Electronic Supplementary Information

Quantized Doping of CdS Quantum Dots with Twelve Gold Atoms

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1. Experimental section

1.1 Chemicals

General: All chemicals were purchased from commercial sources and were directly used without any further purification unless otherwise mentioned. *p*-(trifluoromethyl)benzenethiol (*p*-MBT) [CF₃C₄H₄SH, 98%], oleic acid [OA, 85%], sodium oleate [NaOA, 90%], L-ascorbic acid [AA, 99%], tri-*n*-octylphosphine oxide [TOPO, 95%] and tributyl phosphite [TBP, 95%] were purchased from TCI, chloroauric acid [HAuCl₄·nH₂O, Au-49 wt %] was purchased from STEM, sodium borohydride [NaBH₄, 98%] and cadmium nitrate tetrahydrate [Cd(NO₃)₂·4H₂O, 99.9%] were purchased from Aladdin, elemental sulfur [S, 99%], oleate amine [OAm, 90%], sodium sulfide [Na₂S·9H₂O, 98%] and tri-*n*-octylphosphine [TOP, 90%] were purchased from Acros, silver nitrate [AgNO₃, 99.9%], tetraphenylphosphonium bromide [PPh₄Br, 99%], triphenylphosphine [PPh₃, 99%], trimethylamine [TEA, 99%], sodium chloride [NaCl, 99.9%] and all solvents in analytical purity were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai).

1.2 Apparatus

The transmission electron microscope (TEM) images were recorded on a JEM-2100F transmission electron microscope of JEOL with an acceleration voltage of 200 kV or on a HT7700 transmission electron microscope of Hitachi with an acceleration voltage of 120 kV. Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were recorded on a Themis Z transmission electron microscope of FEI with an acceleration voltage of 300 kV. The UV-Vis absorption spectra were measured on a Lambda365 spectrometer of PerkinElmer. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was measured on an *i*CAP7000 spectrometer of Thermo-Scientific. The luminescence emission spectra were recorded on a F4500 spectrometer of Hitachi.

1.3 Synthetic section

1.3.1 Synthesis of (Au₁₂Ag₃₂S₃₀) clusters



The (Au₁₂Ag₃₂S₃₀) cluster was successfully prepared through an amine-assisted NaBH₄ reduction

method in liquid-liquid phases reported by Zheng *et al.*^[1] Briefly, AuPPh₃Cl (10.0 mg) and AgNO₃ (10.0 mg) were dissolved in a mixed solution of dichloromethane (DCM) (4.0 mL) and methanol (1.0 mL) at 0 °C in a pressure flask by stirring. Immediately, the reaction system turned sticky and light yellow with the addition of *p*-MBT (10.0 μ L). 20 min later, PPh₄Br (12.0 mg) and TEA (50.0 μ L) were added to the flask in order. After another 20 min, 1.0 mL of freshly prepared cold aqueous solution of NaBH₄ (45.0 mg) was rapidly introduced to the flask. The reaction system gradually turned dark in 30 s and was intensely stirred at 0 °C for 12 h. The organic phase was washed with DI water three times and then concentrated to about 0.5 mL by N₂ flow. Slowly, 10.0 mL of hexane was layered on the concentrated solution and the mixture was stored below -15 °C. After 24 h, the precipitated powder was re-dispersed in DCM (4.0 mL) for further characterization.

1.3.2 Synthesis of (Au₁₂Ag₃₂)@Ag nanoparticles (NPs)

 $(Au_{12}Ag_{32}S_{30})$ Cluster + AgNO₃ + AA + OA + NaOA $\frac{NaCl}{EtOH/H_2O, rt, 72h}$ $(Au_{12}Ag_{32})@Ag NPs$ 50.0 µL of DCM solution of the as-prepared (Au_{12}Ag_{32}S_{30}) cluster was added into a centrifuge tube. Subsequently, 16.0 mL of ethanol, 1.20 g of NaOA, 1.6 mL of OA and 24.0 mL of DI water were added in sequence. The mixture was soon agitated by vortex oscillator to form a homogeneous phase. Then, 2.4 mL of aqueous solution of AgNO₃ (10.0 mg), 0.4 mL of aqueous solution of NaCl (0.35 mg, the mol ratio of Cl⁻ to Ag⁺ equals 1/10) and 4.0 mL of aqueous solution of AA (55.0 mg) were added to the system in order, violent oscillation was necessary after each addition of the chemicals. After being kept in dark for 72 h, the mixture was transferred into a separating funnel and mixed with 50 mL of hexane and 50 mL of ethanol. The hexane phase containing (Au₁₂Ag₃₂)@Ag NPs was concentrated to about 5 mL by rotary evaporator and the target product was purified by centrifugation (8,000 r/min × 10 min) with the addition of 5 equivalents of ethanol and re-dispersed in 15.0 mL of hexane.

