Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2015

Supporting Information

Laser-driven ab/desorption of catalysts for producing nanowire arrays in solution

Xue-Min Chen,^a Jing Mao,^a Yu-Zhu Zhou,^a Jing Yang,^a Xi-Wen Du*a and Shi-Zhang Qiao*^b

a School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

b School of Chemical Engineering, the University of Adelaide, SA 5005, Australia

*Email: [xwdu@tju.edu.cn](file:///C:/Users/a1618287/AppData/Local/Microsoft/Windows/Temporary%20Internet%20Files/Content.IE5/UQ1K021O/xwdu@tju.edu.cn) (Xi-Wen. Du); s.qiao@adelaide.edu.au. (Shi-Zhang Qiao)

1. Materials

All chemicals are commercially available and used without further purification. Cadmium powder (Cd, 99%), tellurium powder (Te, 99%), oleic acid (OA, 99%) and tri-noctylphosphine (TOP, 97% in purity) were purchased from Aladdin. Ethanedithiol (EDT, 90%) and acetonitrile (99.8%) were obtained from Tianjin Jiangtian Chemicals. Si (100) wafer (phosphorus-doped) was purchased from Tianjin Institute of Semiconductors.

2. Syntheses of CdTe nanowires

2.1 Substrate Preparation and Au NPs Deposition. A 2-cm² Si (100) substrate was ultrasonically cleaned by acetone, ethanol and deionized water in sequence, and then dried by nitrogen gas. Au film was deposited on the substrate by magnetron sputtering for 25 s at an electrical current of 20 mA. Afterward, the substrate with the Au film was heated to 450 ℃ and kept the temperature for 30 min so as to obtain Au NPs.

2.2 Preparation of Precursors. 11.2 mg Cd powder was dispersed in 20 mL TOP and ultrasonically stirred for 20 min to obtain a TOP suspension of Cd powder (Cd-TOP). 12.8 mg Te powder was added into 20 mL OA, heated to 180 ℃, kept the temperature for 1 hr with magnetic stirring, and then cooled down to room temperature naturally to form an OA solution of tellurium (OA-Te).

2.3 Laser Synthesis of CdTe NWs. In a typical synthetic process, the silicon substrate with Au NPs was first immersed in 2 mL Cd-TOP suspension, and then irradiated with a Nd:YAG pulsed laser. The laser wavelength, pulse width, current, frequency and irradiation time were set as 1064 nm, 15 ms, 110 A, 1 HZ and 5 min, respectively. Afterwards, the substrate was transferred to 2 mL OA-Te solution, and irradiated with the same laser for 3 min.

2.4 Assembling of photodetector. The as-obtained CdTe nanowires on the silicon substrate were rinsed with 1% acetonitrile solution of EDT and then ethanol for several times. Afterwards, a thin Au film of 50 nm was deposited on the top of CdTe nanowires by magnetron sputtering through a shadow mask of cross-finger electrode, and then, a simple device was fabricated for the photoresponse measurement. The transient photocurrents were measured by a Keithley 2611 digital multimeter both in the dark and under AM 1.5G white light irradiation.

3. Characterization

The morphology and structure were determined by SEM (Hitachi S-4800) and TEM (JEOL-2100F). EDS and EELS spectra were acquired by the EDS and EELS units, respectively, attached to TEM. Absorption spectra were recorded on a Hitachi U-4100 spectrometer. The phase structures were investigated by using a Bruker D8 advance XRD. XPS analyses were performed in a PHI Quantum 2000 scanning ESCA microprobe spectrometer. Size distribution of nanoparticles was determined by dynamic light scattering with Malvern Zetasizer Nano ZS90 at 25 ℃. The performance of the photodetector was measured with an AM 1.5 G white light irradiation generated by a simulated sunlight illumination system (100 mW/cm² , Sciencetech, SS150).

4. Calculation on the temperature rise of catalysts

The light absorption of incident laser by the metal particles was directly measured by using a power meter. The energy for temperature rise was calculated by subtracting heat loss from the absorbed energy. Temperature rise was determined by dividing the energy for temperature rise by the specific heat of metallic nanoparticles. Since the solution does not absorb any laser light at 1064 nm wavelength, the energy loss is mainly due to the absorption of metallic nanoparticles (see Figure S6). The absorbed laser energy by the metallic particles per unit mass and per laser pulse, Q (J g^{-1} pulse⁻¹), is calculated by

$$
Q = E/fcV \tag{1}
$$

where E is the laser energy absorbed by the metallic particle per unit time (J s^{-1}) measured by the power meter, f the frequency of the pulsed laser (1 Hz), c the mass concentration of gold (g m⁻³), and V the irradiated volume of the solution (m³).

