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Laser activating gold catalyst for liquid-phase growth of cadmium selenide nanowires

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A laser-activating-catalyst (LAC) technique was developed to grow CdSe nanowires in liquid medium at room temperature. The gold catalysts dispersed in the precursor solution were activated by a pulsed laser so as to decompose the precursor and catalyse the nanowire growth simultaneously. The LAC technique can achieve accurate positioning of nanowires, which is beneficial for device fabrications.

Semiconductor nanowires exhibit unique physical properties appropriate for optoelectronics, transistors, and sensors.¹ Therefore, various techniques have been developed for the growth of nanowires, such as template assisted growth, electric field assisted growth and laser assisted growth.² Among them, catalytic growth is known as a powerful strategy, where metal nanoparticles are employed as catalysts, and precursors are provided through either vapor or liquid phase.³ The catalytic growth in vapor phase usually follows the vapor-liquid-solid (VLS) mechanism⁴ or vapor-solid-solid (VSS) mechanism,³ while that in liquid phase follows a solution-liquid-solid (SLS) mechanism.⁵ The quality of catalytically grown nanowires is determined by the synthetic conditions. For instance, the product morphology depends strongly on the reaction temperature, i.e. nanowires prefer to grow at a relatively lower temperature, while higher temperature favors the fabrications of nanobelts and nanosheets.⁶ Moreover, the growth direction of nanowire relies on the substrate, catalyst, precursor, reaction temperature and pressure etc.,⁷ while the high temperature and/or high temperature facilitate the formation of single-crystalline nanowires, which exhibit excellent optical and electrical properties.^{6,8}

Recently, SLS growth has attracted extensive interests due to its intrinsic advantages, namely, much lower working temperature than that in vapor-phase growth, and easily tuneable product morphologies at the nanoscale.⁹ For example, uniform cadmium selenide (CdSe) nanowires, branched CdSe nanowires, and CdS/CdSe hetero-nanowires have been successfully obtained by SLS growth in liquid.⁹ However, SLS growth needs rigorous prerequisites, for instance, only some catalysts with low melting points (Bi, Sn and In) can be used for SLS growth because they can form eutectics with semiconductors at the limited attainable temperature (usually <350 °C).¹⁰ Moreover, the whole growing

process must be protected by inert gas or vacuum, which makes the synthetic systems very complicated.¹⁰

Pulsed laser ablation is a green, simple and efficient technique for material synthesis, and it has been widely used to synthesize nanostructures such as nanospheres, hollow nanoparticles and heterojunctions.¹¹ Moreover, laser was known for its capability on crystallizing nanomaterial and altering the wettability of substrate.¹² Though the pulsed laser was applied to generate gas precursors in VLS process,¹³ the laser-driven growth of nanowires in solution has never been reported. Considering that the pulsed laser can heat selectively the metal nanoparticles dispersed in liquid to melt, and endows them with high catalytic activity, we propose that pulsed laser irradiation can promote the SLS growth of nanowires in solution even at room temperature and also enable the uses of high-melting-point catalysts (Au, Pt, etc.). Such a laser-activating-catalyst (LAC) technique can break the bottleneck of catalyst oxidization and simplify the experimental setups. Besides, the discontinuous heating and quenching provided by the pulsed laser may create non-equilibrium conditions for the growth of metastable structures.

In the present work, we investigate the LAC synthesis of CdSe nanowires in liquid via pulsed laser irradiation of Au nanoparticles at room temperature. Hexagonal CdSe nanowires are successfully fabricated by adjusting laser energy density, precursor ratio and irradiation time. Our work demonstrates that LAC technique is a green and simple strategy for catalytic growth of nanowires in liquid, and the accurate positioning of laser beam facilitates patterning the growth area of nanowires on the substrate, which is beneficial for the further device fabrications.

The experimental setup is schematically shown in Figure 1. The LAC synthesis was conducted in a quartz beaker containing a face-up substrate with Au catalysts. The beaker was put in ice-bath and irradiated with a long-pulse-width (millisecond) laser for 5 min.

