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# Room Temperature Gas Sensing with Ultrathin Au Nanowires

**Lal N***

*School of Chemistry, University of Leeds, Leeds LS2 9JT, UK*

## Abstract

One-dimensional nanostructures are of particular interest in nanoelectronics because of the ease with which they can be utilized in fabricating nanodevices where their long axis facilitates contact to the structure, while the short axis preserves the quantized nature of electronic levels. It is therefore desirable to synthesize precisely controlled semiconductor and metal nanowires to study their properties. With much advancement achieved in producing high quality and appreciably controlled semiconductor nanowires, approaches to precisely control the dimensions of metal nanowires still needs to be explored. Here, we have investigated room-temperature sensing properties of these gold nanowires for hydrogen, ethanol and $NH_3$. The sensitivity and selectivity of the wires for sensing different gases are explored. The sensing devices were fabricated by drop-casting the nanowire dispersion over pre-patterned electrodes ultimately paving the path for cost effective applications of these nanowires. Simple chemical routes and solution processing techniques has been utilized for their subsequent device applications. The driving force behind the solution processed devices is their low cost, large device area, physical flexibility and compatibility with the existing technologies.

**Keywords:** Nanostructures; Nanoelectronics; Sensing; Nanowires

## Introduction

Gas detection is extremely crucial for determining industrial and automobile emissions, household security and environmental monitoring. Therefore, many ways have been explored for detecting $CO_2$, CO, $SO_2$, $O_2$, $O_3$, $H_2$, Ar, $NH_3$, $H_2O$ and many harmful organic vapours. But, low selectivity and high temperature requirements limit their applications and thus triggered an intense research towards finding new materials with desirable properties. In this scenario, nanomaterials seem to provide a promising solution for these issues due to their high surface area in comparison to their bulk counterparts. Hydrogen is viewed as the emissions-free fuel of the future. It has clean burning qualities with only water being produced as the by-product. Therefore, many efforts are drawn towards the efficient production and storage of hydrogen gas to be used in fuel cells with absolutely no leakage in the whole process which could result in explosions. Detection of ethanol also holds multiple applications in breath analyzers and various fermentation units amongst many others. On the other hand ammonia is an environmental pollutant which requires regular monitoring. Therefore it is of much importance to detect these gases with high sensitivity. In last few years, many semiconductors have been explored extensively for their gas sensing properties [1-5]. ZnO nanostructures have shown much promise in sensing gases and vapors of $NH_3$ and ethanol [6-16]. Such metal oxide based gas sensors work on the principle of adsorption and desorption of oxygen species on their surface (i.e. $O^-$, $O_2$, and $O_2^-$) and when they are exposed to reducing gases such $H_2$, $NH_3$ and ethanol, the captured electrons are sent back to the conduction band which increases the conductivity of the material [17,18]. Most of these sensors require higher temperature (~200°C) to efficiently work. The sensing performance of a material also depends upon its surface to volume ratio (S/V ratio) along with its grain and pore size since it increases the probability of adsorption of the test gas molecules on its surface. Thus, the sensing capability can be tuned by decreasing the dimensions of the desired material. It is for this reason that nanoparticles demonstrate enhanced gas sensitivity than their bulk counterpart [19,20].

However, over a period of time nanoparticles aggregate/sinter at higher temperatures which ultimately degrade the devices [20] and it is difficult to make devices on a single nanoparticle. On the other hand, it is more feasible to make devices with nanowires where their long axis provides the ease of forming electrodes on the material and at the same time their short axis preserves the quantization. Nanowires could be synthesized by simple methods which can be easily scaled up and these structures are much more stable due to their high crystallinity. Nanowires also offer direct, label-free, and real-time electrical signal transduction at room temperature. In general, nanowires of semiconducting materials have been studied more extensively as compared to metal nanowires. Gold nanostructures in conjugation with carbon nanotubes have been explored for sensing applications [21-23]. In gold decorated carbon nanotubes, the schottky junction between metal Au NWs and the semiconducting SWNTs are responsible for the chemical sensing [24,25]. This was the motivation behind investigating the sensing properties of ultrathin gold nanowires.

