Electronic Supplementary Information

Ag-doped InP/ZnS quantum dots for type-I photosensitizers

Can Ren,[a] Die Hu,[b] Yanyan Cui,[a] Peixian Chen,[b] Xiaoqian Xu,[*b]

Jiaji Cheng,[*c] and Tingchao He[*a]

[a]Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China. Email: tche@szu.edu.cn

[b]Key Laboratory of Cell Biology, Ministry of Public Health and Key Laboratory of Medical Cell Biology, Ministry of Education, China Medical University, Shenyang, 110122 China. Email: xqxu@cmu.edu.cn

[c]School of Materials Science and Engineering, Hubei University, Wuhan, Hubei 430062, China. Email: jiajicheng@hubu.edu.cn

Experimental section

Materials and reagents

1-octadecene (ODE, ≥90%), oleylamine (OLA, 80−90%), indium(III) chloride ($InCl_3$, ≥99.995%), tris-(dimethylamino) phosphine ($P(N(CH_3)_2)_3$, 97%), zinc(II) iodide (ZnI_2, ≥99.99%), silver chloride ($AgCl_2$, ≥99.5%), 1-dodecanethiol (DDT, ≥98%), 3-mercaptopropionic acid (MPA, 99%), sodium hydroxide (NaOH, 96%), and other related solvents were purchased from Aladdin without further purification.

Synthesis of InP/ZnS QDs

0.72 mmol $InCl_3$ and 2.16 mmol ZnI_2 were loaded with 6 mL OLA and 4 mL ODE in a 50 mL flask. The mixture was heated to 120 °C and the nitrogen flow was degassed at this temperature for 20 minutes. After the temperature reached 220 °C, 0.25 mL $P(N(CH_3)_2)_3$ was rapidly injected to make the InP core grow. After 15 minutes, 3 ml DDT was dropped into the mixture and growth of ZnS shells was achieved at 200 °C. The mixture was stirred continuously at 200°C for 4 hours. After cooling to ambient temperature, the samples were purified at least 3 times by centrifugation with a mixture of n-hexane/ethanol. The resultant product was dissolved in hexane.

Synthesis of Ag-doped InP/ZnS QDs (Ag/In feed ratio of 6% or 18%**)**

To prepare Ag-doped InP/ZnS QDs, 0.0432 mmol $AgCl_2$ (Ag/In feed ratio: 6%) or 0.129 mmol $AgCl_2$ (Ag/In feed ratio: 18%) was mixed with In and Zn precursors. The other steps were the same to those for the synthesis of InP/ZnS QDs.

Synthesis of water-soluble Ag-doped InP/ZnS QDs

0.5 mL MPA was dissolved in 5.0 mL methanol, and NaOH was added to the above mixture to adjust PH to 12. The 0.5 mL MPA methanol solution was then added into 5.0 mL chloroform solution of InP-based QDs and stirred for 30 min to get the precipitation of the QDs. Then, 5.0 mL distilled water was added into the mixture and kept stirring for another 20 min. After standing for 10 min, the bottom organic phase was discarded and the upper aqueous phase containing QDs was collected. The MPA ligand in the QD aqueous solution was isolated by precipitating the QDs with the addition of acetone. The supernatant was discarded, and the pellet was then redissolved in water.

Absorption and emission optical characterizations

The UV-visible absorption spectra of the QDs in n-hexane solvent were measured by an ultraviolet-visible-near-infrared spectrophotometer (Lambda 950). The emission spectrum and fluorescence quantum efficiencies were determined using a FS5 fluorescence spectrometer (Edinburgh instruments), which is equipped with a 150 W xenon lamp and an integrating sphere accessory.

Cell culture

U251 cells were purchased from Shanghai Institute for Biological Sciences (Shanghai, China). The cells were cultured in Dullbecco's modified Eagle medium (DMEM) (SEVEN) with 10 % fetal bovine serum (FBS) (ExCell Bio) and 1 % penicillin/streptomycin (SEVEN) at 37 °C.