1.3.3 Synthesis of (Au₁₂)@Ag₂S NPs

3.8 mg of elemental sulfur was well dissolved in a mixed solution of OAm (1.0 mL) and OA (5.0 mL) by ultrasonic and the solution was added to that of $(Au_{12}Ag_{32})@Ag$ NPs prepared in the former

step dropwise with vigorous stirring. 30 min later, 75 mL of ethanol was poured into the vessel and the target product, $(Au_{12})@Ag_2S$ NPs, was collected by centrifugation (8,000 r/min × 10 min) and re-dispersed in 15.0 mL of chloroform.

1.3.4 Synthesis of (Au₁₂)@CdS quantum dots (QDs)

$$(Au_{12})@Ag_2S NPs + Cd(NO_3)_2 \cdot 4H_2O \xrightarrow{PPh_3} (Au_{12})@CdS QDs CHCl_3/ MeOH/ OA, 50°C, 10 min$$

15.0 mL of OA and 150 mg of PPh₃ was added into the chloroform solution of $(Au_{12})@Ag_2S$ NPs prepared in the former step and the system was set in an oil bath at 50 °C. Then 5.0 mL of methanol solution containing Cd $(NO_3)_2$ ·4H₂O (150 mg) was injected to the reaction solution quickly. After 10 min, 75 mL of ethanol was poured into the vessel and the target product, $(Au_{12})@CdS$ QDs, was collected by centrifugation (10,000 r/min × 10 min) and re-dispersed in 15.0 mL of dichloromethane.

1.3.5 Synthesis of (Au₁₂)@PbS NPs

$$(Au_{12})@Ag_2S NPs + Pb(Ac)_2 \cdot 3H_2O \xrightarrow{PPh_3} (Au_{12})@PbS QDs CHCl_3/ MeOH/ OA, 50°C, 10 min$$

15.0 mL of OA and 150 mg of PPh₃ were added into the chloroform solution of $(Au_{12})@Ag_2S$ NPs prepared in the former step and the system was set in an oil bath at 50 °C. Then 5.0 mL of methanol solution containing Pb(Ac)₂·3H₂O (180 mg) was injected to the reaction solution quickly. After 10 min, 75 mL of ethanol was poured into the vessel and the target product, $(Au_{12})@PbS$ QDs, was collected by centrifugation (10,000 r/min × 10 min) and re-dispersed in 15.0 mL of dichloromethane.

1.3.6 Synthesis of $(Ag_{44}S_{30})$ Clusters, $(Ag_{44})@Ag NPs$, $(Ag_{44})@Ag_2S NPs$, $(Ag_{44})@CdS QDs$ and $(Ag_{44})@PbS QDs$

The metal precursor was $AgNO_3$ (20.0 mg) with other procedures unchanged in **1.3.1**.

Using (Ag₄₄S₃₀) clusters as starting materials, the preparation of (Ag₄₄)@Ag NPs, (Ag₄₄)@Ag₂S NPs, (Ag₄₄)@CdS QDs and (Ag₄₄)@PbS QDs followed the same procedures depicted in **1.3.2**, **1.3.3**, **1.3.4** and **1.3.5**, respectively.

1.3.7 Synthesis of non-cluster doped Ag NPs, Ag₂S NPs, Ag: CdS QDs and Ag: PbS QDs

16.0 mL of ethanol, 1.20 g of NaOA, 1.6 mL of OA and 24.0 mL of DI water were added into a centrifuge tube. The mixture was soon agitated by vortex oscillator to form a homogeneous phase. Then, 0.5 mL of aqueous solution of Na₂S·9H₂O (0.07 mg, the mol ratio of S²⁻ to Ag⁺ equals 5‰), 2.4 mL of aqueous solution of AgNO₃ (10.0 mg), 0.4 mL of aqueous solution of NaCl (0.35 mg, the mol ratio of Cl⁻ to Ag⁺ equals 1/10) and 4.0 mL of aqueous solution of AA (55.0 mg) were added to the system in order, violent oscillation was necessary after each addition of the chemicals. The addition of Na₂S leaded to the formation of ultrasmall & insoluble Ag₂S nuclei, which functioned as the seeds for the growth of Ag NPs. After aging for three days, the non-cluster doped Ag NPs were obtained with the same procedures depicted in **1.3.2**.

The preparation of non-cluster doped Ag₂S NPs, Ag: CdS QDs and Ag: PbS QDs followed the same procedures depicted in **1.3.3**, **1.3.4** and **1.3.5**, respectively.

2. Characterizations

2.1 (Au₁₂)@CdS QDs



Fig. S1 (a) The TEM image and (b) UV-Vis absorption spectrum of (Au₁₂Ag₃₂S₃₀) clusters.