Figure 2 depicts the morphology and crystal structure of sample 1, whose synthetic parameters are given in Table S1. Scanning electron microscope (SEM) image illustrates many nanowires grown on the substrate with diameters of 55.1 ± 6.2 nm and lengths of 347 ± 30.4 nm (Figure 2a and Figure S1). Quantitative energy dispersion spectrum (EDS) analysis shows that Cd and Se are present in the nanowires with a nearly stoichiometric ratio (Cd 23.83 at%, Se 23.55 at%, and Cu 52.62

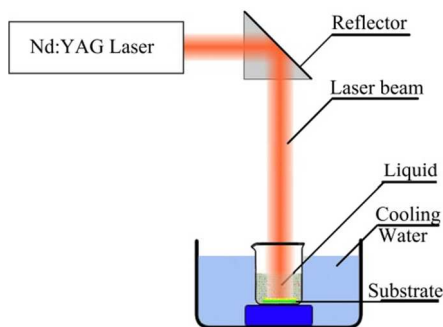


Figure 1. Experimental setup for LAC growth of CdSe nanowires.

at% is from the copper grid) (Figure 2b), indicating the formation of CdSe nanowires. We further made selective area electron diffraction (SAED) analysis on a nanowire with a catalyst particle (shown in Figure 2c). The SAED pattern from the nanowire region shows that the CdSe nanowire possesses a wurtzite structure with $[0\bar{1}11]$ growth direction (Figure 2e), different from $[0001]$, $[10\bar{1}0]$ or

$[11\bar{2}0]$ preferred directions observed in literatures.¹⁴ The quantitative EDS analysis on the catalyst gives an atomic ratio of 71.08:25.67:3.25 for Au: Cd: Se, indicating a composition of Au_3Cd . The SAED pattern from the catalyst suggests a cubic structure (Figure 2d). High resolution transmission electron microscope (HRTEM) image in Figure 2f reveals that the CdSe nanowire possesses a single crystalline structure, with its $(0\bar{1}11)$ planes (lattice spacing 0.32 nm) being parallel to Au_3Cd (202) planes (lattice spacing 0.38 nm). Elemental mapping images (shown in Figures 2h~2j) coincide with the EDS results, implying that the catalyst nanoparticle mainly comprises Au and Cd, with a small amount of Se, while the nanowire is made up of Cd and Se elements. Moreover, the nanowires show a weak absorption band in the wavelength range shorter than 700 nm (Figure S2).

To understand the LAC growth of the CdSe nanowires, we observed the samples obtained at different irradiation periods. In sample 3 by laser irradiation for 60 s, nanowires cannot be found on the substrate (see Figure S3a). Nevertheless, Au catalysts accommodate a lot of Cd and Se atoms according to the line-scan profile shown in Figure S3b. As the irradiation time increases to 180 s (sample 2), some CdSe nanorods grow up from catalysts with a length about 100 nm (Figure S3c). Up to 300 s irradiation (sample 1), tortuous nanowires with a length of about 300 nm are synthesized (Figure 1e). Particularly, the Cd and Se concentrations in Au catalyst decrease with the distance away from the CdSe/Au interface, this tendency is more obvious for sample 1 (see Figures S3d and S3f).

Se concentration in the solution also affects the product morphology. Figure S4 and Table S2 illustrate that, as the Se: Cd ratio increase from 1:2 (sample 4) to 1:1 (sample 1) and then 2:1 (sample 5) (see synthetic details in Table S1), both the Se concentration in catalyst and the nanowire length are enhanced simultaneously, indicating that Se element can promote the nanowire growth remarkably.

The laser intensity is another crucial parameter for the LAC growth of nanowires. As laser intensity increases to 0.4 Jmm^{-2} , the product in sample 6 turns out to be Au-CdSe core-shell structure instead of nanowires, as demonstrated by the elemental mapping images shown in Figure S5. When the laser intensity decreases to 0.05 Jmm^{-2} , the gold particles in sample 7 cannot induce the growth of nanowires (Figure S6).