The measurements of fs-TA spectra

During the measurements, the pump pulses at 400 nm were generated from an OPA system combined with TOPAS, while the probe pulses in the wavelength range of 350-800 nm were generated by irradiating 350 nm fs pulses into a YAG crystal. The solution of the QDs were filled in 1 mm-thick quartz liquid cells.

Detection of •OH production

APF was used to detect the •OH production of QDs in solution. The absorption of the QDs in H_2O at 480 nm was adjusted to about 0.15 OD. Then, 1 μL APF solution (DMF, 5 mM) were added into the QD solution. The mixture was irradiated by a xenon lamp (0.5 W/cm^2) (a 395 nm long-pass filter is placed in front of the light source), The fluorescence change was collected every 4 s until 20 s by a fluorescence spectrometer. The change of fluorescence intensity at about 516 nm was collated and plotted against irradiation time.

Detection of $O_2^{\bullet-}$ production

DHE was used to detect the $O_2^{\bullet-}$ production of QDs in solution. The absorption of the QDs in H_2O at 480 nm was adjusted to about 0.15 OD. Then, 100 μL DHE solution (DMSO, 5 mM) were added into the QDs solution. The mixture was irradiated by a xenon lamp (0.5 W/cm^2) (a

395 nm long-pass filter is placed in front of the light source). The fluorescence change was collected every 4 s until 20 s by the fluorescence spectrometer. The change of fluorescence intensity at about 630 nm was collated and plotted against irradiation time.

Detection of $^1O_2$ production

SOSG was used to detect the $^1O_2$ production of QDs in solution. The absorption of the QDs in H_2O at 480 nm was adjusted to about 0.15 OD. Then, 1 μL SOSG solution (Methanol, 5 mM) were added into the QDs solution. The mixture was irradiated by a xenon lamp (0.5 W/cm^2) (a 395 nm long-pass filter is placed in front of the light source). The fluorescence change was collected every 4 s until 20 s by a fluorescence spectrometer. The change of fluorescence intensity at about 525 nm was collated and plotted against irradiation time.

Cell viability assay

The Cell Counting kit (CCK-8, SEVEN) was used to evaluate the cell viability of U251 cells. Briefly, cells were seeded on a 96-well plate with 1.2×10^4 cells per well. The QDs with different concentrations were then mixed with fresh medium and cultured with U251 cells for 24 h. After incubation, the medium was discarded and replaced with 100 μL fresh medium mixed with 10 μL CCK-8 solution. After incubation at 37 °C for 1 h, the plate was then read by a microplate reader (pectraMax M5, Molecular Device), under the excitation at 450 nm.

Two-photon excited fluorescence imaging

About 1.5×10^5 cells were plated onto 14-mm glass coverslips in a 24-well tissue culture plate and were allowed to adhere overnight. Afterward, the QDs with different concentrations were added to the U251 cells for 24 h. Then, these cells were fixed by 4 % paraformaldehyde. The two-photon excited fluorescence images were taken by using a two-photon confocal microscope (ZEISS).

Live/dead assay of U251 cells incubated with the QDs under laser irradiation.

U251 cells were seeded in 96-well plates with 1.2×10^4 cells per well for 24 h and further incubated with the QDs with a concentration of 2 μM for another 24 h. Then, each well was irradiated by 808 nm laser (1 W/cm^2). After the 96-well plates were left in incubator overnight, they were detected with Live/Dead Cell Viability Assay Kit (Invitrogen) according to manufacturer's instructions. The cells were washed with 1× PBS twice and incubated with 100 μL calcein AM (2×10^{-6} M) and EthD ($1\ 4 \times 10^{-6}$ M) solution for 45 min at room temperature in the dark. After incubation, cells were washed with 1 × PBS twice in the dark and photographed by a fluorescence microscope Olympus IX71 (Tokyo).