Fig. S2 (a-d) TEM images and **(e)** the histogram of diameter distribution of $(Au_{12}Ag_{32})@Ag$ NPs, the diameter distribution is 5.05 ± 0.62 nm, **(f)** the UV-Vis absorption spectrum of $(Au_{12}Ag_{32})@Ag$ NPs.

The $(Au_{12}Ag_{32})@Ag$ NPs were simply modeled to a core-shell structure and the Ag atoms of the shell were assumed to arrange in *fcc* dense stacks. The number of Ag atoms in the matrix shell of $(Au_{12}Ag_{32})@Ag$ NPs was calculated as follows:

$$N_{Ag} = \frac{m_{Ag}}{M_{Ag}} \cdot N_{A} = \frac{\rho_{Ag} \cdot V_{Ag}}{M_{Ag}} N_{A} = \frac{\rho_{Ag} \cdot \frac{4}{3} \pi (r_{Ag}^{3} - r_{Cluster}^{3})}{M_{Ag}} N_{A}$$

= $\frac{10.49g \cdot cm^{-3} \times \frac{4}{3} \pi (2.53^{3} - 0.5^{3}) nm^{3}}{107.87g \cdot mol^{-1}} \times 6.022 \times 10^{23} \cdot mol^{-1} = 3921$
Au %= $\frac{12}{3921 + 32} = 3.03\%$

Fig. S3 The calculated value of (Au to Ag atoms) in $(Au_{12}Ag_{32})@Ag$ NPs. Besides, by the same model, the value of (Au to Ag atoms) in $(Au_{12})@Ag_2S$ NPs varies from $3.09\%^{\sim}3.25\%$ as the density of amorphous Ag₂S varies from $6.85^{\sim}7.23$ g·cm⁻³ and the value of (Au to Cd atoms) in $(Au_{12})@CdS$ QDs equals to 5.47‰.



Fig. S4 TEM images of $(Au_{12}Ag_{32}S_{30})@Ag NPs$ prepared with a specific mR_{CA} in a certain reaction time (Scalebar: 50 nm). **(a)** 2 mol% of Cl⁻ in 24 h, **(b)** 2 mol% of Cl⁻ in 72 h, **(c)** 10 mol% of Cl⁻ in 24 h, **(d)** 10 mol% of Cl⁻ in 72 h, **(e)** 33 mol% of Cl⁻ in 24 h, (inset: the aggregated AgCl), **(f)** 33 mol% of Cl⁻ in 72 h. NaCl was used as Cl⁻ vector in all above cases.



Fig. S5 The schematic illustration for the formation mechanism of (Au₁₂Ag₃₂S₃₀)@Ag NPs.^[2]



Fig. S6 Without the addition of clusters as seeds, TEM images of each product (Scalebar: 50 nm).
(a) 10 mol% of NaCl after 1 d, (b) 10 mol% of NaCl after 3 d, (c) 10 mol% of Cl⁻ (FeCl₃)after 1 d, (d) 10 mol% of Cl⁻ (FeCl₃) after 3 d.



Fig. S7 (a) TEM image and **(b)** the histogram of diameter distribution of $(Au_{12})@Ag_2S$ NPs, the diameter distribution is 5.95 ± 0.66 nm, **(c)** the UV-Vis absorption spectrum of $(Au_{12}Ag_{32}S_{30})@Ag_2S$ NPs.



Fig. S8 (a) TEM image (HRTEM image inset) and **(b)** the histogram of diameter distribution of $(Au_{12})@CdS QDs$, the diameter distribution is 5.94 ± 1.11 nm, **(c)** the UV-Vis absorption spectrum of $(Au_{12}Ag_{32}S_{30})@CdS QDs$.

2.2 (Ag44)@CdS QDs



Fig. S9 (a) TEM image and (b) the UV-Vis absorption spectrum of (Ag₄₄S₃₀) clusters.



Fig. S10 (a) TEM image, **(b)** the histogram of diameter distribution (4.89 \pm 0.6 nm) and **(c)** the corresponding UV-Vis absorption spectrum of (Ag₄₄)@Ag NPs.



Fig. S11 (a) TEM image, **(b)** the histogram of diameter distribution (6.05 \pm 0.89 nm) and **(c)** the corresponding UV-Vis absorption spectrum of (Ag₄₄)@Ag₂S NPs.



Fig. S12 (a) TEM image, **(b)** the histogram of diameter distribution (5.13 \pm 0.64 nm) and **(c)** the corresponding UV-Vis absorption spectrum of (Ag₄₄)@CdS QDs.



Fig. S13 UV-Vis spectra of each final product in the synthesis of $(Ag_{44}S_{30})$ cluster with the addition of different volume of methanol, **(a)** 2.0 mL, **(b)** 4.0 mL, **(c)** 10 mL.

