



# Silicon nanowire-gold nanoparticle heterostructures for Surface-enhanced Raman Spectroscopy



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## ABSTRACT

In this paper, we report a facile approach for the fabrication of silicon (Si) nanowire-gold (Au) nanoparticle heterostructures and their application in molecular sensing using Surface-enhanced Raman Spectroscopy (SERS). Si nanowires were grown via an atmospheric pressure chemical vapor deposition (APCVD) method. The growth conditions such as silicon source feed rate, growth duration, temperature, and catalyst amount were studied to control the morphology and structure evolution of Si nanowires. Further surface decoration of Si nanowires with Au nanoparticles was achieved using a galvanic deposition approach combined with a subsequent annealing process. This process enabled the formation of uniformly- and tightly-packed Au nanoparticles on Si nanowires with controlled size and inter-particle spacing. Such novel Si nanowire-Au nanoparticle heterostructures were subjected to SERS-based chemical detection of water-containing organic dyes. The results indicate that these heterostructured substrates have significantly improved Raman sensitivity and uniformity, and will be potential for future SERS-based bio/chemical sensors.

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## 1. Introduction

Coinage metals such as gold, silver, and copper have been widely used as favorable substrates for Surface-enhanced Raman Spectroscopy (SERS) [1–4]. The significant enhancement for normally-weak Raman signals up to several orders is believed to originate from the Localized Surface Plasmon Resonance (LSPR) of above metallic substrates, which generates a constant electromagnetic field on the surface of plasmonic nanostructures (called near-field) [5]. LSPR can be simply modulated by controlling the size, shape, and distribution of these nanostructures [6,7], or decorating them on special supporting materials [8]. For instance, direct dispersion of gold and silver nanostructures on flat substrates such as silicon wafer has been initially studied [9,10]. However, such substrate geometries was limited due to the uncontrollable spatial density, inevitable aggregation, and nonuniform distribution of

the decorating nanostructures [11]. With this regard, heterostructures by combining these Raman-sensitive plasmonic nanomaterials with low-dimensional nanomaterials (e.g., Si nanowires) have been recently developed in great demand [12–14].

Si nanowires have been studied for several decades due to their unique electronic property, convenient surface tailorability and excellent industrial compatibility [15,16]. It was recently found that the utilization of Si nanowires in chemical sensors is of particular interest due to their good biocompatibility, vast surface-to-bulk ratio, fast response, and their oxide-coated or H-terminated surface [17–19]. However, the as-produced pristine Si nanowires only exhibit moderate sensitivity in SERS due to the lack of plasmonic properties. Towards this end, the subsequent surface modification or decoration of Si nanowires with plasmonic nanostructures can provide an efficient route to develop novel one-dimensional heterostructured substrate. Previously, combination of Si nanowires with foreign nanostructures such as platinum nanoparticles [20], boron and magnesium [21], alkyl and nanotrees [22], diamond-like carbon (DLC) [23] and polymers [24,25] has been reported for electronic and photovoltaic applications. With respect to SERS sensors, Ag nanoparticle-decorated Si nanowires were also demonstrated for the detection of R6G [26], CV [27], DNA [28], and amoxicillin [29]. The significant Raman signal enhancement observed

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on these nanowire heterostructures was attributed to (1) the enlargement of specific surface area, which can absorb more target molecules per unit area, and (2) the closely-packed nanoparticles on the nanowires, which generate abundant “hot-spots” for SERS sensing [30].

Compared with these Ag-based heterostructures, Au nanoparticle-decorated Si nanowires are more potential for electronic sensors and optical devices due to their chemical stability, low-temperature processability (low melting point), and excellent bio-compatibility [31–33]. The concept of combining Au nanoparticles with Si nanowires has been previously proposed in the studies of Tip-enhanced Raman Spectroscopy (TERS) [34–36]. Afterwards, the decoration of Si nanowires with extraneous Au nanoparticles were further explored to develop novel efficient SERS substrate. For instance, Sun et al. studied the charge-selective ability of Au nanoparticles decorated Si–C core–shell nanowires for the detection of Rhodamine 6G (R6G), acridine orange, fluorescein, and methyl orange in aqueous solutions [37]. Chen et al. demonstrated SERS sensing based on the tailorable optical properties of Au nanoparticle-decorated Si nanowires and further tested their photodetection ability [38]. Recently Peng et al. reported the direct decoration of Au nanoparticles on wet-etched Si nanowires as highly sensitive SERS substrate [39]. However, further progress and large scale application of such Au–Si nanowire heterostructures are still a big challenge due to (1) the high production cost, poor structural uniformity, and heavy crystal defects of Si nanowires [16], and (2) lack of methodologies for the effective combination of Si nanowire and Au nanoparticle with controlled particle size and distribution [40].