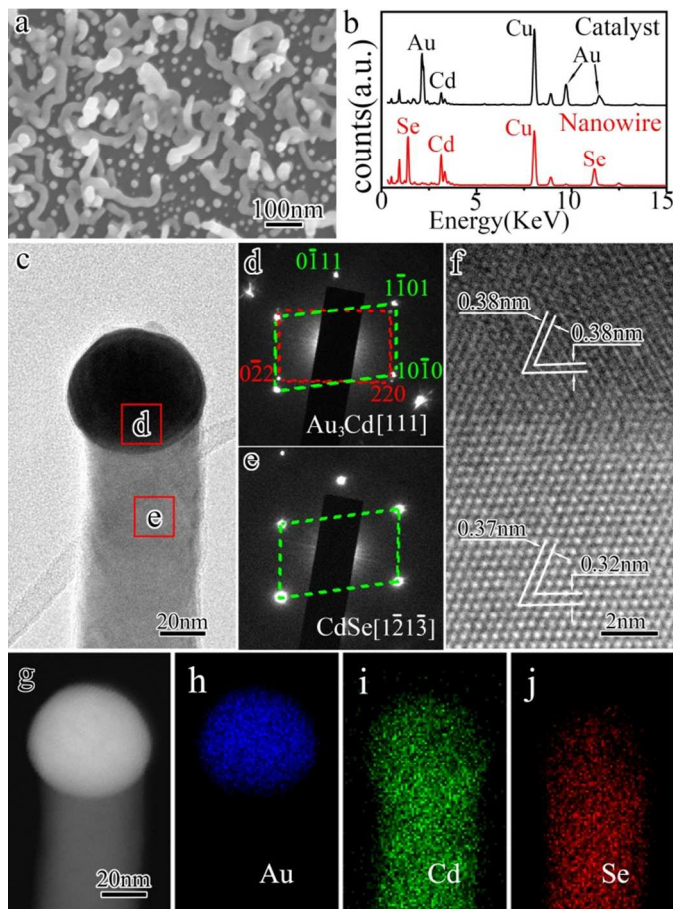


Figure 2. Characterizations of CdSe nanowires prepared under laser irradiation of 5 min with laser intensity of 0.2 Jmm^{-2} and a Se/Cd precursor ratio of 1:1. (a) SEM image, (b) EDS data of catalyst and nanowire, (c) TEM image of a single nanowire; (d) and (e) SAED patterns taken from the areas in (c), (f) HRTEM image at the interface of catalyst and nanowire, (g) STEM image of a single nanowire, (h)~(j) elemental mapping images of Au, Cd, and Se, respectively.

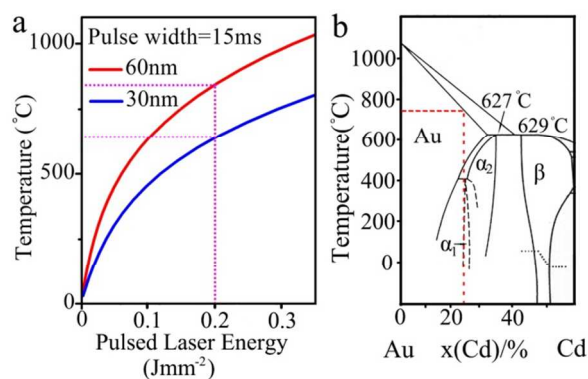


Figure 3. Temperature rise of catalyst under laser irradiation. (a) The theoretical calculation of temperature rise of Au nanoparticle at different laser intensities. (b) Au-Cd binary phase diagram.

We notice that the Au catalysts with larger sizes ($59.2 \pm 7.0 \text{ nm}$) can catalyse the growth of nanowires, while those smaller ones ($31.9 \pm 3.0 \text{ nm}$) cannot (see Figure 2a and Figure S7), then we employ a simple model to estimate the temperature rise of gold nanoparticles

by the pulsed laser irradiation (see the details in supporting calculation and Figure S8),¹⁵ and the results are shown in Figure 3a. At the laser intensity of 0.2 Jmm^{-2} , the 60-nm-sized nanoparticles can be heated to $850 \text{ }^\circ\text{C}$, while the 30-nm-sized ones only to $650 \text{ }^\circ\text{C}$. According to Au-Cd binary phase diagram (Figure 3b), the melting point for Au_3Cd is $730 \text{ }^\circ\text{C}$, thus the bigger Au_3Cd nanoparticles can be molten and work as an effective catalysts for growing nanowires, but the smaller ones are still in the solid state, which is unfavourable for seizing Cd and Se atoms and producing CdSe nanowires.

Based on the above, we propose a possible mechanism of nanowire growth in LAC process (Figure 4). First, Au nanoparticles absorb the energy from pulsed laser and are heated to a certain temperature ($850 \text{ }^\circ\text{C}$ for 60-nm-sized nanoparticle under 0.2 Jmm^{-2} laser irradiation), lower than its melting points ($1063 \text{ }^\circ\text{C}$). Meanwhile, Cd and Se precursors are decomposed by the hot Au nanoparticles, and the resulted Se and Cd atoms diffuse into Au nanoparticle, causing the alloying of nanoparticles. In the second stage, the Cd concentration in nanoparticles gradually increases while the melting point decreases with the number of laser pulses. At last, the nanoparticles transform into Au_3Cd , and can be molten at $730 \text{ }^\circ\text{C}$ under the same laser irradiation. As the third stage, the Au_3Cd nanodroplets serve as efficient catalysts to capture Cd and Se atoms during the laser irradiation and excrete CdSe compound after the laser pulse due to the rapid decrease of temperature and then dissolution in catalysts. The capture-release process repeats in the subsequent laser pulses, leading to the growth of CdSe nanowires.