In recent years, simple wet chemical synthesis techniques have been utilized to produce ultrathin single-crystalline Au nanowires (~2 nm diameter) which paved the path for probing the properties of these molecular-scale metal structures [26-29]. These synthesis methods involved the attachment of ultrafine nanoparticles (having narrow size distribution) in the solution phase or on substrates by selective removal of capping agents from specific crystallographic facets. This results in the formation of long ultrathin nanowires of uniform diameter suitable for transport measurements. In the present study, we have used ultrathin, single crystalline Au nanowires which were synthesized chemically to fabricate gas sensors which could detect hydrogen, ethanol and ammonia at room temperature.

***Corresponding author:** Lal N, School of Chemistry, University of Leeds, Leeds LS2 9JT, UK, Tel: 07405740277; E-mail: N.Lal@leeds.ac.uk

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## Experimental Details

### Solution phase synthesis of ultrathin Au nanowires

Au nanowires were synthesized chemically following an oriented attachment procedure as described earlier in literature [27]. Briefly, 2 mg of $HAuCl_4.3H_2O$ and 40 µl of oleylamine were sonicated in 5 ml of toluene to obtain a yellow coloured solution. The reaction tube was sealed with aluminium foil and parafilm and was heated at 95°C in a silicon oil bath. The reaction was monitored until the color of the solution changed to light pink. Then the reaction tube was moved to a water bath maintained at 40°C for ~10-15 min. To this solution, ~10-12 mg of ascorbic acid was added. The reaction tube was resealed and kept in a water bath maintained at 40°C until the color of the solution becomes dark purple after which the reaction tube was kept at room temperature for cooling. For TEM imaging the sample from this purple solution was diluted with toluene and dropped on a Cu-formavar TEM grid for imaging. TEM imaging was performed by FEI Tecnai G20 operated at 200 kV.

**Care:** All glasswares used in the above experiments were cleaned with freshly prepared aqua regia, rinsed thoroughly with distilled water and then dried overnight in a hot air oven maintained at 120°C.

### Device fabrication

The gas sensing devices were fabricated by forming an interdigited pattern on $SiO_2$/Si substrate by photolithography. The electrodes consist of Cr (10nm) /Au (300 nm) electrodes via e-beam evaporation. The distance between the two electrodes was 10 µm and the width of each finger was 20 µm. The length of the finger was ~500 µm [30]. Au nanowires dispersion was drop-casted precisely over the fabricated electrodes. The devices were air dried initially and then were kept overnight in a vacuum chamber to completely evaporate the solvent.

### Gas sensing setup

A custom-built, computer-controlled set up consisting of a test chamber, sensor holder, a Keithley multimeter-2400, mass flow controllers and a data acquisition system was used for measuring gas sensing properties as shown in Figure 1.

The test gas was mixed with dry air to achieve the desired concentration and the flow rate was maintained using mass flow controllers. The current flowing across the sensor can be related to the resistance of the sensor in dry air or in the test gas. Gold nanowires show a change in resistance upon their exposure to test gases and vapours. The performance of any gas sensor can be described by sensitivity magnitude 'S' which is the ratio of $\Delta I/I_{air}$ where $\Delta I$ is the difference of current flowing through the device in the presence of the test gas and in dry air, $I_{air}$ is the current in device under dry air [31]. The resistance of the sensors presented in this study was in the range of ~100 MΩ (Figure 2). Another crucial parameter for sensors is sensitivity time, defined as the time required for the resistance to reach 90% of the equilibrium value after the test gas is injected and recovery time is taken as the time necessary for the sensor to attain a resistance 10% above the original value in air. To measure alcohol sensing characteristics, $N_2$ gas was bubbled at a constant flow rate (100 sccm) through a gas bubbler containing alcohol to get alcohol vapours with desired alcohol concentration in the test chamber.

