Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supporting Information

Microwave activated gold nanoparticles for catalytic growth of monocrsytal CdSe nanowires in solution

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Contents

Experimental Section

Reagents. cadmium powder (Cd, 99%), selenium powder (Se, 99%) and oleic acid (OA, 90%) were purchased from Aladdin.

Preparation of Au catalyst. FTO substrates with an area of 2×2 cm^2 were ultrasonically cleaned in deionized water and ethanol, subsequently, Au nsnoparticles was deposited on FTO substrates by magnetron sputtering with a sputtering current of 20 mA for 25 s.

Preparation of precursors. 89.9 mg Cd powder and 80 mL OA were added into a 100 mL reagent bottle and then heated in an oil bath at 200 ℃ with magnetic stirring for 1 hr. 63.0 mg Se powder and 80 mL OA were added into a 100 mL regent bottle and then heated in an oil bath at 200 ℃ with magnetic stirring for 1 hour. Then the two solutions of precursor were cooled naturally down to room temperature.

Synthesis of CdSe NWs. The FTO substrate with Au NPs was immersed in 5 mL OA suspension of Cd powder and 5 mL OA suspension of Se powder, and the reactor was radiated by microwave at 2.45 GHz with maximum power of 300 W. The temperature inside the reactor was monitored in real time. After reaction, the sample on FTO substrate was taken out from the microwave reactor and washed with acetone and ethanol. For comparison, nanowires were also synthesized using SLS mechanism carried out with laser-activating-catalyst technique[1], where the same precursors was irradiated with a Nd:YAG pulsed laser. The laser wavelength, pulse width, current frequency and irradiation time were 1064 nm, 15 ms, 110 A, 1 HZ and 5 min, respectively.

Characterization: The morphology and structure were determined by SEM (Hitachi S-4800) and TEM (JEOL-2100F), the latter instrument is equipped with a field emission gun, EDS and EELS units. The products on the substrate were directly observed by SEM, while for TEM characterization, the nanowires were scraped from substrate, dispersed in ethanol, and the dipped onto a cooper grid with carbon film. The phase structures were investigated by XRD (D8 advance). Absorption spectra were recorded with a Hitachi U-4100 UV-Vis near-infrared spectrophotometer.

Sample Preparation for Photocatalysis Experiments: The sample was

prepared by adding CdSe–Pt nanorods/nanonet (1.6 mL) with typical optical density (OD) of 0.55 at wavelength 473 nm (the wavelength of the irradiating laser), with pH set to 7,

ethanol (0.4 mL), and a stir bar
to an air-tight cuvette. The sample was then bubbled with dry nitrogen
gas for 2 min. All of the experiments were carried out in a dark room

under vigorous stirring. MB solution was prepared by dissolving MB powder in TDW to receive a blue solution with OD of 1.5 at 667 nm, the main absorption peak of MB. To measure

the concentration of Pt dots solution, an extinction coefficient of 1000 M □1 cm □1 at 473 nm per Pt

atom was used [38]. Statistical measurements on the CdSe–Pt isolated rods show that the average number of Pt dots per rod was ca. 40, thus by assumption that only hemispheres of Pt

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Photocatalytic Experiments: The photocatalytic activities were evaluated by degradation of methyl blue (MB) at room temperature. In each experiment, samples were put into 8 mL MB solution (20 mg L^{-1}) and then irradiated with a 500 W Xe-lamp (200 nm < λ < 700 nm). At a given time interval, the residual concentration of MB was tested by UV-Vis spectrophotometer.

