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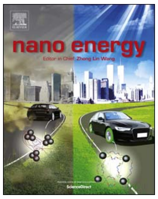

Surface plasmon resonance enhancement of production of H_2 from ammonia borane solution with tunable $Cu_{2-x}S$ nanowires decorated by Pd nanoparticles

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ABSTRACT

Localized surface plasmon resonances (LSPR) in near-infrared (NIR) region have been extensively studied for copper chalcogenide nanostructures, not only for the absorption enhancement but also tunable LSPR characteristics with their free carrier concentrations or defects. In the present work, one-step cation exchange method has been used to synthesize $Cu_{2-x}S$ nanowires with x varied between 0 and 1, including Cu_2S, Cu_7S_4 and CuS and so forth. The plasmonic band of $Cu_{2-x}S$ nanowires shifts to a shorter wavelength with the increase in x, as observed in vis-NIR spectra, which is attributed to the increase in density of copper vacancies. The $Cu_{2-x}S$ nanowires have been used as catalysts towards the photocatalytic generation of H_2 from ammonia borane (AB). Among samples with different Cu-S compositions, Cu_7S_4 samples exhibited the highest activity in terms of H_2 evolution rate (25.54 mmol/g h). Moreover, a marked enhancement of the H_2 evolution rate (157.04 mmol/g h) could be achieved after decorating the $Cu_{2-x}S$ nanowires with Pd nanoparticles to form the hybrid structures. The results of the present investigation may lead to an effective strategy for the design and development of LSPR materials for photocatalytic applications.

Compared to metal, a crucial advantage of using semiconductors for plasmonics is their tunable free carrier concentrations, by doping, heating, or phase transition, as this is a physical parameter that determines the localized surface plasmon resonances (LSPR) frequency of the plasmonic material. The tunability of LSPR not only allows the applications of LSPR enhanced photovoltaics, but also control or switching within active devices such as optical transistors or logic gates [1]. LSPR of semiconductor materials could be alternated from the terahertz (THz) to near-infrared (NIR) or visible frequencies, provided that controlled doping is attainable, either via the creation of intrinsic defects or the addition of extrinsic impurities [2,3]. In infrared region, which constitutes about 44% of the sunlight, semiconductor show higher potential than noble metal whose LSPR is generally in the visible region, making possible to extend the light response of photocatalysts. The near field enhancement owing to LSPR is shown to be comparable with that of noble-metal nanoparticles, indicating that highly enhanced light absorption rate can be expected for the applications in photocatalysis.

Metal-like LSPR have since been found in a variety of semiconductor systems, including copper chalcogenides, germanium telluride, or transition metal oxide, etc [4–6]. Among those materials, researches of copper sulfides ($Cu_{2-x}S$) in photovoltaics- and photocatalysis-related energy conversion and environment treatment have been widely conducted in recent years because of their intrinsic characteristics, a p-type self-doped semiconductor composed of highly earth-abundant elements with stoichiometry-dependent band gap ($E_{g,Cu2S}$~1.2 eV; $E_{g,CuS}$~2.1 eV) [7–13]. The plasmonic absorption tunability of $Cu_{2-x}S$ produced by the introduction of Cu vacancies in the $Cu_{2-x}S$ lattice leads to the increase of hole carrier concentrations and band gap. The characteristic especially in the NIR region makes $Cu_{2-x}S$ promising candidates for building plasmonic-enhanced photocatalyst.

For the purposes of tuning plasmonic properties of $Cu_{2-x}S$, compositional control is the effective means to vary optoelectrical properties of LSPR. Various methods to fabricate the tunable materials, such as atomic layer deposition, template-assisted synthesis form Cu_2O crystals, reduction from CuS, and oxidation from Cu_2S by oxidizing agent or exposure in oxygen atmosphere, have been reported [9–15]. However, the difficulties in composition control, impurities as well as slow, complex, and high temperature procedures are the common challenges of those methods.

