

## **Electronic Supplementary Information**

### **Microwave Induced Center-Doping of Silver Ions in Aqueous CdS Nanocrystals with Tunable, Impurity and Visible Emission**

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## Experimental Section

### 1.1 Materials.

3-mercaptopropionic acid (MPA, 99%) and cadmium chloride (99%) were purchased from Alfa Aesar. Glutathione (GSH, 99%), thioglycolic acid (TGA, 99%) and L-cysteine (Cys, 98.5%) was obtained from Sigma. Ag<sub>2</sub>S (99%) was from Aladdin. AgNO<sub>3</sub> (99.8%), Na<sub>2</sub>S (98%), NaOH (99%) were purchased from Shanghai Chemical Reagents Company.

### 1.2 Preparation of Aqueous CdS:Ag NCs through core/shell-doping scheme.

Firstly, appropriate amounts of CdCl<sub>2</sub> (1 mmol) and MPA (2.5 mmol) are dissolved in 400 ml deionized water together, and the cadmium complexes are received. 1 M NaOH solution is next used to adjust the pH of cadmium complexes solution to between 8 and 9. Secondly, AgNO<sub>3</sub> and MPA are added together into 95 ml deionized water with constant stirring, and these silver complexes with the specific molar ratio (Ag<sup>+</sup>: MPA=1:2.5) are then mixed with 5 ml 0.1 M Na<sub>2</sub>S solution. The pH of aforementioned solution is also adjusted to the basic range using 1 M NaOH solution. Thirdly, the precursor solution is obtained by mixing those two solutions, and the molar ratio of Ag<sup>+</sup>: Cd<sup>2+</sup>: MPA: HS<sup>-</sup> is equal to 0.05:1:2.6:0.5. For comparison purpose, other capping molecules, GSH, TGA and Cys are also used and the procedure is the same as that for MPA. Meanwhile, different molar ratios of Ag<sup>+</sup>/Cd<sup>2+</sup>/MPA/HS<sup>-</sup> are also tested for precursor solutions: 0.05 (0.1 and 0.025):1:2.6:0.5. Finally, a 10 mL quartz autoclave filled with 5 ml precursor solution is maintained at 100 °C in a microwave synthesizer (Initiator Exp. from Biotage Comp.) for different intervals of time.

### 1.3 Formation of Aqueous CdS:Ag NCs through nucleation-doping strategy.

Typically, Na<sub>2</sub>S solution was injected into aqueous solutions containing CdCl<sub>2</sub>, AgNO<sub>3</sub> and MPA with a molar ratio (Ag<sup>+</sup>: Cd<sup>2+</sup>: MPA: HS<sup>-</sup>=0.05:1:2.6:0.5), yielding the precursor solution. Before adding Na<sub>2</sub>S, 1 M NaOH solution is used to adjust the pH to between 8 and 9. Moreover, the precursor solution is maintained at 100°C in

microwave oven for different intervals of time.

#### **1.4 Synthesis of Aqueous CdS:Ag NCs through growth-doping route.**

As shown above, cadmium complexes and silver complexes are prepared and the pH of these solutions is adjusted to between 8 and 9. However, the cadmium complexes is added into 1M Na<sub>2</sub>S solution firstly, and then silver complexes is mixed with the solution with constant stirring. The molar ratio of Ag<sup>+</sup>/Cd<sup>2+</sup>/MPA/HS<sup>-</sup> is 0.05:1:2.6:0.5. The precursor solution is maintained at 100°C in microwave oven for different interval of time.

#### **2. Characterization.**

At room temperature and ambient conditions, fluorescence spectra are measured by a Perkin Elmer LS55 spectrofluorimeter. Ultraviolet-visible absorption spectra are obtained using a Shimadzu UV-2450 UV-Vis spectrophotometer. X-ray diffraction (XRD) analysis are done on a Simens D5005 diffractometer (40 kV, 30 mA) at Cu-K $\alpha$  edge with a wavelength of  $\lambda = 0.15418$  nm, and diffraction patterns are collected in the 2 $\theta$  range of 10-60° at a scanning rate of 1°/min. The TEM and HRTEM images, EDX and SAED spectra are recorded by means of FEI Tecnai G20 high resolution transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MKII spectrometer with a Mg K $\alpha$  excitation (1253.6 eV).

The PL QY of NCs samples is measured at room temperature with Rhodamine 6G (99%, Aldrich. ethanol as solvent) as the reference standard (QY = 95%),<sup>[1]</sup> and the same samples are used directly in optical characterizations, such as PL and UV/Vis absorption. The as-prepared samples are centrifuged by acetone and dried under ambient condition for XRD and XPS characterizations.