Supporting Calculation

Calculation on temperature rise. The precursor solution does not absorb microwave due to low dielectric property of OA solvent, the microwave energy was mainly absorped by metal nanoparticles and conductive FTO substrates. The temperature rise is then calculated by

$$P \cdot t \cdot C_{abs} = c(T - 423\ K) \quad (1)$$

where P is the microwave energy absorbed by the gold particle at 300 W, t is the time for temperature rising to goal temperature (423 K), c is the specific heat of Au (0.131 J g^{-1} K^{-1}). C_{abs} is per particle absorption cross-section at 12.2 cm (microwave wavelength) which could be modelled by the Mie's theory. When gold nanoparticles size is less than mean free path of electrons (42 nm), such as 10 nm, the size effect should be considered for determining its dielectric constant:

$$\varepsilon(\omega,R) = \varepsilon_1(\omega,R) + i \cdot \varepsilon_2(\omega,R) = \varepsilon^{bulk}(\omega) - \varepsilon_D^{bulk}(\omega) + \varepsilon_D(\omega,R) \quad (2)$$

$$\begin{cases} \varepsilon^{bulk}(\omega) = \left[n(\omega)^2 - \kappa(\omega)^2\right] + i \cdot 2n(\omega)\kappa(\omega) \\ \varepsilon_D^{bulk}(\omega) = 1 - \dfrac{\omega_p^2}{\omega^2 + i\omega/\tau}, \qquad \omega_p^2 = \dfrac{n_e e^2}{\varepsilon_0 m_e^*} \\ \varepsilon_D(\omega,R) = 1 - \dfrac{\omega_p^2}{\omega^2 + i\omega/\tau(R)}, \qquad \tau(R)^{-1} = v_F\left(\dfrac{1}{l} + \dfrac{1}{R}\right) \end{cases}$$

Among them, for gold, the first two items are equal in equation (2). According to experimental study of Raschke et al.[2], $\hbar\omega_p$=8.5 eV, l/v_F= 14 fs.

So, the complex dielectric constant of gold nanoparticles is calculated by

$$n = \frac{1}{\sqrt{2}}\sqrt{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1} \qquad \kappa = \frac{1}{\sqrt{2}}\sqrt{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1} \tag{3}$$

References

1. C. Huang, J. Mao, X. Chen, J. Yang and X. Du, *Chem. Commun.*, 2015, **51**, 2145.
2. R. L. Olmon, B. Slovick, T. W. Johnson, D. Shelton, S.-H. Oh, G. D. Boreman and M. B. Raschke, *Phys. Rev. B*, 2012, **86**, 235147.

Supporting Figures

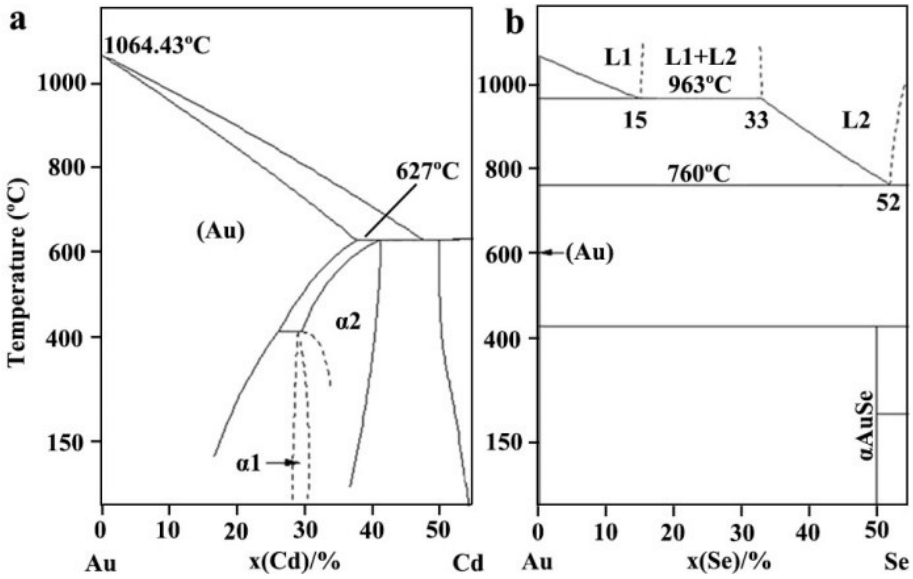

Fig. S1 (a) Au-Cd and (b) Au-Se binary phase diagrams.

