

## Thermally activated Cu/Cu<sub>2</sub>S/ZnO nanoarchitectures with surface-plasmon-enhanced Raman scattering



Yan-Gu Lin<sup>a,\*</sup>, Yu-Kuei Hsu<sup>b,\*</sup>, Chin-Jung Chuang<sup>b</sup>, Yu-Chang Lin<sup>a</sup>, Ying-Chu Chen<sup>c</sup>

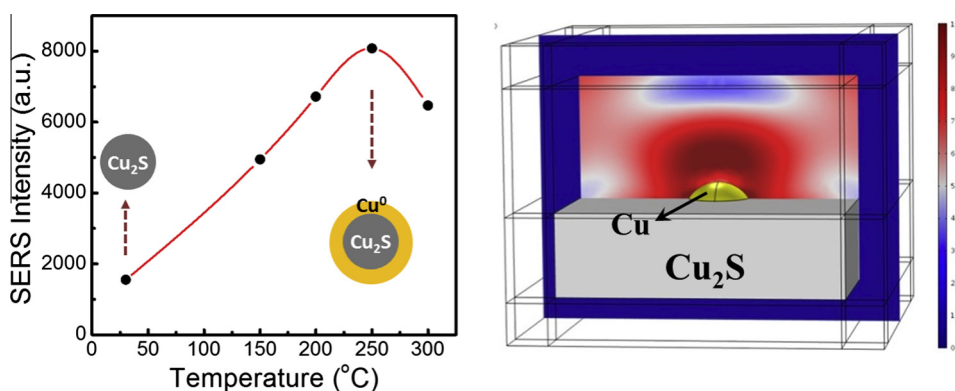
<sup>a</sup>National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

<sup>b</sup>Department of Opto-Electronic Engineering, National Dong Hwa University, Hualien 97401, Taiwan

<sup>c</sup>Karlsruhe Institute of Technology (KIT), Institut für Anorganische Chemie, Engesserstraße 15, D-76131 Karlsruhe, Germany

### GRAPHICAL ABSTRACT

Thermally activated Cu/Cu<sub>2</sub>S/ZnO nanoarchitecture has been demonstrated as a promising surface-plasmon-enhanced Raman scattering substrate.



### ARTICLE INFO

#### Article history:

Received 8 June 2015

Revised 15 October 2015

Accepted 17 October 2015

Available online 14 November 2015

#### Keywords:

Copper(I) sulfide

Copper

Nanostructures

Surface-enhanced Raman scattering

### ABSTRACT

Hierarchical Cu/Cu<sub>2</sub>S/ZnO nanoarchitectures were fabricated via an electroplated ZnO nanorod array in the first step, followed by the growth of Cu<sub>2</sub>S nanostructures for the application of surface-enhanced Raman scattering (SERS) detection. The Cu/Cu<sub>2</sub>S nanostructures as grown were thermally treated at 150–300 °C under a nitrogen atmosphere to improve the crystalline quality, and, unexpectedly, to induce plasmonic Cu nanoshells on the surface of Cu<sub>2</sub>S. With 4-aminothiophenol (4-ATP) as probing molecules, SERS experiments showed that the thermally treated Cu/Cu<sub>2</sub>S/ZnO nanostructures exhibit excellent detection performance, so that they can serve as active and cost-effective SERS substrates for ultrasensitive detection. The enhancement is attributed to the coupling between Cu<sub>2</sub>S and plasmonic Cu, as confirmed by electromagnetic field simulations. This novel hierarchical substrate shows satisfactory reproducibility and a linear dependence of intensity on analyte concentration, revealing an advantage of this method for easily scaled production.

© 2015 Elsevier Inc. All rights reserved.

\* Corresponding authors.

E-mail addresses: [lin.yg@nsrc.org.tw](mailto:lin.yg@nsrc.org.tw) (Y.-G. Lin), [ykhsu@mail.ndhu.edu.tw](mailto:ykhsu@mail.ndhu.edu.tw) (Y.-K. Hsu).