#### **3. Results and Discussion**

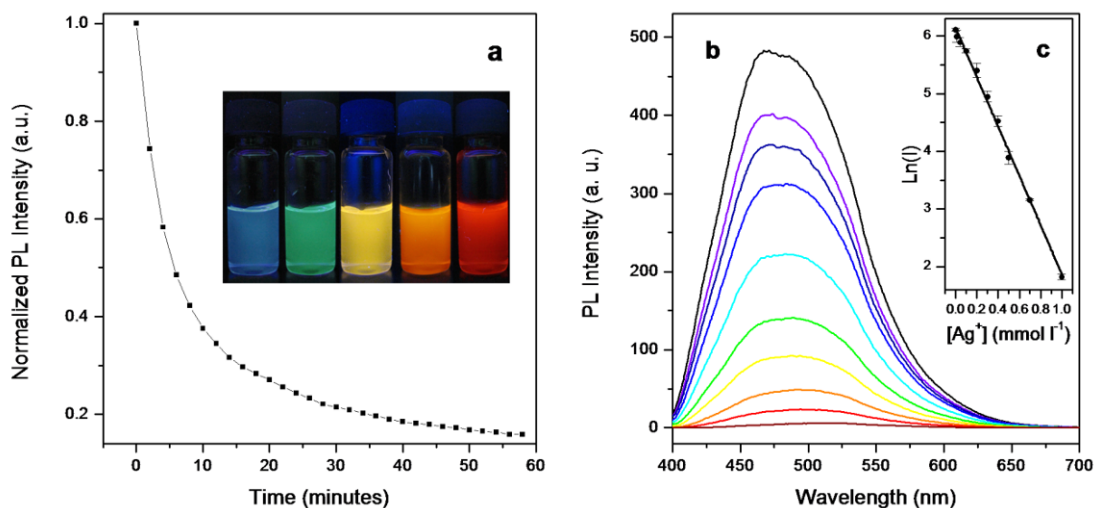


Figure S1 (a) Photoluminescence decay curves of MPA-capped CdS NCs with time, the inset is the images of doped CdS:Ag NCs under UV lamp with emitting colors of cyan, green, yellow, orange and red, which covers most visible windows; (b) The effect of silver ions concentration on the PL of GSH-capped CdS NCs showing that silver ions quench the emission of CdS NCs; (c) a straight line calibration curve that can be expressed as  $y=6.140-4.276x$ ,  $R^2=99.6\%$ .

