

Electronic Supporting Information

Layer-by-Layer Assembled PMMA-SH/CdSe-Au Nanocomposite Thin Films and the Optical Limiting Property

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1. Preparation of cadmium myristate

Cadmium myristate was synthesized and purified by the reported method.¹ Cadmium nitrate tetrahydrate (1.542 g, 5 mmol) was dissolved in anhydrous methanol (50 mL). A sodium myristate solution was prepared by dissolving sodium hydroxide (0.600 g, 15 mmol) and myristic acid (3.420 g, 15 mmol) in anhydrous methanol (500 mL). Then the cadmium-nitrate solution was added dropwise into the sodium-myristate solution with vigorous stirring. After the addition of all the cadmium-nitrate solution, the reaction was continued for 30 min for complete reaction. The resulting white precipitate was washed with methanol three times to remove unreacted precursors, and then dried at 65 °C under vacuum overnight.

2. Preparation of Au (I) toluene solution

Synthesis of the organometallic complex Au(I)–SR according to the previously reported procedure.² The Au(I)–SR complex was prepared by using Au(III) organometallic compound and alkanethiol. In a typical synthesis, tetraoctylammonium bromide (200 mg) was dissolved in toluene (20 mL). Then, H₂AuCl₄ aqueous solution (20 mL, 10 mM) was added under magnetic stirring. The upper organic layer turned to wine color after 30 min and was washed three times with deionized water (30 mL once) in a separation funnel. After the separation of the mixture, dodecyl mercaptan (0.2 mL) was added to the organic solution. After ultrasonication for about 5 min, the solution became transparent and colorless, indicating the formation of Au (I)–SR organometallic complex, which was then used as the Au (I) stock solution.

3. Synthesis of trimethylolpropane tris(3-mercaptopropionate)(Trithiol)

Trimethylolpropane tris(3-mercaptopropionate) (denoted as trithiol) was synthesized according to the reported procedure.³ In brief, 1,1,1-tris(hydroxymethyl) propane (6.715 g,

0.05 mol), toluene (40 mL), and H₂SO₄ (0.401 g) were added and mixed in a three-neck flask equipped with reflux condensing tube, constant pressure drop funnel, and Dean-Stark trap. After bubbled by N₂ for 30 min, 3-mercapto-propanoic acid (17.504 g, 0.15 mol) was dropped slowly into the reaction system through the constant pressure drop funnel. The reaction was carried out in the nitrogen atmosphere by heating the flask to 130 °C. Four hours later, the reaction was terminated by cooling down to room temperature. Then, the reaction solution was washed with deionized water to neutrality. The organic phase was separated, and dried over anhydrous MgSO₄. The resultant product was obtained by the removal of toluene using the rotary evaporator.

4. Photoconductive atomic force microscope (PCAFM) measurement

For the PCAFM measurement, dilute solution of CdSe-Au NCs was dropped on highly oriented pyrolytic graphite (HOPG) and dried with N₂. All current-voltage measurements were carried out at room temperature in dark room with a NT-MDT-NTEGRA Spectra system. The instrument was operated in two pass. The first pass was conducted in non-contact mode to get topography images of the CdSe-Au NCs on the HOPG substrate. The second pass was carried out in contact mode with tip-sample interaction force of about 350 nN. A DC bias was applied to the substrate with respect to tip and the I-V curves were acquired by choosing CdSe-Au NCs of interest and positioning the gold-coated tip above its center. For photo-excitation, a beam of continuous 532 nm laser was focused on the sample at the apex of the tip with an intensity of 0.059 MW/cm². Data acquisition consisted of first taking I-V curve without laser irradiation, then recording I-V curve under laser irradiation to explore the effects of photo-excitation.

