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3D-printed millifluidic chip for synthesizing plasmonic semiconductor nanocrystals as sensors substrate

W.-C. Law*, T.-L. Cheung, N.X. Rao

Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, P. R. China.

*Corresponding author: roy.law@polyu.edu.hk.

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Abstract

In the past, plasmonics always referred to the collective oscillation of free electrons on metals surface such as gold (Au) and silver (Ag). This has been changed when plasmonic behavior was experimentally demonstrated in semiconductor, i.e. self-doped copper sulfur, nanocrystals ($Cu_{2-x}S$ NCs) in 2009. In fact, $Cu_{2-x}S$ NC possesses different plasmonic behavior than Au and Ag, which the resonant condition is governed by another regime (free holes as the carriers) and its sensing capability has not yet been fully explored. In this contribution, the as-prepared (organic phase) $Cu_{2-x}S$ NCs were transferred in the water and tested with glycerin-water mixtures and anions. The results suggested that $Cu_{2-x}S$ NC is very sensitive to the variation of refractive index in the surrounding environment. Furthermore, we found that the plasmonic properties of these NCs are also very sensitive to the presence of anions. By taking the advantages of this "additional" effect, $Cu_{2-x}S$ NC can be used as a potential substrate for the fabrication of sensor device with enhanced sensitivity.

Keywords

Plasmonics, Copper Sulfide, Semiconductor Nanocrystals, Millifluidic, 3D-printed

Introduction

A key component of a reliable biosensor is the detection technique. Over the past two decades, a variety of technique such as electrochemiluminescence (ECL), surface enhanced Raman scattering (SERS), molecular beacon, surface plasmon resonance (SPR) and giant magnetoresistive (GMR) has been developed [1-6]. Among them, plasmonic based sensing technique has emerged as an efficient approach with high

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detection sensitivity. Different types of plasmonic nanostructures, including gold nanorods, nanostars, nanoshells, and nanocages, silver nanorods, etc, [7-13] have been synthesized to provide distinct absorption spectra and local electromagnetic field enhancement. Typically, plasmonic refers to the free oscillating electrons on a particular type of metal surface such as Au and Ag. Under the resonant condition (collective oscillation of electrons), their optical properties are very sensitive to the changes of dielectric media and particle shapes. Conventionally, plasmonic based biosensors were composed of a nanoscaled metallic structure where the surface plasmons are very sensitive to the surrounding environment. Through monitoring the optical properties, this sensitive substrate allowed us to detect and monitor the biomolecular interactions.

Very recently, new plasmonic nanomaterials have been developed. In 2009 and 2011, copper-based semiconductor nanocrystal structures ($Cu_{2-x}E$, E = S, Se) which the plasmon resonance is supported by the oscillation of free holes was experimentally demonstrated by two prestigious research groups [14, 15]. Since then, studies have shown that the optical properties of $Cu_{2-x}S$ are very sensitive to the organic solvents (e.g. chloroform and toluene) [16]. Manna's group demonstrated the possibility of reversibly tuning the plasmonic peak of $Cu_{2-x}Se$ by oxidizing these plasmonic NCs using a cerium (IV) complex [17]. In addition, superior performance of these novel

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NCs have also been shown over the gold nanostructures [18]. Korgel group have depicted the potential of $Cu_{2-x}Se$ as a photothermal (PT) therapeutic agent [19]. In their work, under the 800 nm light irradiation, $Cu_{2-x}Se$ NCs generated significant PT heat with efficiency comparable to the conventional PT agent such as gold nanorods [20] and better than the gold nanoshells [21]. It implies that the plasmonic aroused from the free hole may have comparable or even better energy transfer efficiency, localized plasmonics field and near-field enhancement. Although pioneering work in the synthesis of $Cu_{2-x}S$ NCs with clear NIR plasmonic absorbance has been observed, drawbacks including large nanoparticles with a different crystal structure and insufficient number of free holes were also found [16]. In addition, while the physical properties of these NCs and the underlying principle of free holes resonance are still under investigation, the sensing capability of $Cu_{2-x}S$ NCs has yet been fully explored. In this paper, $Cu_{2-x}S$ NCs were synthesized in a millifluidic chip and comprehensive studies were performed to evaluate the sensing performance of $Cu_{2-x}S$ NCs in aqueous solution.

