Direct Patterning of Metal Chalcogenide Semiconductor Materials

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Lithography is one of the most widely used methods for cutting-edge research and industrial applications, mainly owing to its ability to draw patterns in the micro and even nanoscale. However, the fabrication of semiconductor micro/nanostructures via conventional electron or optical lithography technologies often requires a time-consuming multistep process and the use of expensive facilities. Herein, a low-cost, high-resolution, facile, and versatile direct patterning method based on metal–organic molecular precursors is reported. The ink-based metal–organic precursors are found to operate as negative resists, with the material exposed by different methods (electron-beam/laser/heat/ultraviolet (UV)) to render them insoluble in the development process. This technical process can deliver metal chalcogenide semiconductors with arbitrary 2D/3D patterns with sub-50 nm resolution. Electron beam lithography, two-photon absorption lithography, thermal scanning probe lithography, and UV photolithography are demonstrated for the direct patterning process. Different metal chalcogenide semiconductor nanodevices, such as photoconductive selenium-doped Sb$_2$S$_3$ nanoribbons, p-type PbS single-nanowire field-effect transistors, and p-n junction CdS/Cu$_2$S nanowire solar cells, are fabricated by this method. This direct patterning technique is a versatile and simple micro/nanolithography technology with considerable potential for “lab-on-a-chip” preparation of semiconductor devices.

1. Introduction

The fabrication of microscale and nanoscale structures is vital for many applications, for example, microfluidics, display units, small electronics systems, and optoelectronic devices. Among the existing nanopatterning methods, electron beam and optical lithography have the advantages of high degree of automation, precisely controlled operation, and nanometer-sized resolution. For conventional lithography, an electron or photoresist and complex prototyping processes are required.[1] Upon electron beam/UV light exposure, the positive resist degrades and negative resist polymerizes in the designed patterns. The unexposed positive resist[2] (polymethylmethacrylate (PMMA), polyolefin sulfones, polyisocyanates, etc.) has a very low solubility in developer solution, while the exposed (degraded) part becomes soluble. Negative resists (poly(methyl vinyl ketone, poly(vinyl methyl ether), poly(vinyl alcohol), etc.) behave in the opposite manner, allowing to simply rinse off the unexposed photoresist, whereas the exposed and polymerized resists withstand the rinsing process.[3,4] After such a development step, the pattern of the resist on the substrate can be further used to transfer the pattern into the desired material, for example, by thin film deposition, oxidation, etching, or doping on the substrates through the pattern of the resist mask. In the last step, a liftoff is carried out to remove the remaining resist. The multistep consecutive processing of conventional lithography leads to a long fabrication time and is error-prone as a result of these multiple processing steps. Due to charge back scattering and the proximity effect, radiation resists always serve as the primary resolution limitation factor of electron beam lithography (EBL).[3,4] Ideally, one would prefer a resistless direct patterning method that overcomes the disadvantages of conventional lithography process. Direct patterning is an efficient method that directly transfers target materials to the substrates.[5–8] This method is featured as patterning methodology-based electron beam/UV-induced decomposition/cross-linking of metal–organic precursors. However, the current direct patterning technology is limited to the patterning of metallic,[5,6] ceramic,[7] and metal oxide[8–10] materials, which greatly limit its application. Here, we describe a novel and versatile strategy for micro- and nanopatterning of metal chalcogenide materials, which provides a direct fabrication path for 2D and 3D nanostructures with sub-50 nm resolution.