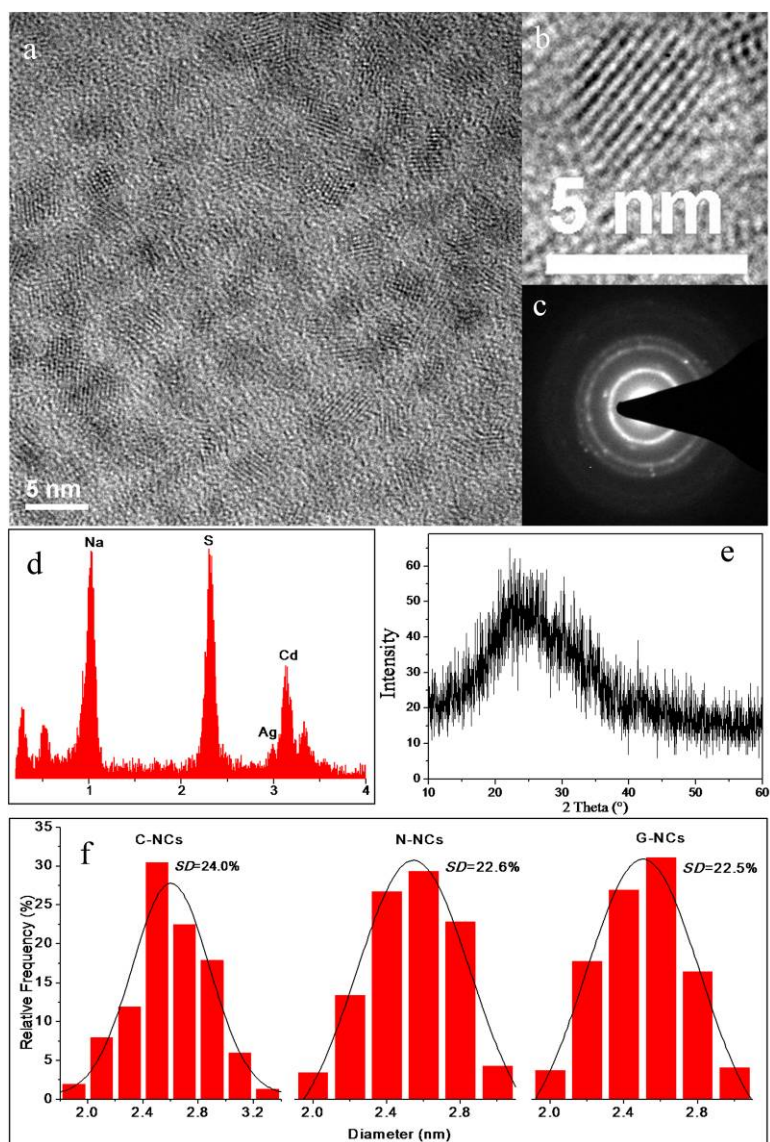


Figure S2 TEM and HRTEM images of Ag<sup>+</sup>-doped CdS C-NCs (a&b), SAED patterns (c) and EDAX spectrum (d) obtained from a selected area of (b), XRD patterns of C-NCs (e), the particle size distribution of doped NCs (f).

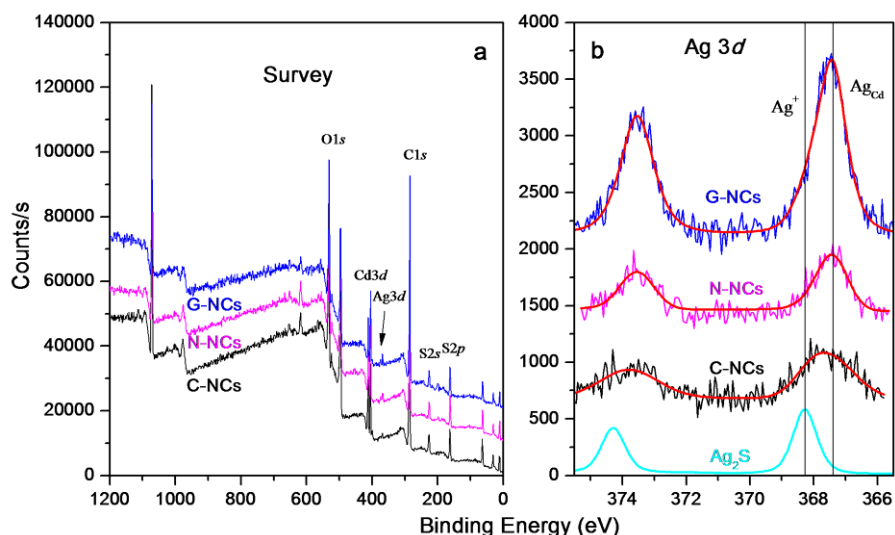


Figure S3 XPS spectra of CdS:Ag NCs. The Ag/Cd feed ratio was around 0.05/1. (a) XPS spectra of NCs. The presence of the characteristic Cd 3d peak at 405 eV, Ag 3d peak at 367.5 eV and 374 eV, S 2s/2p peak at 228 eV and 163 eV, indicated the presence of Cd, Ag and S element in the resulting NCs. (b) Ag 3d spectra of three NCs. The C-NCs, N-NCs and G-NCs had shown Ag 3d<sub>5/2</sub> peak at 367.81 eV, 367.46 eV and 367.47 eV respectively.

Fig.S3 present XPS measurement of silver doped CdS NCs. The presence of the characteristic Cd 3d peak at 405 eV, Ag 3d peak at 368 eV, S 2p peak at 163 eV, indicated the presence of Cd, Ag and S element in the resulting NCs (see Fig.S3a). Meanwhile, the XPS characteristic Ag 3d<sub>5/2</sub> peaks of C-NCs, N-NCs and G-NCs were centered at 367.81 eV, 367.46 eV and 367.47 eV, respectively, indicating the doped Ag was in the form of Ag<sup>+</sup> (Ag<sub>2</sub>S or Ag<sup>+</sup> occupied the the octahedral site of the CdS lattice) and Ag<sub>Cd</sub> (Ag<sup>+</sup> occupied the Cd<sup>2+</sup> site of the CdS lattice).<sup>[2]</sup> The Ag 3d<sub>5/2</sub> peaks shifted with the deepness of Ag doped into the center of NCs, as shown in Fig.S3b. In the case of C-NCs, the Ag 3d<sub>5/2</sub> peak is in between Ag<sup>+</sup> and Ag<sub>Cd</sub> peak because the core of C-NCs is Ag<sub>2</sub>S and the Ag<sup>+</sup> would diffuse on interface between the nanocluster core and the CdS overcoating layers by cation exchange, while Ag<sup>+</sup> occupying the Cd<sup>2+</sup> site of the host lattice. For G-NCs, the Ag<sup>+</sup> is attached on the surface of CdS nuclei and occupied the Cd<sup>2+</sup> site in the growth process by microwave irradiation, so the Ag 3d<sub>5/2</sub> peak is closer to Ag<sub>Cd</sub> peak greatly. Furthermore, the Ag 3d<sub>5/2</sub> peaks of G-NCs is evidently higher than C-NCs and