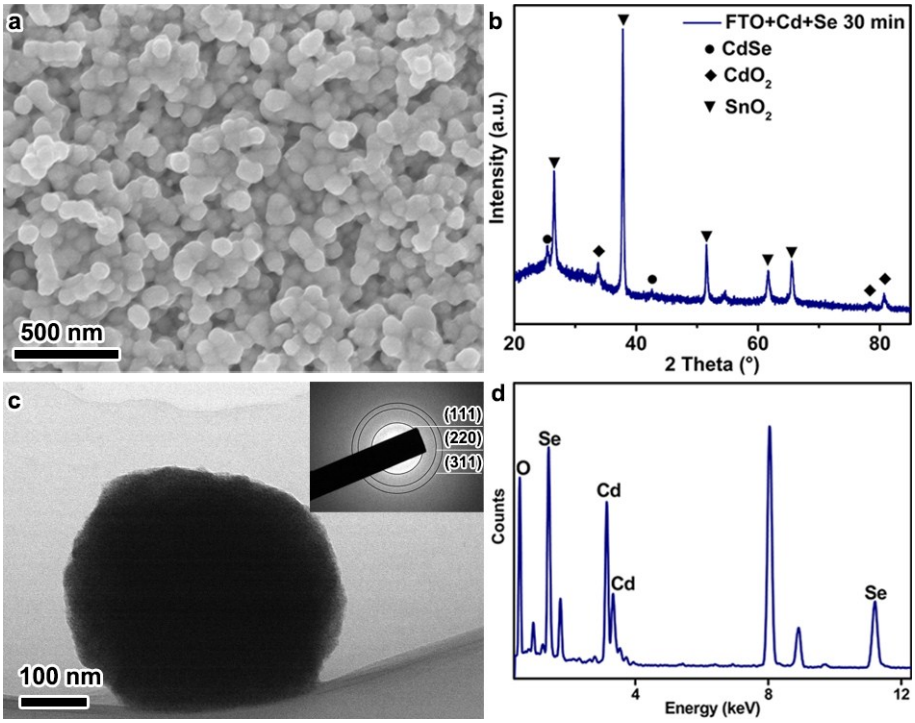

Fig. S2 Characterizations of products prepared by using bare FTO glass without gold catalysts. (a) SEM image, (b) XRD profile, (c) TEM image, the inset is SAED pattern, (d) EDS profile.

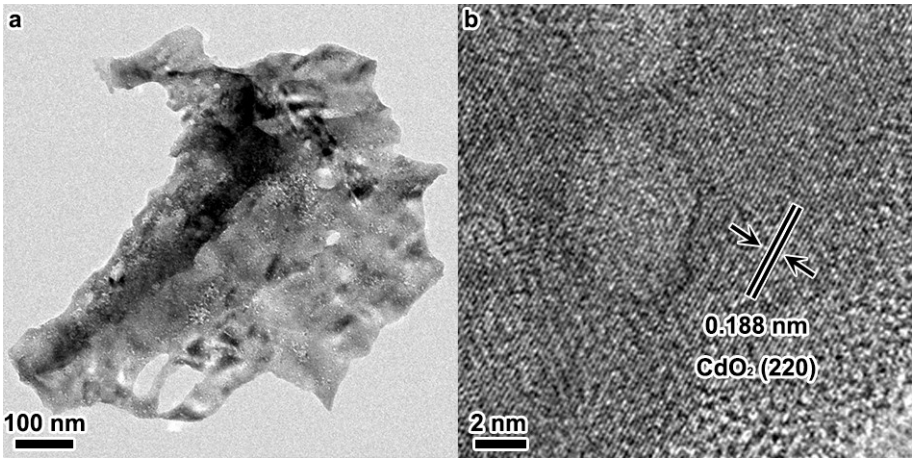

Fig. S3 TEM images of products obtained without substrate. (a) Low magnification TEM image, (b) high resolution TEM image