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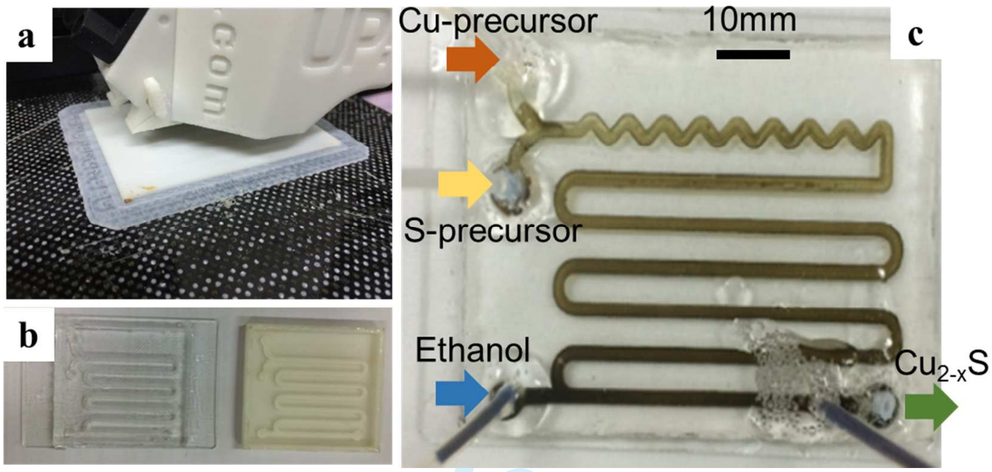
Experimental

Fabrication of Millifluidic Chip

A 3D printer from PP3DP was applied to print the mould of 3D channels followed by pouring pre-mixed polydimethylsiloxane (PDMS) into the mould [22]. The PDMS was then cured at 65 °C for 4 hours (Scheme 1a and 1b). Finally, the PDMS was carefully bonded to a glass slide and connected with polytetrafluoroethylene (PTFE) tubes.



Scheme 1. (a) 3D printed acrylonitrile butadiene styrene mould for fabricating millifluidic chip. (b) The mould (right) and the PDMS millifluidic chip (left). (c) Synthesis of $Cu_{2-x}S$ NCs using continuous-flow regime in the millifluidic chip.

Synthesis of $Cu_{2-x}S$ NCs

Spherical $Cu_{2-x}S$ NCs were synthesized using our previous protocol [22]. In brief, 6 mmol of copper (I) chloride was dissolved in 10 ml of oleylamine and 1 mmol of sulfur was dissolved in 10 ml of oleic acid. Both of them were heated at 120 °C with stirring. By using a syringe pump, the precursor solutions were simultaneously injected into the millifluidic chip which was placed on a pre-heated hot plate at 120°C (Scheme 1c). The winding path was designed for precursors mixing and initizing the

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nucleation process. It was followed by the growth of $Cu_{2-x}S$ NCs along the channel and the NCs were subsequently quenched at the final stage by ethanol. The purified NCs were redispersed in chloroform.

Characterization of $Cu_{2-x}S$ NCs

Transmission electron microscope (TEM) images were taken by a JEOL JEM-2011. UV-vis-NIR absorbance spectra measurements were conducted using a PerkinElmer Lambda 950 UV/Vis/NIR Spectrophotometer System. Rigaku Smart-Lab powder XRD diffractometer was used to measurement the powdered X-ray diffraction (XRD) profiles.

Phase transfer of $Cu_{2-x}S$ NCs into water

Ligand exchange of $Cu_{2-x}S$ NCs was performed by vigorous stirring the mixture containing $Cu_{2-x}S$ NCs and L-glutathione (GSH) under the pH 10-11 for 30 minutes. The $Cu_{2-x}S$ NCs were then purified using ethanol and redispersed in water.

Results and Discussion

The TEM image of $Cu_{2-x}S$ NCs is shown in Figure 1a. The size distribution was obtained by manually measuring the NCs which the average size is around 9.1 nm with standard deviation of 1.8 nm, indicating the high monodispersity of the NCs. This was achieved under the molar ratio of precursors (Cu:S 6:1) and the flow rate

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(3000 μl). Figure 1b shows the XRD profile that the $Cu_{2-x}S$ NCs exhibit the djurleite crystal structure [22].