2. Patterning Process

2.1. Precursor Solution

The basis of this work is a metal-butyldithiocarbamic acid (BDCA)[11]-based molecular precursor solution that we adopted...
for direct patterning. BDCA is nontoxic, cheap, and thermally degradable and can be easily synthesized by the reaction of carbon disulfide and 1-butylamine. The ethanol solution of BDCA can be directly applied to dissolve various types of hydroxides and metal oxides, such as In(OH)₃, Cd(OH)₂, Mo(OH)₄, W(OH)₄, Bi(OH)₃, Cu₂O, PbO, ZnO, and Sb₂O₃. In our work, we also demonstrate that selenium doping in the chalcogenide semiconductors can be realized simply by adding SeO₂ in the precursor solution. The various chalcogenide precursor solutions adopted in our work are shown in Figure 1b. We have demonstrated this new fabrication method with a variety of metal–organic precursor solutions. Upon high-temperature annealing (300–500 °C), the thermal decomposition of metal–organic molecular precursors will generate chalcogenide materials, such as InS, CdS, MoS₂, WS₂, Bi₂S₃, Cu₃S, PbS, ZnS, and Sb₂S₃, depending on the metal–organic precursor components. Chalcogenide materials have been extensively studied in many applications, such as infrared window material[12] (ZnS), optoelectronic devices[13] (PbS, Sb₂S₃, InS), and low-dimensional layered transistors[14] (WS₂, MoS₂). Currently, the research of transition metal chalcogenides (e.g., TMDs, WS₂, MoS₂, and WTe₂) is a hot spot in semiconductor devices. TMDs are conventionally fabricated via chemical vapor deposition (CVD).[15] The high cost resulting from the clean environment and high temperature required for CVD largely limits the application of TMD-based devices. The direct patterning method reported in this article could avoid high-cost equipment and dramatically reduce the process steps, as would be required in traditional TMDs device integration.

2.2. Processing

In a previous study, the thermal decomposition mechanism of metal diethylthiocarbamate (Zn(DETC)₂) has been demonstrated.[16] Upon low-temperature annealing (80–100 °C),
a metal complex intermediate is formed due to a thermal decomposition process. This metal complex is then insoluble in organic solvents. However, electron, laser, and UV radiation may also induce chemical reaction (normally the polymerization of precursor molecules) during the direct patterning process.[8,17,18] The polymerized chemicals are featured as insoluble in the development solution as a result. In our study, we found that upon heat/electron beam/laser/UV irradiation, the BDCA acid-based metal–organic precursors undergo a similar chemical change, rendering them insoluble in various solutions (such as ethanol, acetone, isopropyl, etc.), which allows to use it for direct writing of nanostructures. We assume that in our process, the local heating and chemical reaction induced by the electron beam,[19] light,[20] and localized heat irradiation are the working mechanism of the direct patterning process.

Depending on the desired type of chalcogenide, the associated metal–organic precursor solution is deposited onto the substrates (step 1 of Figure 1a). Patterning of the precursor film is carried out by exposure electron beam, confocal laser, localized heat, or UV light (step 2 of Figure 1a). In case of EBL, the electron radiation doses used to expose the precursor films are 7200 mC cm$^{-2}$ for Sb$_2$S$_3$/Sb$_2$S$_3$$_x$Se$_{1-x}$, 3600 mC cm$^{-2}$ for ZnS/ZnS$_{1-x}$Se$_{x}$, and 4800 mC cm$^{-2}$ for PbS/PbS$_{1-x}$Se$_{x}$. The electron beam exposure causes the phase change of the metal–organic precursor, which can be clearly seen in dark-field microscopy (see Figure 1c). After electron beam exposure, the structures are developed by immersing the exposed sample for 1 h in isopropanol (step 3 of Figure 1a). In the developing process, the unexposed part of the precursor film is removed, leaving the exposed patterns on the substrate. The designed patterns are displayed after development in both bright- and dark-field microscopy images (see Figure 1d). The obtained nanostructures were subsequently annealed at 300, 550, and 400 °C in nitrogen atmosphere for Sb$_2$S$_3$/Sb$_2$S$_3$$_x$Se$_{1-x}$, ZnS/ZnS$_{1-x}$Se$_{x}$, and PbS/PbS$_{1-x}$Se$_{x}$, respectively, to decompose the metal–organic complex completely, remove residual solvents, and crystallize the material to form the respective chalcogenide materials. The chemical composition of the as-synthesised nanostructures is ascertained by energy-dispersive spectroscopy (EDS) (see Figure S1, Supporting Information).

### 2.3. Nanopatterns

High-resolution 2D nanometer scale patterns of various chalcogenide semiconductors have been prepared on silicon substrates by the EBL direct writing method (see Figure 2). In the scanning electron microscopy (SEM) images in Figure 2a,b, we show 2D arrays composed of uniform Sb$_2$S$_3$ nanoparticles of 120 and 50 nm width. In Figure 2c,d, we depict Sb$_2$S$_3$ nanowire (NW) arrays with widths of 80 and 35 nm. As can be seen, the method allows writing of arbitrary semiconductor patterns with controlled size and position. We expect that further parameter optimization will enable to deliver sub-10 nm resolutions. The Konstanz University logo composed of 50 nm diameter ZnS lines shown in Figure 2e yields high fidelity and contrast, indicating our direct patterning method’s capability of handling complex patterns.