## Results and Discussion

Ultrathin Au nanowires in solution were synthesized by homogeneous nucleation of faceted Au nuclei in toluene followed by elongation of these nuclei through oriented attachment mechanism

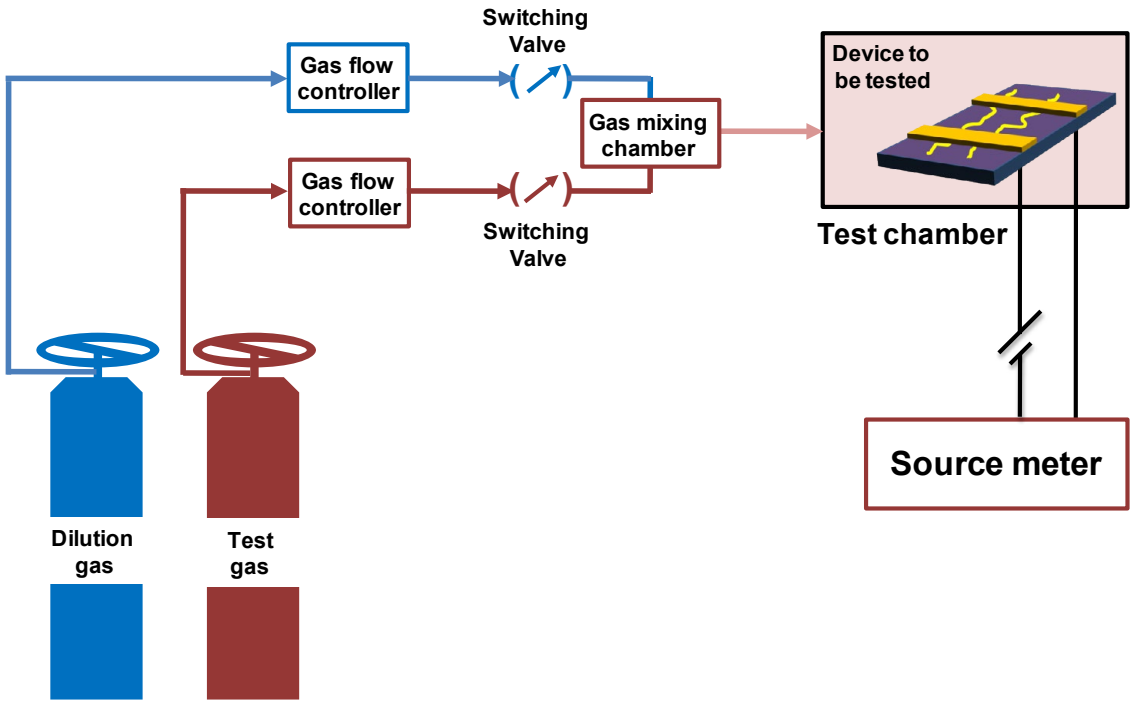


**Figure 1:** Schematic of the gas sensing setup that was used for the detection of various gases.

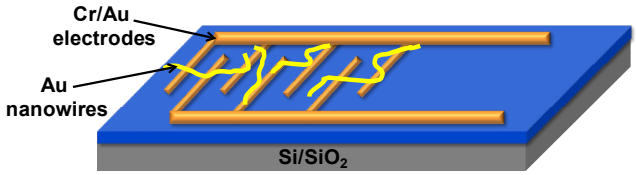


**Figure 2:** Schematic diagram of Au nanowire based gas sensing device.

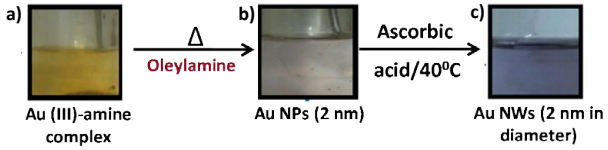


**Figure 3:** Optical image of different stages of ultrathin Au nanowires synthesis in solution.

[27]. In the chemical reaction, $HAuCl_4$ and oleylamine are mixed together in toluene to form a yellow colored solution having Au (III)-amine complex (Figure 3a) which upon heating becomes colorless and Au gets reduced to +1 oxidation state and form cube shaped intermediates. Further heating turns the solution to pale-pink in colour and forms ultrafine Au nanoparticles (Figure 3b). Addition of ascorbic acid at this stage selectively removes oleylamine from {111} facets of Au nuclei present in the solution. Exposed {111} facets of two Au nuclei come together and attach with each other to reduce their total surface energy and their subsequent smoothening results in the formation of Au nanowires with elongation along <111> direction. It turns the reaction mixture to dark violet/purple in colour (Figure 3c) suggesting the completion of nanowire synthesis.