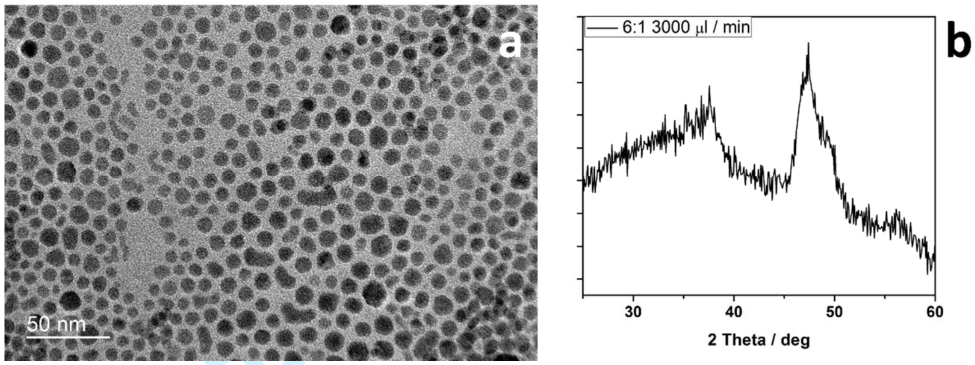

Figure 1. (a) TEM image and (b) XRD profile of $Cu_{2-x}S$ NCs.

The $Cu_{2-x}S$ NCs were initially dispersed in chloroform which is a non-polar organic solvent, then were transferred to water by replacing the hydrophobic ligands with glutathione (GSH) [23]. GSH is a short-chain thiol ligand to facilitate the dispersion of $Cu_{2-x}S$ NCs in water. It is essential to quantitatively evaluate the performance of the NCs for sensing applications. In our first experiment, glycerin-water mixtures from 0 wt.% to 35 wt.% were prepared and their corresponding refractive index change is from 1.3330 to 1.3906 [24]. The shift of plasmonic absorption peaks is illustrated in Figure 2a. The red shifts were caused by the increase in the concentration of glycerin, indicating that $Cu_{2-x}S$ was sensitive to the local change of the dielectric constant. Figure 2b shows the change in peak position versus concentration of glycerin. The detection limit was estimated to be 4×10^{-4} refractive index unit. Under the resolution of 0.3 nm, this is also corresponding to 0.3% of glycerin.

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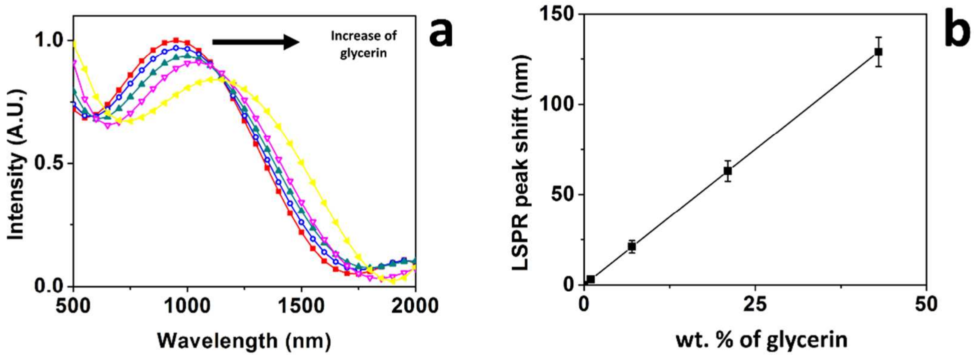

Figure 2. (a) UV-Vis-NIR measurements of $Cu_{2-x}S$ mixed with glycerin-water with various weight ratios. (b) Variation of plasmonic shift vs glycerin concentration.