As an effort to explore our direct patterning method’s potential application in 3D modeling, a microstructure consisting of many sets of gears was fabricated (see Figure 3a). This 3D structure was prepared in an additive multilayer manner, demonstrating the chalcogenide semiconductor precursors’ potential acting as ink-based materials for 3D stereolithography (SLA)[23] or selective laser sintering (SLS).[22] To our knowledge, the current SLA and SLS technologies can only produce polymer- and plastic-based 3D structures. By employing the additive manufacturing method, a 3D heterostructure composed of Sb$_2$S$_3$ and ZnS on the top of silicon substrate...
has been prepared (Figure 3b). Such 3D heterojunction structures are of great interest for microelectromechanical systems (MEMS)\cite{23} as well as “lab-on-a-chip” applications.

2.4. Conversion Mechanisms

We also adopted thermal scanning probe lithography (TSPL) (see Figure S2, Supporting Information), UV light lithography (UVL) (see Figure S3, Supporting Information), and two-photon absorption lithography (TPAL) (see Figure 3c,d) for the direct patterning of micro/nanostructures. TSPL\cite{24} is featured as patterning via highly localized heat at the tip-sample contact area. Under this direct local heating, we observed the same transformation of our precursor film forming the insoluble metal–organic complex. For EBL and UVL, we found that the success patterning does not depend on the acceleration voltage but on the dose of the radiation (for Sb$_2$S$_3$). Take Sb$_2$S$_3$, for example, the successful patterning of EBL required electron radiation dose of at least 7200 mC cm$^{-2}$, despite the acceleration voltage. For UVL, the minimum exposure time with 405 nm light source (25 mW cm$^{-2}$ intensity) is 2 h. For TSPL, on the other hand, the key parameter is the temperature of the cantilever (700 °C for Sb$_2$S$_3$). That is to say, the direct patterning by EBL and UVL is dose dependent while TSPL is intensity dependent. These facts lead to the indication that for EBL and UVL direct patterning, the working mechanism is radiation-induced chemical reaction. Such conclusion is also supported by the fourier transform infrared (FTIR) absorption spectrums analysis (see Figure 3e) of the metal–organic precursor film before and after UV/heat treatment. As it depicts in Figure 3e, intense peaks corresponding to BDCA acid were clearly visible.\cite{25} It is important to notice that no new vibration mode was detected after thermal annealing and UV radiation, indicating that no new chemicals formed during the annealing/radiation process. This fact is in agreement with previous report.\cite{26} After 140 °C annealing and UV radiation, the IR peaks related to BDCA acid diminished strongly. This phenomenon can be attribute to the decomposition of the precursor film.\cite{26} Under thermal annealing, metal BDCA acid decomposes to form metal chalcogenides (MS$_x$). The thermal-induced decomposition mechanism is given in reaction equation\cite{25}

$$\text{M(S,CNHC,H$_4$)$_x$} \rightarrow \text{MS}_x + x \text{(S$_2$CNHC,H$_4$)} \quad (1)$$

Based on above information, we can see that both the chemicals and decomposition processes involved in the direct patterning are very simple, which is a huge advantage over the conventional complex organic-compound-based direct patterning process. The photolytic decomposition of BDCA acid is reported here for the first time. According to the FTIR spectrums, the UV radiation-induced decomposition is very similar with thermal annealing. In addition, it is fascinating to find that, compared with thermal annealing, UV radiation rendered more thorough decomposition of the precursor film. After a final 300 °C annealing of the UV-radiated sample, no IR peak can be detected in the resulting product, indicating the final product is free of BDCA acid.\cite{27} For EBL, we envision the working mechanism is electron beam induced decomposition of BDCA acid.