Figure 4 shows the TEM image of the ultrathin Au nanowires obtained in solution. Using these nanostructures, solution based devices was fabricated as described in experimental details. Once the device is fabricated, the first step to be performed is to confirm the contacts of the electrodes to the material of interest. In the present study, Figure 2 shows the schematic diagram of the device and the confirmation of the contacts between electrodes and gold nanowires is given in Figure 5. The device exhibits resistance of the order of ~100 MΩ. This order of resistance for Au nanowires is in agreement with the previous studies reported from our laboratory [32,33]. In the present study, the non-linear in the I-V characteristics can be attributed to the capping agents present over Au nanowires. The device was then tested for its sensing properties under various gases.

In Figure 6a we show the I-V characteristics of the sensor under dry air and 1000 ppm of $H_2$ gas. The stability of the device was confirmed by testing the device for multiple cycles with 1000 ppm of $H_2$ as shown in Figure 6b.

The device shows significant sensitivity towards hydrogen which is nearly 90% for 1000 ppm at 300 K. The interesting thing about the device lies in the fact that it senses $H_2$ at room temperature as most of the oxide sensors operate at 200°C. The response and recovery times are about 100 s and 80 s, respectively. The network like geometry of nanowire films may allow the target molecules to pass through the materials easily thus increasing the sensitivity further towards the analyzed molecules. Figure 7a compares the I-V characteristics of Au nanowires based device in air and in increasing concentration of ethanol. The device shows excellent ethanol sensing properties with