## 1. Introduction

Surface-enhanced Raman scattering (SERS) that produces greatly enhanced vibrational signals, small detection requirements and effective selectivity for adsorbates [1–3] has drawn considerable interest since its discovery; its applications are featured in physics, biomedicine, environmental monitoring, analytical chemistry, etc. Over the past decade, SERS-active substrates of two types – noble metals (Ag, Au, and Cu) and transition metals (Pt, Pd, Ru, Rh, Fe, Co, and Ni) with rough surfaces that have an enhancement factor (EF)  $10^6$ – $10^{11}$  – were primarily investigated [4–6]. This factor is attributed mainly to an electromagnetic mechanism (EM), which involves a surface-plasmon resonance (SPR) on the metal surface under the excitation of an incident laser beam and which leads to an enhanced local electromagnetic field that in turn enhances the Raman signal of adsorbed analytes. Various semiconductor nanoparticles such as NiO, ZnO, TiO<sub>2</sub> and Cu<sub>2</sub>O have been found also to generate weak SERS activity directly; typical prominent EFs range from  $10^1$  to  $10^4$  [7–10]. The main SERS originating from those nanostructures is proposed to be associated with a charge-transfer (CT) mechanism, according to which a transfer of charge occurs between the adsorbed analytes and the substrate. Although the semiconductor nanomaterials exhibit a small enhanced Raman signal of adsorbed analytes, a SERS substrate much cheaper than noble-metal substrates is highly expected. Recent reports reveal further that SPR is not fundamentally limited to metals but occurs in semiconductors with appreciable densities of free carriers [11]. A utilization of plasmonic semiconductor nanomaterials might hence also be beneficial for SERS detection.

Copper(I) sulfide (Cu<sub>2</sub>S) is an important *p*-type semiconductor material (band gap 1.2 eV) and has been the object of particular attention for photovoltaic and electron-storage applications [12–14]. Importantly, as Cu<sub>2</sub>S can support numerous copper-deficient stoichiometries, it is highly self-doped, corresponding to vacancy density  $\sim 10^{21}$  cm<sup>-3</sup>. This feature enables Cu<sub>2</sub>S to exhibit a remarkable SPR in the near-infrared region [15]. The main objectives to improve SERS activity have been to fabricate a nanostructural substrate that can provide numerous sites of strongly enhanced field, the so-called *hot spots*. The fabrication of Cu<sub>2</sub>S nanostructures to enhance SERS activity is hence highly desirable, but reports on Cu<sub>2</sub>S nanostructures for SERS application are rare [16]. In this work, we propose a facile and simple route to produce hierarchical Cu/Cu<sub>2</sub>S/ZnO nanoarchitectures as highly effective SERS substrates. Our results provide a new opportunity to use SERS to explore the molecule–semiconductor interaction, a fundamental but essential question for the design of novel devices.

## 2. Experimental sections

Hierarchical Cu/Cu<sub>2</sub>S nanostructures were fabricated via electrodeposited ZnO nanorod array templates, and were subsequently synthesized through successive ionic layer absorption and reaction (SILAR), shown in Scheme 1. First, ZnO nanorod arrays were prepared in a typical electrodeposition; a piece of Pt foil and a standard silver/silver chloride electrode (Ag/AgCl) served as counter and reference electrodes, respectively. Glass coated with indium tin oxide (ITO) as substrate served as the working electrode. Aqueous solutions containing KCl (0.1 M) with ZnCl<sub>2</sub> at varied concentrations served as electrolyte; H<sub>2</sub>O<sub>2</sub> was a source of oxygen. Electrodeposition was performed with an electrochemical analytical instrument (CHI 627D). The potential –0.7 V versus Ag/AgCl was applied for 30 min; the temperature of the solution was controlled at 80 °C. Subsequently, for the SILAR, Cu<sub>2</sub>SO<sub>4</sub> (10 mM, pH 5) and Na<sub>2</sub>S (75 mM, pH 13) served as the precursor solutions of

Cu- and -S ions. The ZnO template was immersed in the solution with order and time as Cu<sub>2</sub>SO<sub>4</sub> 20 s, DI water 30 s, Na<sub>2</sub>S 240 s, DI water 30 s, Cu<sub>2</sub>SO<sub>4</sub> 20 s and DI 30 s in each cycle; this cycle was repeated and reproduced various times to fabricate the Cu<sub>2</sub>S nanostructure on the ZnO nanorod arrays. The samples were then thermally treated at temperatures 150, 200, 250 and 300 °C, under a nitrogen atmosphere for 1 h. Following this thermal treatment, all samples were immersed in a solution of 4-aminothiophenol (4-ATP) at various concentrations for adsorption. After at least 3 h, the samples were removed from the solution and rinsed five times with distilled water.