Thus, in this paper we report a fundamental study on the cost-effective and large-scale production of Si nanowires and their further surface decoration with Au nanoparticles. The form was conducted *via* a modified atmosphere pressure chemical vapor deposition (APCVD) method while the later was achieved using a unique galvanic deposition–annealing approach. The influence of growth parameters such as SiH<sub>4</sub> flow rate, duration, temperature and catalyst amount on the morphology and structure of Si nanowires were studied in detail. Si nanowires with different structure were further selected and subjected to a galvanic deposition process for the deposition of surface Au nanostructures (shell or flakes), of which the morphology and dispersion were optimized in a subsequent high-temperature annealing process. The obtained final products, Si nanowire–Au nanoparticle heterostructures, as well as various pristine Si nanowires were used as the SERS substrates for the chemical sensing of R6G in aqueous solution. Their Raman sensitivity (detection limit) and uniformity were evaluated and compared in detail.

## 2. Experimental details

### 2.1. Materials and methods

(100), n-type silicon wafer was purchased from IWS (Colfax, CA). Gold (III) chloride trihydrate (HAuCl<sub>4</sub> · 3H<sub>2</sub>O, 99.9%) was purchased from Sigma-Aldrich (St. Louis, MO). Sodium borohydride (NaBH<sub>4</sub>, 98%) was purchased from Acros Organics (New Jersey, NJ). DI water (18.1MΩ-cm) was obtained using a Barnstead International DI water system (E-pure D4641). All chemicals were used without further purification. Gold sputtering was carried out in a Bio-Rad gold sputtering and coating system, (Agawan, MN). Growth and annealing of the Si nanowires were conducted in a GSL-1100X Tube Furnace (MTI Corporation).

### 2.2. Growth of Si nanowires

An atmosphere-pressure chemical vapor deposition (APCVD) method was used for the growth of Si nanowires. Briefly, the Si

substrate was treated in piranha solution for 30 min at 100 °C. This was followed by sputtering of gold film with required thickness. The substrate was then placed in the center of the quartz tube for the growth of Si nanowire according to the vapor–liquid–solid (VLS) mechanism. Various growth parameters were used to optimize the CVD process and further control the morphology and structure of Si nanowires (see Table S1 in supplementary information for detailed experimental parameters the sample labeling). 10% H<sub>2</sub>/Ar with a feeding rate of 100 sccm (standard cubic centimeters) was constantly used as the carrier gas. When the growth was completed, the furnace was cooled down to room temperature with protection of Ar.

### 2.3. Fabrication of Si nanowire–Au nanoparticle heterostructures

The as-produced Si nanowires were treated with BOE solution for 5 s and then placed in a galvanic deposition solution (1 mM KAuCl<sub>4</sub> + 1% HF) for gold deposition [41,42]. The samples were then washed with DI-water and immediately dried in N<sub>2</sub>. This was further followed by a high-temperature annealing process (10 min) at various temperatures. Such treatment leads to the fabrication of final product, Si nanowire–Au nanoparticle heterostructures, an efficient SERS substrate for detection of trace-amount organic dye molecules.

### 2.4. Detection of water-containing R6G

Both the as-produced Si nanowires and the Si nanowire–Au nanoparticle heterostructures were used for the detection of R6G *via* SERS. The nanostructures were first treated in BOE solution for 10 s to create surface Si–H bonds, which can effectively anchor R6G molecules onto the substrates. The samples were then washed with DI-water, dried in N<sub>2</sub> and immediately incubated in the R6G-containing solution for 10 h under slight stirring. The dye-attached samples were washed with DI-water and dried in N<sub>2</sub> for Raman test.

### 2.5. Characterizations

Morphological and structural analysis of the Si nanowires and the Si nanowire–Au nanoparticle heterostructures were conducted using JEOL-7000 FE-SEM and Tecnai F-20 TEM. The average nanoparticle size and inter-particle spacing was estimated according to ~200 nanoparticles or nanowires counted from SEM and TEM images. Raman test on R6G-attached substrates were carried out on the Bruker Senterra Raman System (Bruker Optics Inc. Woodlands, TX), where a neon laser source with wavelength of 785 nm was used. The applied laser power was 1 mW and the integration time was 10 s. The average intensity of Raman peak for R6G were estimated from ~15 spectra obtained at various regions on the substrate.

## 3. Results and discussion

### 3.1. Atmosphere-pressure chemical vapor deposition of Si nanowires

**Scheme 1** illustrates the process for the fabrication of Si nanowire–Au nanoparticle heterostructures and their application as SERS substrate. As mentioned above, Si nanowires were grown *via* an atmospheric-pressure chemical vapor deposition (APCVD) process, of which the growth mechanism can be directed from the well-defined vapor–liquid–solid (VLS) principle [16]. As shown in **Scheme 1**, first sputtering of gold film was conducted on silicon substrate. This was followed by a high-temperature annealing process, which led to the dewetting of gold film to form island-like Au nanoparticles. These Au nanoparticles were further served as

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