system, Figure S8: response and recovery time of the Cu$_2$O/Pt nanopattern sensors to 1 to 4 ppm NO$_2$, Figure S9: selectivity characterization of the Cu$_2$O/Pt nanopattern sensor, Figure S10: long-term stability of the Cu$_2$O/Pt nanopattern sensor. Table S1: NO$_2$ gas sensing performance comparison based on CuO or Cu$_2$O materials.

Author Contributions: Conceptualization, validation, writing—review & editing, and writing—original draft preparation, funding acquisition, resources, project administration, J.Y.K. and S.-Y.C.; methodology, investigation, S.Y.; data curation, visualization, formal analysis, S.-Y.C.; supervision, and writing-review & editing, H.-T.J.

Funding: This research was supported by a National Research Foundation of Korea (NRF) grant funded by the Ministry of Science, ICT and Future Planning, Korea (NRF-2018R1A2B3008658) and a Global Frontier grant funded by the Center for Advanced Soft Electronics under the Global Frontier Research Program of the Ministry of Science, ICT and Future Planning, Korea (MSIP, NRF-2012M3A6A5055744).

Conflicts of Interest: The authors declare no conflict of interest.

References
8. Thirumalairajan, S.; Girjia, K.; Mastelaro, V.R.; Ponpandian, N. Surface morphology-dependent room-temperature LaFeO$_3$ nanostructure thin films as selective NO$_2$ gas sensor prepared by radio frequency magnetron sputtering. ACS Appl. Mater. Interfaces 2014, 6, 13917–13927. [CrossRef]
11. Hu, J.; Zou, C.; Su, Y.; Li, M.; Han, Y.; Kong, E.S.-W.; Yang, Z.; Zhang, Y. An ultrasensitive NO\textsubscript{2} gas sensor based on a hierarchical Cu\textsubscript{2}O/CuO mesocrystal nanoflower. J. Mater. Chem. A 2018, 6, 17120–17131. [CrossRef]


34. Zhang, W.; Yang, J.; Lu, X. Tailoring galvanic replacement reaction for the preparation of Pt/Ag bimetallic hollow nanostructures with controlled void number of voids. *ACS Nano* 2012, 6, 7397–7405. [CrossRef] [PubMed]  


38. Ji, R.; Sun, W.; Chu, Y. One-step hydrothermal synthesis of Ag/Cu2O heterogeneous nanostructure over Cu foil and their SERS applications. *RSC Adv.* 2014, 4, 6055–6059. [CrossRef]  


44. Mane, A.A.; Moholkar, A.V. Palladium (Pd) sensitized molybdenum trioxide (MoO3) nanobelts for nitrogen dioxide (NO2) gas detection. *Solid-State Electron.* 2018, 139, 21–30. [CrossRef]