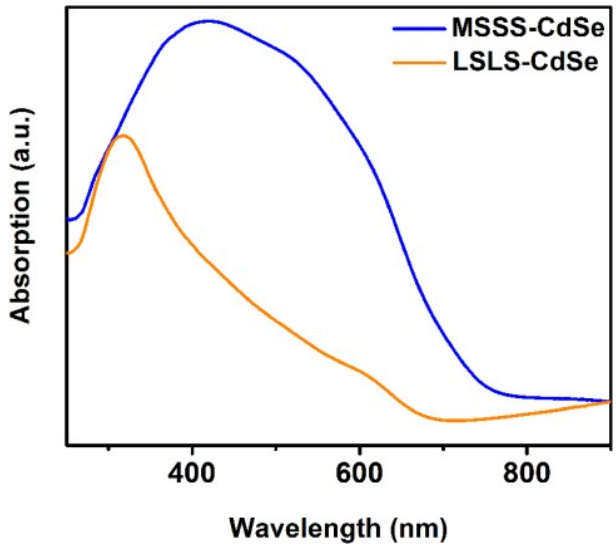

Fig. S4 Absorbance spectra of CdSe NWs by SSS growth under microwave heating (MSSS-CdSe, blue line) and SLS growth by laser heating (LSLS- CdSe, orange line).

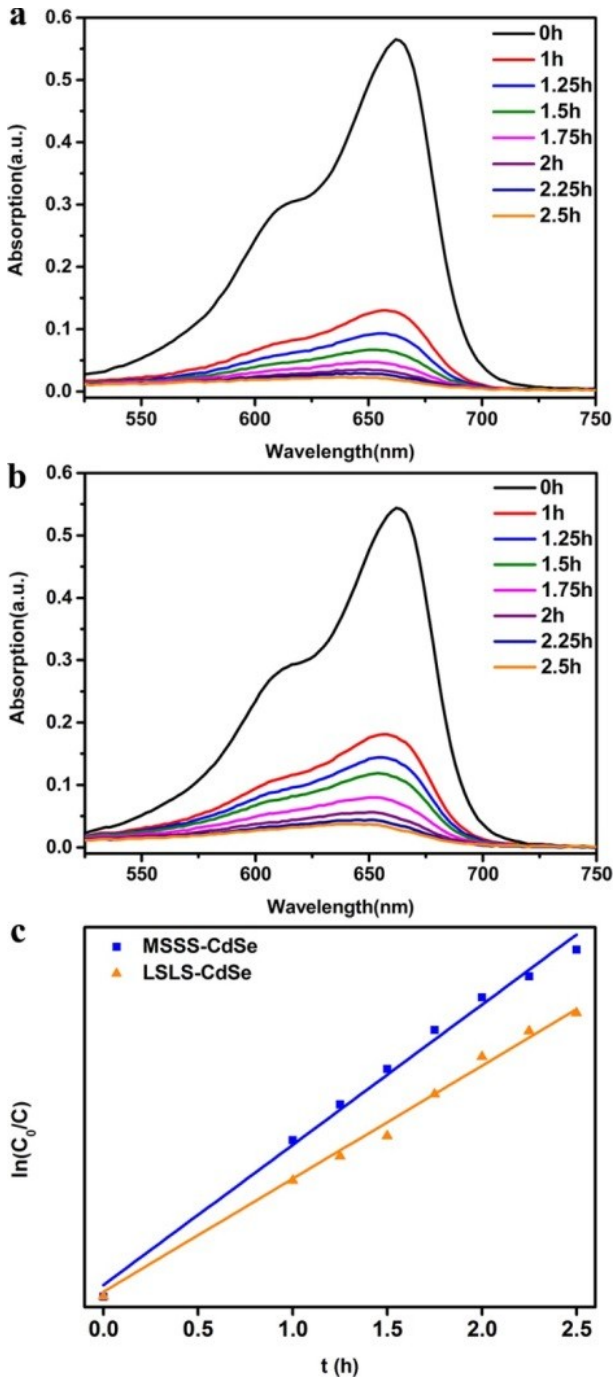

Fig. S5 Absorbance spectra of the mixture of CdSe NWs with MB solution (a) NWs by microwave heating, (b) NWs by laser heating. (c) Plot of the natural logarithm of the concentration (C) of MB normalized against the concentration (C_0) before the photocatalytic reactions as a function of the reaction time (t).

End ESI