As demonstrated by Manna's group, the reversibly tuning absorption band of $Cu_{2-x}Se$ could be done by oxidizing the NCs using a cerium (IV) complex. As electron and hole serve as a complimentary partner, we hypothesize that when an electron-rich material is brought very close to the $Cu_{2-x}S$ NC, it can deplete the number of free holes carrier and lead to a large red-shift or vanish of plasmonic peak. It is important because in traditional plasmonic-based sensing, Au and Ag were usually used. The resonant oscillations, which occur at metal/dielectric interface, are very sensitivity to the refractive index change. As the resonant condition of $Cu_{2-x}S$ is supported by another regime (free holes), the plasmonic properties will not only be sensitive to the surrounding medium but also the concentration of free holes in the NCs. This "additional" effect would enable to develop a new sensing mechanism with enhanced detection sensitivity. To justify our hypothesis, in our second experiment, different concentrations (0 mM, 5 mM, 10 mM, 15 mM and 20 mM) of $AuCl_4^-$ solutions were

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prepared. As shown in Figure 3a, when the concentration of $AuCl_4^-$ increases, it altered the number of free hole carriers in valence band [25] and led to decrease and eventually vanish of plasmonic peak, showing the agreement with our hypothesis. A linear relationship between the intensity of LSPR peak and the concentration of anions is obtained in Figure 3b. The detection limit was estimated to be 5.5 μM.

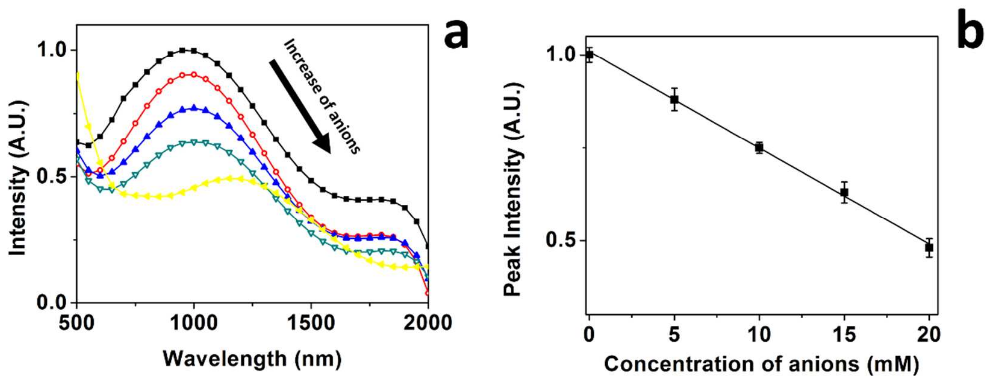

Figure 3. (a) Change of plasmonic profiles of $Cu_{2-x}S$ NCs due to the depletion of free hole carriers. (b) Variation of peak intensity vs anion concentrations.

Conclusion

In summary, we have demonstrated that the plasmonic peak of $Cu_{2-x}S$ NCs was sensitive to the surrounding dielectric in aqueous solution and the number of free hole carriers in the NC. The millifluidic chip is a valuable too allow us for synthesizing $Cu_{2-x}S$ NCs with high monodispersity in organic medium. GSH was employed to transfer organic $Cu_{2-x}S$ NCs into water without losing the plasmonic features. In fact, the unique plasmonic features of $Cu_{2-x}S$ NCs will enable us to develop new sensing mechanism and fabricate ultrasensitive nanoprobes. We believe that the work will have important impacts to the field of plasmonic semiconductor NCs synthesis and

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the nanoparticle-based sensing.

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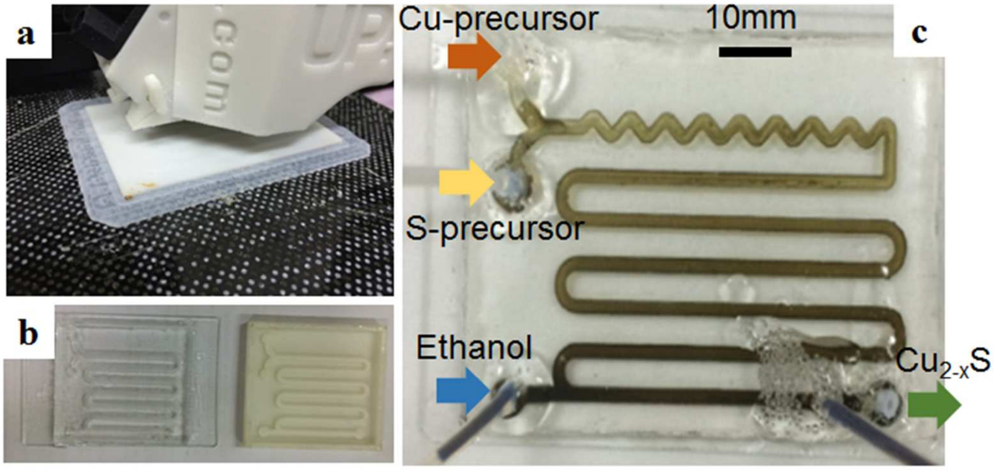