Figure 3. 3D semiconductor nanostructures generated by a,b) EBL and c,d) TPAL. a) Sb$_2$S$_3$ 3D structure composed of three layers. b) 3D heterostructure composed of Sb$_2$S$_3$ and ZnS. c) Monolayer 3D honeycomb structure composed of Sb$_2$S$_3$. d) Double-layer 3D honeycomb structure composed of Sb$_2$S$_3$ written with TPAL (Nanoscribe 3D laser microprinting). e) FTIR spectra of Cu$_2$S precursor film (black), baked at 140 °C (red), 405 nm UV irradiated for 2 h (blue), and post-annealed at 300 °C (yellow). f) Transmittance spectrums of the precursor solutions of Sb$_2$S$_3$ and Cu$_2$S.
For TSPL, on the other hand, photoabsorption-induced decomposition and heating may trigger the chemical transformation of BDCA acid. TPAL is a direct 3D lithography that has great potential for constructing arbitrarily shaped 3D devices in a single-step process.[28] By tightly focusing a near-IR laser beam into the photoresist, subsequent multiphoton absorption (normally two-photon absorption)-induced polymerization occurs only in the vicinity of the focal point, allowing the fabrication of a 3D structure. However, the current TPAL is only limited to patterning with photopolymers,[29] metals,[6,30] and metal oxides,[31] which are insufficient for many practical applications in areas such as photonics, electronic, and MEMS devices. As it depicts in Figure 3c, monolayer honeycomb-shaped 3D photonic structure was fabricated with TPAL based on the precursor solution of Sb₂S₃. By simply writing a second monolayer honeycomb structure above the first one, a double-layered honeycomb structure (Figure 3d) can be formed just in one lithography process (see Video S1, Supporting Information). Additive 3D direct patterning of metal chalcogenide-based functional structure is realized for the first time. Figure 3e shows the transmittance spectrums of the Sb₂S₃ and Cu₂S precursor solutions (metal-BDCA acid). For TPAL, the wavelength of the laser is 780 nm. According to the transmittance spectrums, the precursor solutions exhibit no absorbance at 780 nm, that is, transparent at one-photon condition. However, the precursor solutions show strong absorbance at 390 nm (two-photon absorption). These phenomenon forms the base of the TPAL direct writing. The multiphoton absorption-induced chemical reaction or thermal effects are both possible for the working mechanism of TPAL direct patterning. In our experiment, we found that with very slow scan speed (1 µm s⁻¹), the direct patterning process is very efficient. However, the disadvantage of the slow scan speed is the boiling of precursor solution, that is, bubbles were formed from the focus point of the laser beam, which significantly reduced the resolution of the resulting product. We believe the bubbles were formed as a result of overheated precursor solution.

Besides EBL, TPAL TSPL, and UVL, we expect other advanced lithography technologies, such as X-ray,[32] and laser-interference lithography,[33] can be adopted for the direct patterning of chalcogenide materials based on the BDCA acid metal–organic precursors to fabricate 2D and 3D micro- and nanostructures.[32–34]

3. Applications

Finally, we demonstrate the potential of the method exemplarily for different applications. A Se-doped Sb₂S₃ single nanoribbon photodetector was fabricated by EBL direct patterning. The top inset of Figure 4a is a schematic diagram of the device configuration for the photocurrent measurement. The SEM

![Image](https://www.afm-journal.de/)

**Figure 4.** Device current–voltage characteristics. a) I–V curves of individual Sb₂S₃–Se nanoribbon with 5 µm width in the dark and under various illumination intensity (450 nm continuous-wave laser light). b) Back gate-dependent I–V curves of single PbS NW with 200 nm width. c) I–V curves of CdS/Cu₂S heterojunction NW in dark and under 1 sun (AM 1.5G) illumination.
image of the device is shown in the bottom inset of Figure 4a. The Sb$_2$S$_3$ nanoribbon was created above the parallel Au electrodes on a SiO$_2$/Si commercial substrate (for more details, see Experimental Section). The diameter of the nanoribbon and the channel length are 5 and 2.5 µm, respectively. In Figure 4a, we plot the I–V curves of a single Se-doped Sb$_2$S$_3$ nanoribbon measured under dark condition and under 450 nm light illumination with varying intensity.

In the dark, the Se-doped Sb$_2$S$_3$ nanoribbon is highly insulating with resistivity of around 2.7 × 10$^9$ Ωm. The current across the nanoribbon dramatically increases under laser illumination. For semiconductor materials, photo-generated carriers significantly increase the conductivity when illuminated by photons with energies overcoming the band gap. The conductivity increases linearly with illumination intensity. This indicates that the as-synthesised Se-doped Sb$_2$S$_3$ nanoribbon is a promising candidate for high-sensitivity nanophotodetectors as well as nanophotonic switches.\cite{15} As these nanodevices can be implemented on the desired position on a chip, they allow simple fabrication of arrays of such devices for advanced detector functionalities.