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In the present study, we demonstrated that tuned $Cu_{2-x}S$ nanowires with x ranging from 0 to 1 could be synthesized via a novel one-step cation exchange method. The confirmed structures and components including Cu_2S, Cu_7S_4, and CuS were examined by Cs-corrected TEM, EDS and XRD. Furthermore, the modulation of their optical properties could also be observed in the VIS-NIR spectra. This approach represents a new route for the preparation of precisely tailored copper chalcogenides nanostructures containing monovalent and bivalent copper cations. We further employed the bare $Cu_{2-x}S$ nanowires, as well as $Cu_{2-x}S$-supported Pd nanoparticles as catalysts towards the H_2 from ammonia borane (NH_3BH_3; AB) under visible light irradiation ($\lambda > 420$ nm), attaining in this latter case higher light harvesting efficiency than with the bare nanowires. The results herein included not only shed light on the innovative synthesis method, but may lead to an effective strategy for the design and development of LSPR materials for photocatalytic applications.

Herein, $Cu_{2-x}S$ nanowires with x varied between 0 and 1 were fabricated via one-step cation exchange from CdS nanowires. By controlling the amount of copper ions (Cu^+ and Cu^{2+}) in ethylene glycol and the reaction temperature (75 ~ 95 °C), nanowires with various compositions could be obtained by this method. Fig. 1 shows the schematics of the processes of one-step cation exchange method to synthesize tunable $Cu_{2-x}S$ nanowires from CdS nanowires. As in our previous work, CdS nanowires were grown along [0,1,1] direction with a vapor-solid-liquid (VLS) process, and CuCl was used as source of Cu^+ for the growth of Cu_2S nanowires [16]. In these synthesis, Cu^{2+} ions of $CuCl_2$ were also mixed into the reaction solution for tuning the stoichiometry of $Cu_{2-x}S$. The detailed synthesis parameters are listed in supporting information Table S1. The morphology, crystal structure and composition characteristics of the nanowires were examined by field-emission scanning electron microscopy (FESEM, JEOL JSM-6500F), Cs-corrected high resolution transmission electron microscopy (HRTEM, JEM-ARM200F) and scanning transmission electron microscopy with energy-dispersive spectroscopy (STEM-EDS).

LSPR, which is known for its near-field enhancement phenomenon, is arising from resonant excitation. Collective oscillations of free carriers in nanostructured materials could powerfully concentrate and strengthen the incident light intensity. The property that could harvest light for energy applications has been used in diverse areas. One promising application of LSPR is photocatalysis. The role of semiconductor with LSPR characteristics to enhance photocatalytic efficiency and their corresponding mechanism have been well reviewed in the literatures [1,2,17–20].

Several samples grown in diverse Cu^+/Cu^{2+} concentration conditions were synthesized and then examined by STEM-EDS. Fig. 2 is the plot of x values of $Cu_{2-x}S$ nanowires produced with various synthesis conditions, and it reveals that the x value increases with the Cu^{2+} concentration in the reaction solution. To avoid the deviation of diverse interaction volume at each nanowire, samples with similar diameters were chosen to be analyzed by STEM-EDS. Even though a slight difference exists at each reaction condition, an obvious trend still indicates that Cu vacancies are boosted with the increase in Cu^{2+} concentration. In the present study, five different sets of samples (Samples 1 to Samples 5) were prepared under varied growth conditions for the subsequent analysis and measurements. In Fig. 3, the structures of Cu_2S (monoclinic) in Sample 1, Cu_7S_4 (orthorhombic) in Sample 3 and CuS (orthorhombic) in Sample 5 can be seen. The structures were determined from the analysis of diffraction patterns, and the Cu-S ratios were obtained with EDS. The crystallinity of the structures was further analyzed with X-ray powder diffraction (XRD) patterns as shown in supporting information Fig. S1. The various distinct sets of diffraction peaks could be assigned to Cu_2S, $Cu_{1.8}S$, Cu_7S_4, and CuS, respectively. For Sample 2 and Sample 4, the Cu-S ratios were found to be between the three confirmed structures (Cu_2S, Cu_7S_4 and CuS), revealing the nonstoichiometric properties.