The nanoparticles dispersed in a solvent lose heat via two ways:

convection heat transfer

$$
\Delta Q_1 = \mathbf{h}(T - T_0)S(d_0)\tau \tag{2}
$$

radiation heat transfer

$$
\Delta Q_2 = \varepsilon \delta T^4 S(d_0) \tau \tag{3}
$$

Herein,*h* is the convection heat transfer coefficient (50< *h*<1000 in solution), *T0=302 K* (room temperature), the surface area of nanoparticle *S(d0)=πd⁰ 2* , τ is the pulse width of the laser, ε is the emissivity of nanoparticle (emissivity, 0<ε<1), δ is the Stefan-Boltzmann constant (5.67 \times 10⁻⁸ W m⁻² K⁻⁴)。

The energy for temperature rise can be calculated by

$$
\Delta Q = c_p \left(T - T_0 \right) = Q - N \Delta Q_1 - N \Delta Q_2 \qquad (T \le T_m)
$$
 (4)

$$
\Delta Q = c_p \left(T - T_0 \right) = Q - \Delta H_m - N \Delta Q_1 - N \Delta Q_2 \quad (T_m < T \le T_0)
$$
\n
$$
(5)
$$

and the final temperature is determined as

$$
T = (Q - N\Delta Q_1 - N\Delta Q_2) / C_p + T_0 \qquad (T \le T_m)
$$
 (6)

$$
T = (Q - \Delta H_m - N\Delta Q_1 - N\Delta Q_2) / C_p + T_0 \qquad (T_m < T \le T_b)
$$
 (7)

Cp is the specific heat of metallic nanoparticles, $N = \frac{1}{\rho V(d_0)}$ the number of $V(d_{\alpha})$ *N* $\rho_{V}(a_0)$ $=\frac{1}{\sqrt{1-\lambda}}$ the number of

nanoparticles in 1 g metal, ρ the density of metal, ΔH _{*m*} the fusion enthalpy.

Table S1. Quantitative EDS results of AuCd_x alloy nanoparticles.

Table S2. Quantitative XPS results of AuCd_x alloy nanoparticles.

Table S3. FWHM values of Cd 3d bands of AuCd_x alloys in XPS.

Table S4. Quantitative TEM-based EDS results corresponding to the profiles shown in

Table S5. Experimental parameters for preparing CdTe nanowires shown in the figures of main text.

Figure 4d, respectively.

Figure S1 Representative TEM, HRTEM images and selected area diffraction (SAED) patterns of intermediate products at different irradiation times in the absorption step. (a) (b) (c) are TEM, HRTEM images and SAED pattern, respectively, of the product obtained at 0 min, (d), (e),(f) are TEM, HRTEM images and SAED pattern, respectively, of the product obtained at 3 min, (g), (h),(i) are TEM, HRTEM images and SAED pattern, respectively, of the product obtained at 5 min.

Figure S2. Representative low-resolution SEM image of CdTe NWs prepared by LDAD

method with laser energy intensity of 0.3 J/mm²

Figure S3 (a) High magnification, and (b) corresponding side-view SEM images of NWAs.

Figure S4 SEM image and size distribution of Large AuCd₉ NPs used for desorption

experiment.

Figure S5 Representative TEM images of nanowires obtained under the same laser irradiation (energy density 0.3 J/mm², irradiation time 5 min) but with different precursors, (a) the nanowire obtained by irradiating large $AuCd₉$ NPs in OA solution of tellurium, (b) the nanowire obtained by irradiating gold NPs in the mixture OA solution of tellurium and TOP suspension of Cd powder.

Figure S6 The absorption spectra of Au catalysts and Cd powder in TOP.

Figure S7 The calculation on temperature rise of Au NP (50 nm) and Cd NP (120 nm) at different laser intensities. At the laser intensity of 0.3 J/mm², the 50-nm-sized Au nanoparticles can be heated to 990 °C, and 120-nm-sized Cd nanoparticles can be heated to nearly 750 °C.

Figure S8 Au-Cd binary phase diagram

Figure S9 Typical I-V curves of CdTe NWAs measured in the dark and under white light illumination. The lower inset is the photocurrent response throughout two onoff cycles of light illumination at a constant bias of -1.0 V.