EBL direct patterning was used to fabricate NW field-effect transistors. As shown in the bottom inset of Figure 4b, a single 200 nm wide PbS NW was deposited on the same substrate as described in the previous paragraph. The schematic diagram of the device configuration for the field-effect measurement is given in the top inset of Figure 4b. The Au contacts function as source and drain electrodes and the silicon substrate serves as the back gate. As depicted in Figure 4b, the PbS NW shows a typical ohmic current–voltage characteristic. A positive gate voltage $V_g$ leads to a decrease in conductivity while a negative $V_g$ enhances the conductivity, implying the synthesised PbS NW being p-type.\cite{36} The hole concentration, $p$, is estimated to be 2.8 × 10$^{19}$ cm$^{-3}$ and the hole mobility $\mu_p$ to be 1.8 cm$^2$ V$^{-1}$ s$^{-1}$.

As an effort to explore the potential application of our direct patterning method in photovoltaic devices, a hetero-p-n junction composed of CdS and Cu$_2$S NWs has been fabricated by the additive manufacturing method. This NW p-n junction is 95 µm long and 5 µm in width. Typical I–V properties of the CdS/Cu$_2$S NW junction in the dark and under 1 sun (AM 1.5G) were measured (Figure 3c). In dark, the junction is insulating due to the high resistivity of CdS. Under 1 sun illumination, the NW junction exhibited typical photodiode characteristics,\cite{37} yielding a short-circuit current $I_{SC}$ of 0.31 nA and an open-circuit voltage $V_{OC}$ of 0.36 V.

These are different examples that show the versatility of such simple and controlled fabrication method for different device applications. Our novel preparation method allows transferring the high functionality of different chalcogenide materials and applications directly to nanoscale devices. As we nano-meter control over their position, arrays and special arrangements of different device types can be implemented for further advancement of functionality.

4. Conclusion

In summary, direct patterning of metal chalcogenide nanostructures via various conventional/unconventional lithography technologies (EBL/TPAL/TSPL/UVL) based on metal–organic precursor solutions has been realized for the first time. Such direct patterning process could apply to a wide range of metal chalcogenide systems. We expect other advanced lithography technologies, such as X-ray\cite{32} and laser-interference lithography,\cite{33} can be adopted for the direct patterning of chalcogenide materials based on the BDCA acid metal–organic precursors to fabricate 2D and 3D micro- and nanostructures.\cite{32–34} This technology offers significant advantages over traditional micro- and nanopatterning methods in terms of resolution, flexibility, and convenience. We showed that both heat transfer and photochemical reaction are decisive for the direct patterning process. Additive 3D direct patterning of non-photoresist-based functional structure by TPAL is realized for the first time. The demonstration of direct patterning via UVL indicates the application in wafer-scale circuit integration. The described approach is well-suited for fabrication of 2D and 3D heterostructures of various functional materials for micro- nanomechanic and optoelectronic applications, which makes it very interesting for lab-on-a-chip fabrication. We envision, for example, a semiconductor circuit, which deploys NW transistor circuits powered by NW solar cells on the same chip.

5. Experimental Section

Materials: Antimony(III) oxide (Sb$_2$O$_3$, 99.99%), zinc oxide (ZnO, 99.99%), cadmium oxide (CdO, 99.99%), copper(I) oxide (Cu$_2$O, 99.99%), lead(II) oxide (PbO, 99.99%), carbon disulfide (CS$_2$, 99.9%), ethanol (99.99%), and 1-butylamine (99%) were obtained from Sigma-Aldrich. All chemicals were used without further purification. The substrates used for the I–V measurements were OFET Gen.4 chips purchased from Fraunhofer Institut für Photonische Mikrosysteme. These substrates feature contacts of 30 nm Au on 10 nm indium tin oxide, which are deposited on 230 nm SiO$_2$/n-doped silicon wafers.

Preparation of Metal–Organic Precursor Solution: The precursor solutions were prepared according to reported protocols.\cite{31} A total of 1.0 mmol of metal oxide, 2.0 mL of ethanol, and 1.5 mL of CS$_2$ were added into a 50 mL three-neck vial with magnetic stirring at room temperature. A total of 2 mL 1-butylamine was slowly injected into the vial and the complex was continuously stirred for 12 h, resulting in a homogeneous solution. For EBL and TSPL patterning, 1 mL of the above solution was diluted with 2 mL ethanol. For TPAL, the as-synthesised solution was used.