The morphology and EDS mapping of hierarchical Cu/Cu<sub>2</sub>S/ZnO nanostructural films was examined with a scanning electron microscope (SEM, JEM-4000EX); the structure of the samples was analyzed with an X-ray diffractometer (XRD) at a beamline 17B in NSRRC. X-ray absorption spectroscopy (XAS) analyses were performed at a beamline 20A in NSRRC. The chemical states of the elements were determined with X-ray photoelectron spectra (XPS) at a beamline 24A in NSRRC. To record Raman spectra (LabRAM HR 550 system, equipped with a thermoelectrically cooled CCD multi-channel detector, 50× objective; accuracy better than 1 cm<sup>-1</sup>), a He–Ne laser (wavelength 632.8 nm, power 5 mW) served for excitation. Data were accumulated for only 20 s with 4-ATP on the Cu<sub>2</sub>S film as grown and the thermally treated Cu<sub>2</sub>S films. The local distribution of the E-field was simulated with commercial software (COMSOL EM).

## 3. Results and discussion

### 3.1. Characteristics of Cu<sub>2</sub>S nanostructural films

Fig. 1a shows the morphology of pristine ZnO nanorods with a well defined hexagonal shape and length approximately 1 μm. After SILAR (three cycles), the deposit over the ZnO nanorods shows a uniform coverage and a dense distribution (Fig. 1b); the ZnO nanorods seemed to stand on the ITO substrate as the support for deposits without severe erosion. After SILAR (nine cycles), the density and amount of deposit loaded on ZnO surfaces increased (Fig. 1c); the thickness of the deposits increased but the interspace between nanorods gradually shrank. Those deposits were significantly constructed as porous networks on connecting together each deposit over a ZnO nanorod. The EDS (Fig. 1d) clearly show that the hierarchical composite arrays were composed of ZnO and Cu<sub>2</sub>S. The elemental composition ratio Cu:S  $\sim 2$  confirms the formation of Cu<sub>2</sub>S in the SILAR; the detected Zn signal indicated that the ZnO nanorods were preserved in the SILAR. The structural formation of Cu<sub>2</sub>S nanostructures through the SILAR was studied with Raman analyses, as shown in Fig. 2. After SILAR (three cycles), only two phonon modes at  $\sim 260$  and  $473.5$  cm<sup>-1</sup> were observed: the dominant feature at  $473.5$  cm<sup>-1</sup>, assigned to the S–S stretching mode of S<sub>2</sub> ions at 4e sites, and a weaker signal at  $261$  cm<sup>-1</sup>, associated with CuS [14]. The main line gradually shifted,  $473.5$  cm<sup>-1</sup>  $\rightarrow$   $471.7$  cm<sup>-1</sup>, with increasing SILAR cycles. Raman studies of Cu<sub>x</sub>S exhibited lines of Cu<sub>2</sub>S and CuS located at  $472$  cm<sup>-1</sup> and  $474$  cm<sup>-1</sup>, respectively [17]. A phase transformation from CuS to Cu<sub>2</sub>S occurred during the SILAR over nine cycles. The reason for the phase transformation is that with more numerous SILAR cycles the duration of immersion of the sample in the Na<sub>2</sub>S solution increased; Na<sub>2</sub>S could play a significant role in sulfonation and in reducing Cu<sup>2+</sup> to Cu<sup>1+</sup> [18], which resulted in the formation of Cu<sub>2</sub>S.

To improve further the crystal structure of the Cu<sub>2</sub>S nanostructures as grown, a thermal treatment at varied temperatures under N<sub>2</sub> atmosphere was undertaken. The morphologic evolution of these thermally treated samples is shown in Fig. 3. The shape

Download English Version:

<https://daneshyari.com/en/article/606446>

Download Persian Version:

<https://daneshyari.com/article/606446>

[Daneshyari.com](https://daneshyari.com)