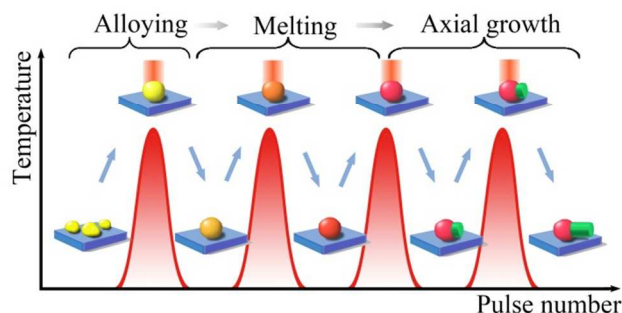


Figure 4. Proposed mechanism for the LAC growth of CdSe nanowires.

The influence of Se concentration and laser energy can be well understood according to the above mechanism. Since the Se solubility in Au_3Cd catalysts is lower than that of Cd, the supply of Se atoms is the control of the growth of nanowires, and the enhancement of Se/Cd ration in solution can improve the Se concentration in the Au catalyst then the growth rate of nanowires. On the other hand, the higher laser intensity (0.4 Jmm^{-2}) can drive the Au_3Cd catalysts to higher temperature and kept them melting for a longer time. Resultantly, the Au_3Cd nanodroplets absorb more Cd and Se atoms during one laser pulse, which precipitate so fiercely that a complete CdSe shell instead of separated particles forms on the surface of the catalyst, causing the formation of Au-CdSe core-shell structures. Similar phenomenon was found in previous study of SLS synthesis.¹⁶

The movement and output of laser beam can be manipulated precisely, thus it is easy to control the irradiating position and pattern the nanowire area on the substrate. The proposed patterning protocol is presented in Figure S9a. The silicon substrate with Au catalysts is placed in a container with the solution of precursors, and the container is driven by a motorized positioning system following a programmed path while being irradiated by the repetitive laser beam. The nanowires grow up in the exposed region after several rounds of laser irradiation, showing a dark pattern on the substrate (Figure

S9b). We believe that this patterning technology can be applied for fabricating micro-devices, since the synthesis and patterning can be accomplished simultaneously, and the process flow can be simplified to a large extent.

Based on the above, the LAC technique exhibits several unique features distinct from common SLS synthesis. First, metal nanoparticles play the dual roles of catalysts and heat source. Second, the nanowires grow up in an ambient-temperature solution. Third, the growth of nanowires is intermittent. Fourth, noble metal nanoparticles with high melting points can be utilized as catalyst, which does not need gas protection any more. Fifth, the growth area can be precisely defined by laser exposure. Therefore, the LAC technique demonstrates simple and facile merits, and show great potential for device application. However, the products usually contain a lot of defects due to the intermittent growth and fierce temperature undulation.

Conclusions

In summary, we have demonstrated a laser-activating-catalyst growth of CdSe nanowires in solution. The pulsed laser can heat Au nanoparticles to a molten state, which decomposes the precursors and capture Se and Cd atoms for the catalytic growth of nanowires. The irradiation time, precursor ratio and laser intensity are identified as the crucial factors determining the formation of nanowires. Our strategy possesses several advantages over the traditional solution techniques, namely, great variety of catalysts (expanded to noble metals with high melting points), simple experimental set-up (without any protective gas), and easy positioning and patterning (by controlling laser path). Thus this LAC technique shows promise for extending to a wide range of semiconductor systems, breaking the limit of traditional catalytic growth and integrating nanowires into devices.

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Electronic Supplementary Information (ESI) available: [experimental details, calculation on the temperature rise of metal catalysts, diameter and length histograms of as-grown CdSe nanowires, absorption spectra of as-grown nanowires, characterizations on the CdSe nanowires prepared with Se:Cd of 1:1 at different times, characterizations on the CdSe nanowires prepared at different Se:Cd ratios, characterizations of Au-CdSe core-shell nanostructure obtained under high-intensity laser irradiation for 5 min, TEM image of Au nanoparticles irradiated by low-intensity pulsed laser for 5 min, diameter distributions of Au nanoparticles with or without nanowires, absorption spectra of OA-Cd and TOP-Se precursors, patterned growth of CdSe nanowires on substrate]. See DOI: 10.1039/c000000x/

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