N-NCs, indicating the silver impurities are rich in the surface of G-NCs. Therefore, the XPS results is caused by the diverse doped strategies of NCs, which is in accordance with the speculations about three doped routes.

The thicker outer-shell of hosts grow, the better optical properties of NCs should be obtained, such as broad excitation and emission scope, high PL QY and stability. This suggests that the PL scope and PL QY of doped CdS NCs are tunable by controlling the position of hosts into which silver impurities are doped. The remaining question that we have to answer is how the silver impurities depress the quenching of MPA-capped CdS host and tune the emission from 480 nm to 630 nm?

In the theory of Wuister et al., the lower energetic position of the valence band for bulk CdS results in hole trapping of the photogenerated hole on the thiol molecule of MPA.<sup>[4]</sup> After doped treatment, the emission is due to shallow traps acting as recombination centers for photogenerated charge carriers,<sup>[5]</sup> and the top of the doped NCs valence band is above the thiol redox energy level, then the hole trapping is inhibited by an energy barrier. As a result, the doped NCs cannot efficiently convert thiols into disulfides via a photocatalytic reaction. Besides, the reason of C-NCs with tunable visible emission is that as central diffusion of  $\text{Ag}^+$  into host lattice(Fig. S3b)<sup>[6]</sup> and the outer-shell grew thicker, the crystal field for each dopant ion become more symmetric in long range.<sup>[7]</sup> Consequently, the crystal field splitting of the d-orbitals become smaller, which results in a PL red shift. Peng et al. found the strong PL from MnSe:ZnSe NCs could be tuned from about 575 nm to 595 nm (20 nm red-shift) in organic solvents. For the C-NCs, the PL emission covers most of the visible window and partially depends on the irradiation of microwave.