Scheme1

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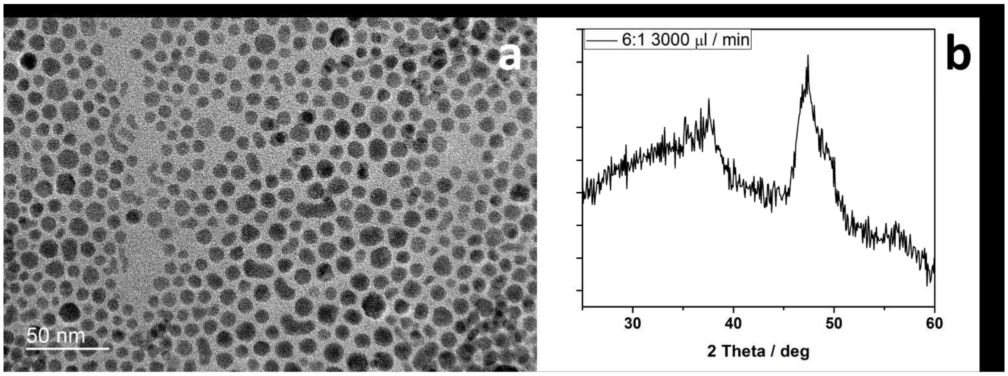

Figure1

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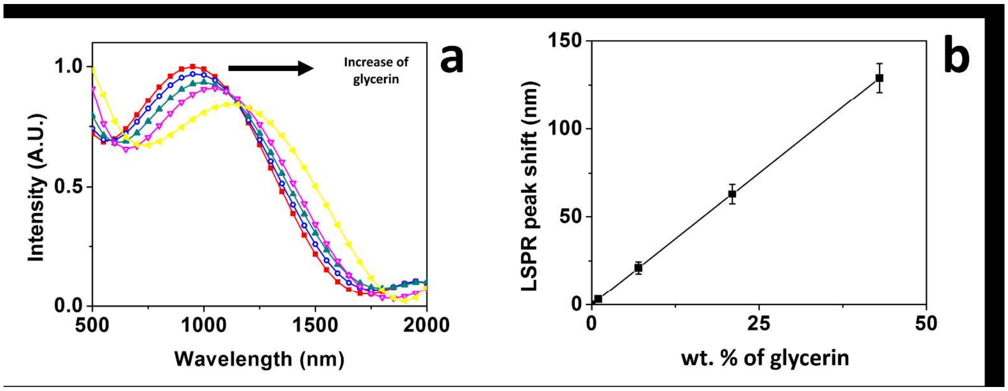

Figure2

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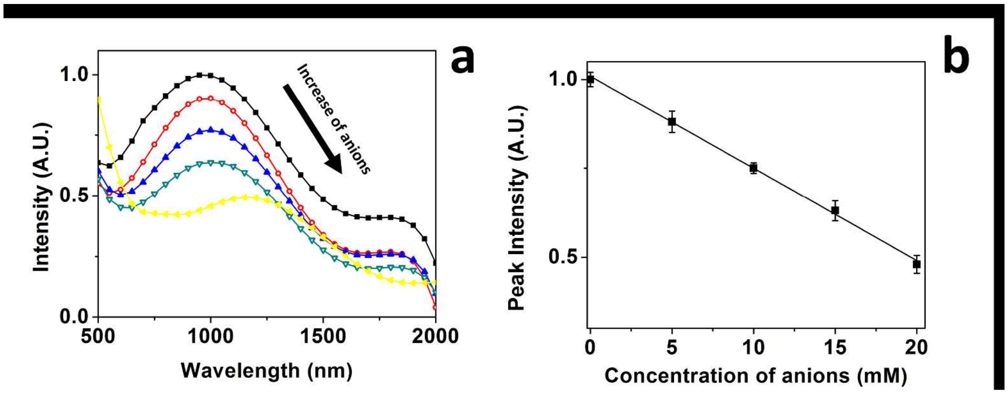

Figure3

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