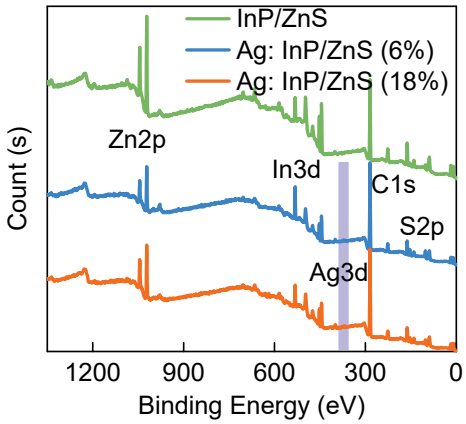

Figure S1. XPS patterns of three samples.

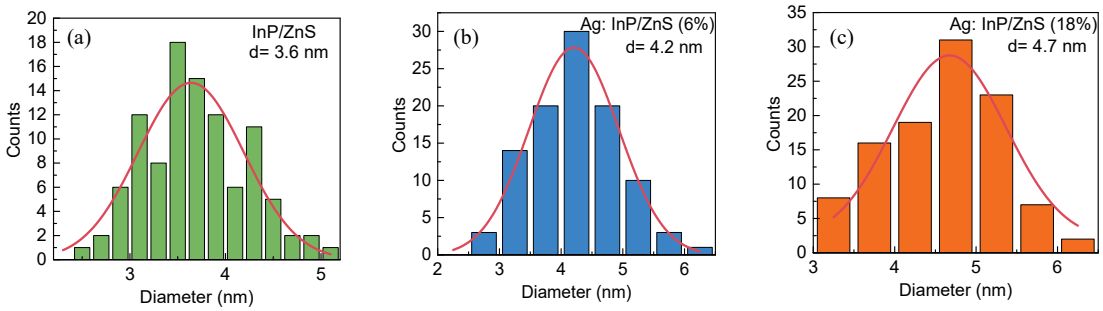

Figure S2. The size distributions of (a) InP/ZnS QDs, (b) Ag: InP/ZnS QDs (6%) and (c) Ag: InP/ZnS QDs (18%).

Table S1. The basic optical parameters for three samples.

Ag/In feed ratio	τ_{500nm} (ns)	τ_{580nm} (ns)	QY (in hexane)	QY (in water)
0%	53.1	-	26.38	6.29
6%	70.6	222.4	34.99	8.94
18%	68.0	231.8	29.12	4.66

Table S2. MPA cross sections for three samples.

Ag/In feed ratio	σ_2 (GM)	σ_3 (10^{-80} cm^6 s^2 photon^{-2})
0%	3.5×10^3 (940 nm)	2.9×10^3 (1280 nm)
6%	1.7×10^4 (820 nm)	1.7×10^4 (1260 nm)
18%	1.2×10^4 (860 nm)	1.4×10^4 (1260 nm)

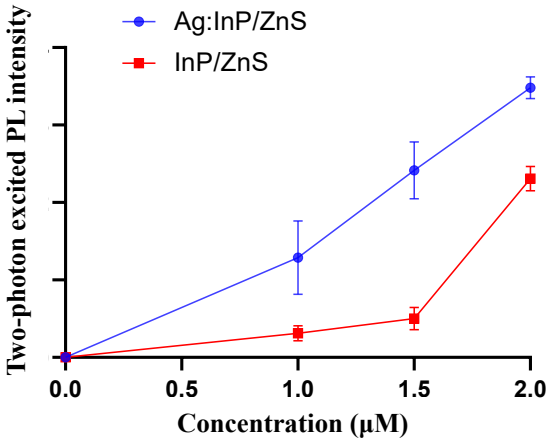

Figure S3. Two-photon excited PL intensity from the U251 cells incubated QDs with different concentrations.

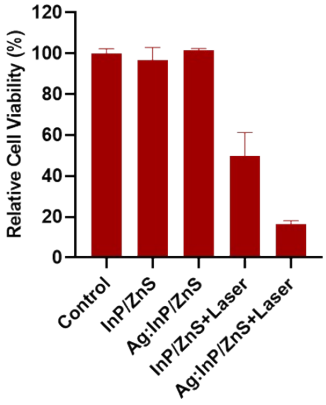

Figure S4. Cell viability of U251 cell incubated with the QDs after 808 nm irradiation.