Three key points should be noticed in the synthesis of noble metal clusters. Firstly, a low temperature ensures a dramatic decline in the reaction kinetics. Secondly, the addition of amine is necessary for the formation of relatively stable borane-amine complexes, leading to a low reducing agent decomposition rate and an enduring reductive atmosphere which is beneficial for the formation of clusters. At last, the biphasic synthetic strategy is a general consensus widely accepted in cluster synthesis, whether in a liquid-liquid or a liquid-gas protocol. It's of vital importance for the metal precursors to be reduced in the interface of phases to prevent the rapid formation of nanoparticles. As shown in **Fig. S13**, with the increasing addition of methanol, the quality of (Ag₄₄S₃₀) clusters became poorer and Ag NPs were finally obtained in a methanol-overwhelming homogenous system.

2.3 The contrast experiments



Fig. S14 TEM images and corresponding UV-Vis spectra of **(a-b)** Ag NPs, **(c-d)** Ag₂S NPs and **(e-f)** Ag: CdS QDs (Scalebar: 50 nm).



Fig. S15 TEM images of PbS QDs prepared by cation exchange reaction (Scalebar: 50 nm).
(a) (Au₁₂)@PbS QDs, (b) (Ag₄₄)@PbS QDs, (c) Ag: PbS QDs.

2.4 The optimization procedures



Fig. S16 The optimization procedures in the synthesis of $(Au_{12})@Ag_2S$ NPs. TEM images of $(Au_{12})@Ag_2S$ NPs prepared in different solvents. **(a)** toluene, **(b)** cyclohexane, **(c)** chloroform, all of the Ag_2S NPs in the above cases aggregated seriously and **(d)** the UV-Vis absorption spectrum of product-**(c)**. The scattering absorption at 800 nm also indicated the poor dispersity.



Fig. S17 The optimization procedures in the synthesis of $(Au_{12})@CdS QDs$. TEM images of $(Au_{12})@CdS QDs$ prepared in toluene using different kinds of phosphorus ligands: **(a)** TBP, **(b)** TOP, **(c)** TOPO and **(d)** PPh₃. PPh₃ showed a slight superiority in dispersity. TEM images of $(Au_{12})@CdS$ QDs prepared in different solvents using PPh₃ as phosphorus ligand with the addition of 5.0 mL of OA: **(e)** toluene, **(f)** cyclohexane, **(g)** hexane and **(h)** chloroform. The solvent of chloroform or hexane showed a better dispersity.



Fig. S18 TEM images of $(Au_{12})@CdS$ NPs prepared in hexane or chloroform using PPh₃ as phosphorus ligands with the addition of 15 mL of capping ligand (OA or OAm). (a) in hexane with 15 mL of OAm, (b) in hexane with 15 mL of OA, (c) in chloroform with 15 mL of OAm, (d) in chloroform with 15 mL of OA. (e) UV-Vis absorption spectrum of the four products.



2.5 Optical Properties

Fig. S19 The time-resolved fluorescence decays of as-prepared (a) CdS QDs and (b) PbS QDs.^[3]

(Au ₁₂)@CdS	(Ag ₄₄)@CdS	Ag: CdS	(Au ₁₂)@PbS	(Ag ₄₄)@PbS	Ag: PbS
37.9	29.1	11.4	37.5	28.1	7.7

 Table S1
 The photoluminescence quantum yield (PLQY) of all as-prepared CdS QDs and PbS QDs

Table S2 Double-exponential fitting results of the time-resolved fluorescence lifetime (τ) of CdS QDs in **Fig. S19a**.

	(Au12)@CdS	(Ag44)@CdS	Ag: CdS
τ ₁ /ns	809.6	875.9	1063.2
 τ ₂ /ns	2826.0	3194.5	4066.4

Table S3 Single-exponential fitting results of the time-resolved fluorescence lifetime (τ) of PbS QDs in **Fig. S19b**.

	(Au ₁₂)@PbS	(Ag ₄₄)@PbS	Ag: PbS
τ/ns	349.1	482.9	534.4



Fig. S20 (a) The photoluminescence excitation (PLE) spectra of $(Au_{12})@CdS QDs$, $(Ag_{44})@CdS QDs$ and Ag: CdS QDs, **(b)** the normalized "subtract" signal (black line) derived via subtraction of Ag: CdS QDs PLE signal from $(Ag_{44})@QDs$ PLE signal in **(a)** and overlapped with the absorption spectrum of $(Ag_{44}S_{30})$ clusters (red line).^[4] Seeded from $(M_{12}Ag_{32}S_{30})$ cluster (M=Au or Ag), the $(Ag_{44})@CdS QDs$ showed a similar optical property in PLE as $(Au_{12})@CdS QDs$.



2.6 XRD data

Fig. S21 XRD patterns of the as-prepared CdS QDs or PbS QDs by cation exchange reaction.

3. References

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