Electron Beam Lithography: For EBL, an ELPHY Plus electron-beam system operated at 30 kV acceleration voltage and 8 nA beam current was utilized. The precursor solutions were spin-cast onto various substrates. The thickness of the precursor films can be tuned by the spin-coating speed and the concentration of the precursor solutions. In our study, 100 nm thick precursor films were obtained by spin-casting the diluted solution mentioned above at a speed of 8000 rpm for 30 s. The high spin-coating speed ensures homogeneous coverage and the formation of a pinhole-free precursor film. The samples covered with precursor were directly subjected to EBL.

Two-Photon Absorption Lithography: For TPAL, a 3D laser microprinting (Nanoscribe GmbH, Photonics Professional GT) was adopted. The precursor solution was solidified by multiphoton absorption using a confocal laser with center wavelength of 780 nm and 90 fs pulse length with 50 mW average power. A 63× objective lens (numerical aperture NA = 1.4, Carl Zeiss) was dipped directly into the precursor solution. Working volume of 150 µm × 150 µm × z was scanned using galvanic mirrors with 25 µm s$^{-1}$ scan speed. Each layer was stitched together using a piezo stage with 5 µm slicing distance. The 3D honeycomb models were created with commercial software Autodesk Fusion 360 and compiled into machine code using software Describe from Nanoscribe GmbH.
Thermal Scanning Probe Lithography: For TSPL, a commercial NanoFrazor TSPL tool (SwissLitho AG) was used. The precursor solutions were spin-casted onto various substrates. In our study, 100 nm thick precursor films were obtained by spin-casting the diluted solution mentioned above at a speed of 8000 rpm for 30 s. In this work, the thermal cantilever was set to a scan speed of 300 µm s⁻¹, temperature of 700 °C, and dwelling time of 30 µs per pixel.

UV Light Lithography: For UV light, a commercial mask aligner (SÜSS MicroTec, MJB 4) was adopted. The Cu₂S precursor solutions were spin-coated on FTO substrate at 6000 rpm for 40 s. Samples were exposed to UV light irradiation (405 nm with 25 mW cm⁻² intensity) for 2 h in air. The photomask was fabricated with chromium-covered soda-lime glass (Compugraphics Jana GmbH).

Material and Device Characterization: Optical images were taken on a Zeiss Axio Imager microscope equipped with EC Epiplan Neofluar objective lenses. SEM images were obtained with a Zeiss CrossBeam 1540XB electron-beam system. SEM EDS characterization was performed with an Oxford X-Max system. I–V characterization was performed with a Keithley 2600 dual-channel source-measure unit. Attenuated total reflection (ATR)/FTIR spectra were recorded with a PerkinElmer Spectrum 100 spectrometer equipped with a diamond crystal-based ATR accessory.

Gate-Dependent Measurements: The mobility of single-NW field-effect transistor was estimated from the following equation[28]

\[
\frac{dl}{dV_g} = \frac{\mu CV}{L^2}
\]

(2)

where \(l\) is the source-drain current, \(V_g\) is the gate voltage, \(\mu\) is the carrier mobility, \(C\) is the capacitance, and \(L\) is the length of the NW. The capacitance is given by

\[
C = \frac{2\pi\epsilon_0\epsilon h}{\ln(2h/r)}
\]

(3)

where \(\epsilon\) is the dielectric constant, \(h\) is the thickness of the silicon oxide layer, and \(r\) is the radius of the NW.

The carrier concentration was calculated as[28]

\[
n_{th} = \frac{C \times V_{th}}{\epsilon r^2 L}
\]

(4)

where \(V_{th}\) is the threshold gate voltage required to completely deplete the NW.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors have a patent application pending for this preparation method of semiconductor nanostructures (EP 19187135.9).

Author Contributions
L.S.M. and W.W. conceived the idea. W.W. designed the experiment and synthesized the material. W.W. and P.P. performed the EBL process. W.W. performed the TPAL process. W.W. wrote the manuscript and all authors contributed to the writing of the manuscript. L.S.M. supervised the study.

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