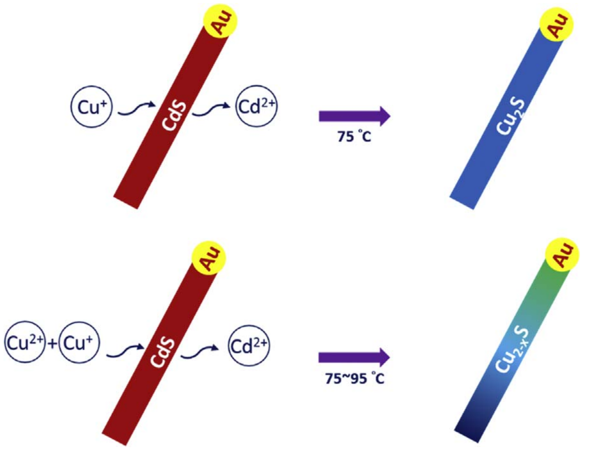

Fig. 1. Schematic representation for the processes to synthesize tunable nanowires from CdS nanowires via one-step cation exchange method.

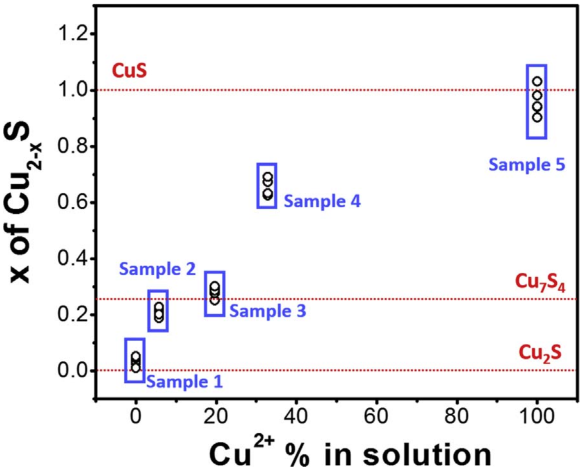

Fig. 2. The plot of x values of $Cu_{2-x}S$ nanowires produced with various synthesis conditions. Samples 1 to Sample 5 are treated as the targets for further investigations. The three red lines indicate the three confirmed structures in crystallographic database (Cu_2S, Cu_7S_4 and CuS).

From the structure information listed in Table 1, it can be seen that the fractional volume difference with respect to CdS range from 0.88% (CdS/Cu_2S) to −55.23% (CdS/CuS). The excess volume change caused porosity inside the CuS structure during the reaction processes. From the high magnification SEM and TEM images shown in Fig. 3, it can be seen that the roughness of nanowires increases with the Cu^{2+}% in the reaction solution, which indicates that the voids may be generated inside the nanowires structure. In addition, a decrease in the nanowire diameter caused by a necking phenomenon at the junction with Au catalyst due to the volume change was also observed (Supporting Information Fig. S2). On the other hand, the $Cu_{2-x}S$ nanowires preserved their single-crystal structures, as inferred from the analysis of diffraction patterns.

To elucidate whether the optical characteristics could be tuned with the Cu-S composites, VIS-NIR spectra obtained are shown in Fig. 4. The VIS-NIR spectra of the synthesized $Cu_{2-x}S$ nanowires show a broad blue shift from Sample 1 to Sample 5 around NIR region. In Fig. 4, Sample 1 shows inconspicuous peak. However, with the increase of copper vacancies, the peak shifted to shorter wavelength (from ~930 nm in Sample 2–740 nm in Sample 5) and its intensity increases simultaneously. The shift is attributed to the increase in density of copper vacancies, indicating the tunability of LSPR with different Cu-S compositions.

In the present work, The $Cu_{2-x}S$ nanowires with LSPR, have been used as catalysts towards the H_2 production from hydrolysis of AB. As