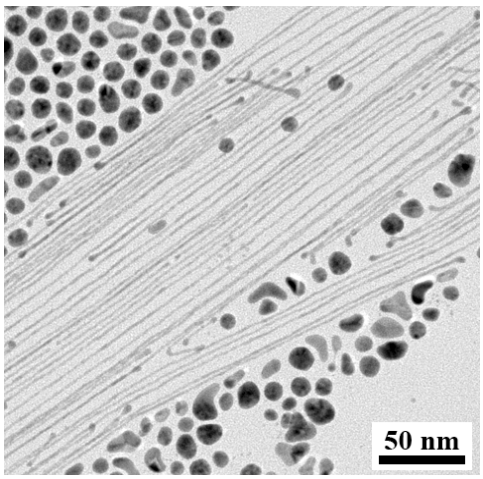


**Figure 4:** TEM image of as synthesized ultrathin Au nanowires.

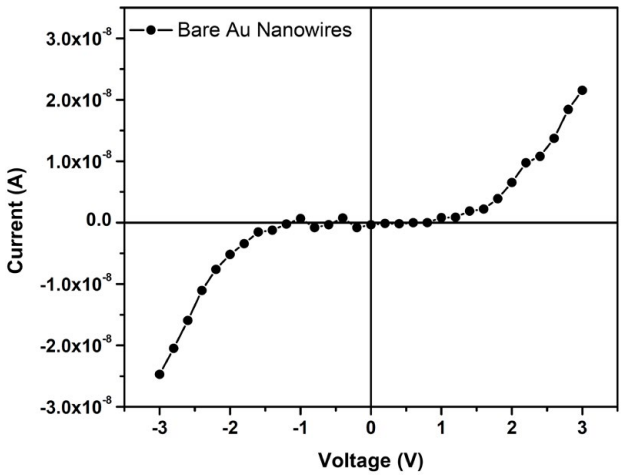


**Figure 5:** Confirmation of the contacts between gold nanowires and the electrodes.

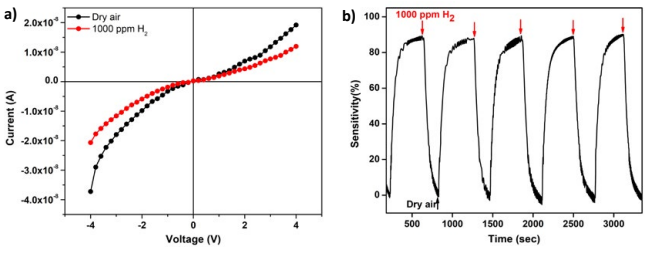


**Figure 6:** (a) I-V comparison of the device in dry air and in 1000 ppm of $H_2$ (b) Sensitivity of the device under multiple cycles of 1000 ppm of $H_2$ at room temperature.

the sensitivity values being 3340% for 200 ppm of ethanol at 300 K as shown in Figure 7b. It also confirms the stability of the device under multiple cycles of 200 ppm of ethanol at 4 V (Figure 7b). Moreover, the sensitivity and recovery times are about 130 s and 50 s, respectively. Au nanowires were also tested for their sensitivity towards $NH_3$ and it was observed that Au nanowire based device exhibits a sensitivity of 160% towards pure $NH_3$ (Figure 8).

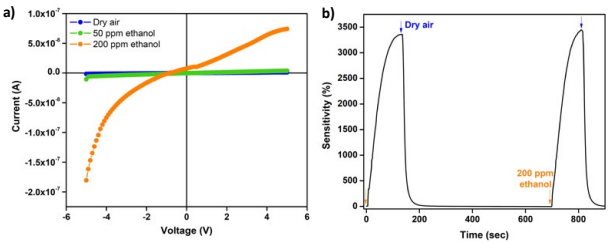


**Figure 7:** (a) I-V characteristics of the sensor in dry air and in increasing concentration of ethanol (b) Sensing cycles of the device in 200 ppm of ethanol at room temperature.

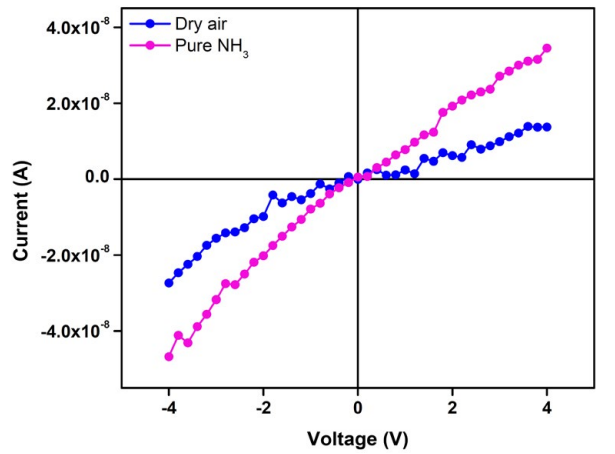


**Figure 8:** I-V characteristics of an Au nanowire based device in dry air and pure $NH_3$.

## Conclusion

The sensors fabricated from chemically synthesized ultra-thin gold nanowires have been studied for their sensing properties towards various gases such as $H_2$, ethanol and $NH_3$. The sensors showed excellent sensitivity towards these gases. Solution processing was employed for making the sensing devices and the encouraging fact about these devices lies in their room temperature operation.

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