5. Experimental setup for the measurement of optical limiting performance

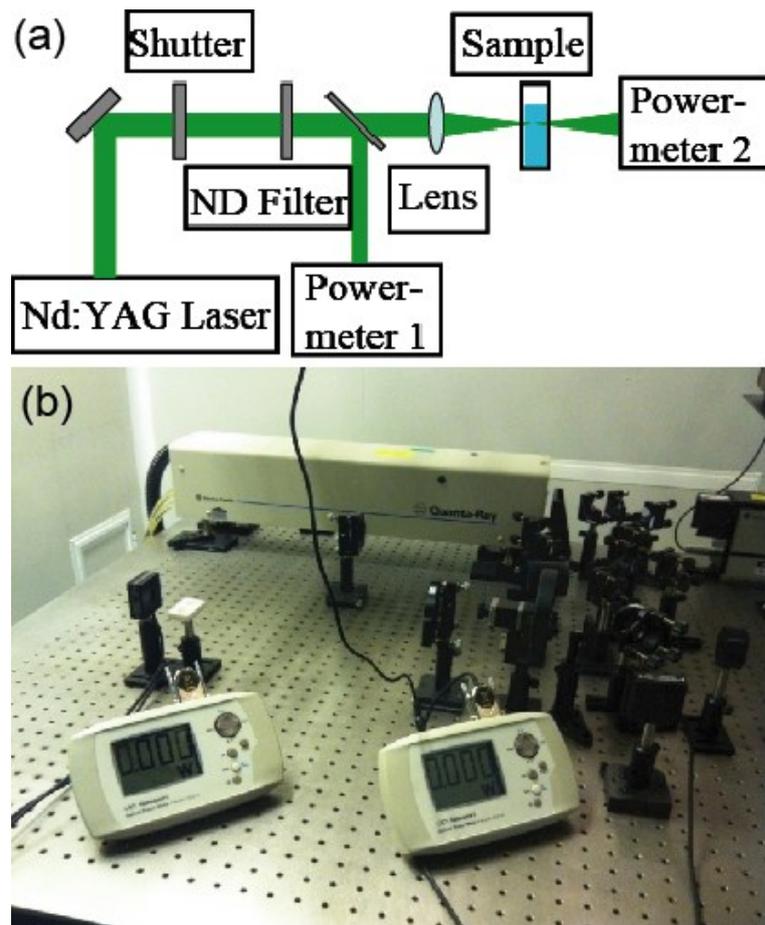


Fig. S1 (a) Schematic representation and (b) photograph of the experimental setup for the measurement of optical limiting performance.

6. Chemical structures of the components of the photopolymerizable resin

Components of the photopolymerizable resin

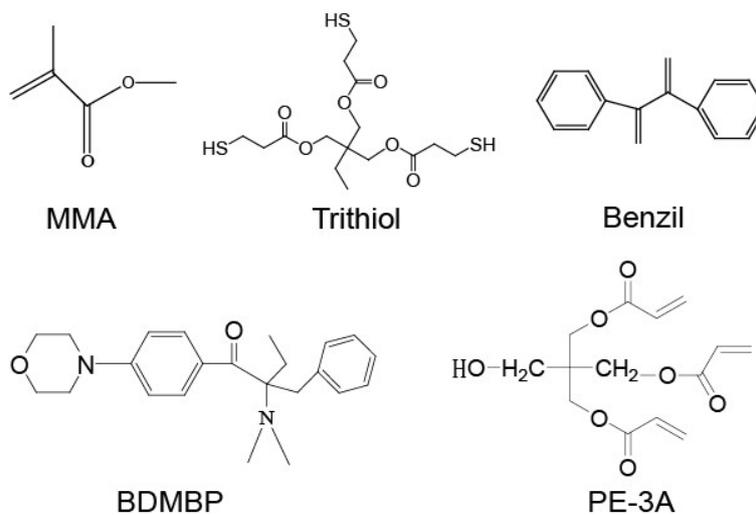


Fig. S2 Chemical structures of the components of the photopolymerizable resin.

7. Size Distribution of CdSe NC seeds and Au nanoparticles deposited on the CdSe NC Seeds

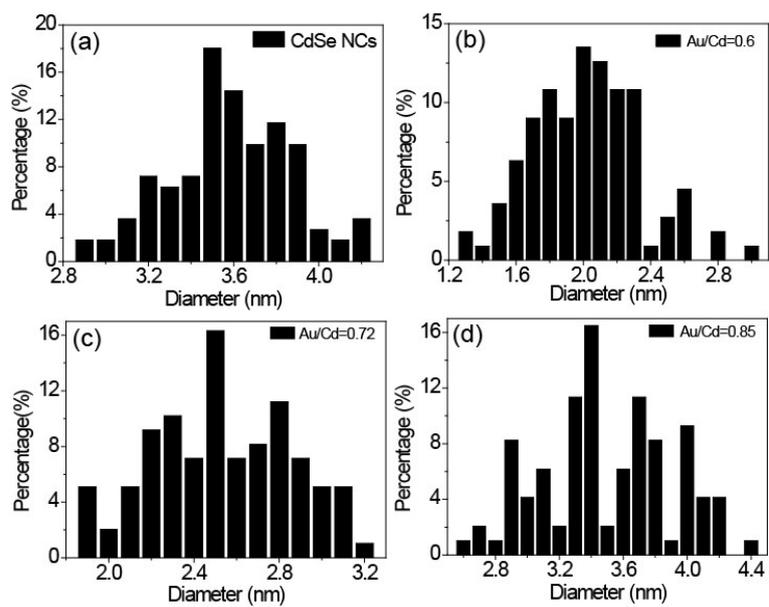


Fig. S3 Size Distribution of (a) CdSe NC seeds and Au nanoparticles deposited on the CdSe NC Seeds with Au/Cd ratio of (b) 0.6, (c) 0.72, and (d) 0.85.

8. Table S1. The components of the photopolymerizable resin

Sample No.	MMA (wt %)	Trithiol (wt %)	PE-3A (wt %)	Benzil (wt %)	Sensitizer (wt %)
1 [#]	28.4	31.4	38.3	1.1	0.8

9. Table S2. Optical properties of CdSe-Au NPs with different Au/Cd ratios

Sample No.	Au/Cd ratio ^{a)}	$\lambda_{\text{abs}}^{\text{b)}$ nm	$I_{\text{PL}}^{\text{c)}$	Au size ^{d)} nm	$E_{\text{th}}^{\text{e)}$ J/cm ²
control	0	567	3783	-	-
1 [#]	0.6	563	1.1	2	26.4
2 [#]	0.72	559	2.1	2.5	21.3
3 [#]	0.85	558	1	3.4	11.8

^{a)}Au/Cd ratio: Au(I)/CdSe mole ratio; ^{b)} λ_{abs} : the first excitonic absorption wavelength; ^{c)} I_{PL} : photoluminescence intensity at 580 nm; ^{d)}Au size: the size of the deposited Au domains on the CdSe-Au nanoparticles; ^{e)} E_{th} : threshold laser energy exhibiting optical limiting response.

Reference

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