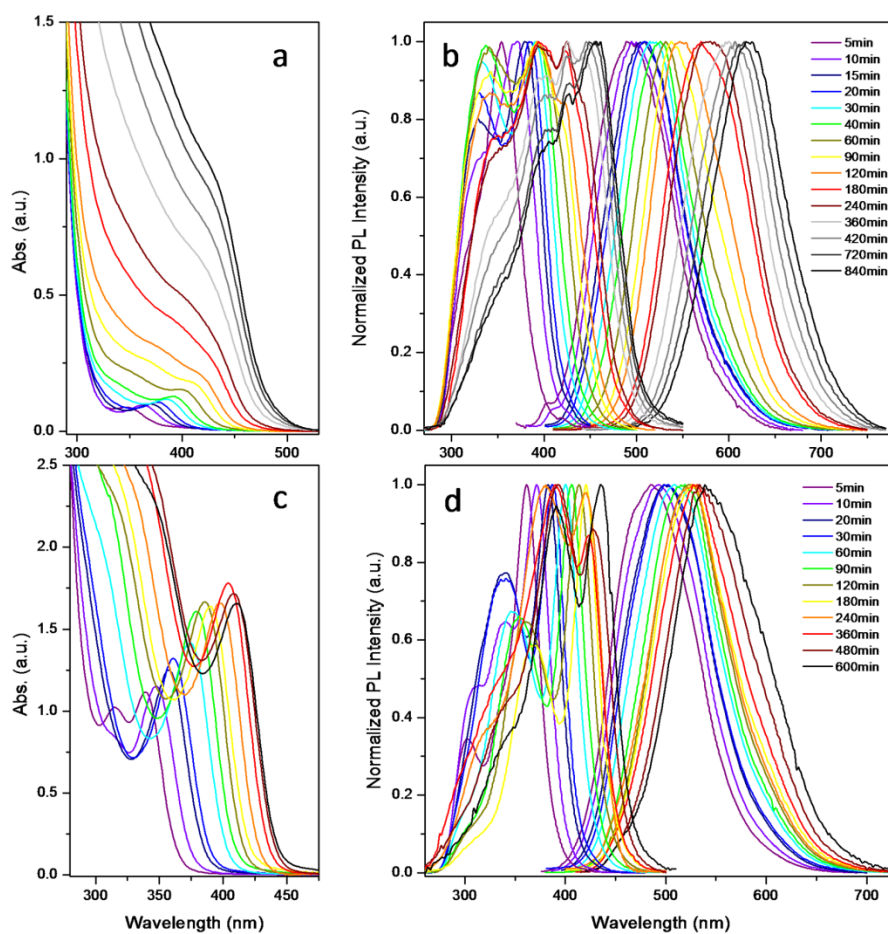


Figure S4 Temporal evolution of the absorption spectra (a&c) and PL emission spectra (b&d) of  $\text{Ag}^+$ -doped CdS NCs with different ratio of  $\text{Ag}^+$  to  $\text{Cd}^{2+}$  in precursors solution synthesized through core/shell-doping strategy: 1:10 (a&b) and 1:40 (c&d).



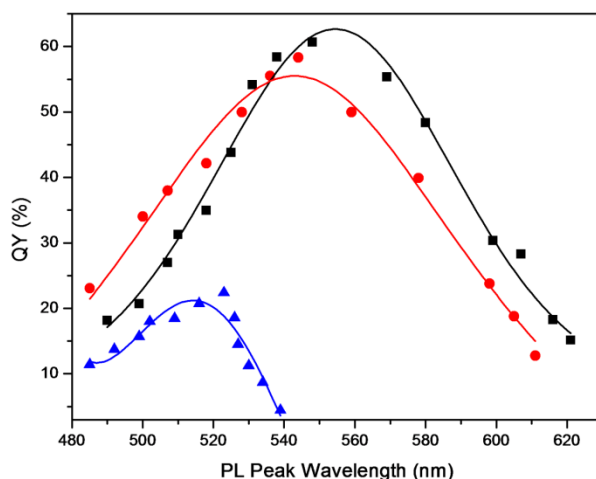


Figure S5 PL QY curves of  $\text{Ag}^+$ -doped CdS NCs with different ratio of  $\text{Ag}^+$  to  $\text{Cd}^{2+}$  in precursors solution synthesized through core/shell-doping strategy: 1:10 (■), 1:20 (●) and 1:40 (▲).

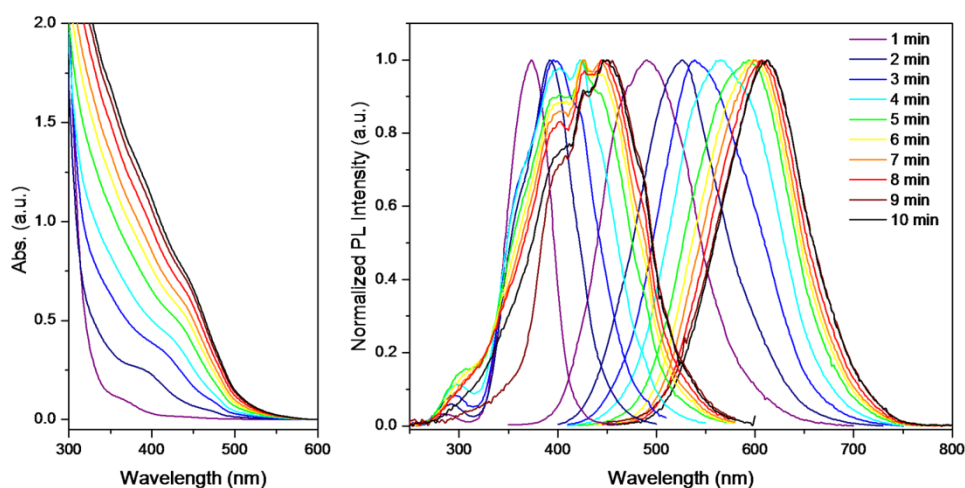


Figure S6 Temporal evolution of the absorption spectra (left) and PL emission spectra (right) of  $\text{Ag}^+$ -doped CdS NCs samples with GSH as mercapto-ligand obtained at different time intervals.

We have attempted to prepare the C-NCs by refluxing of precursors at  $100^\circ\text{C}$ , but the PL emission of colloidal solution is not reproduced. This indicates that the silver ion has not been doped into the host or only attached on the surface of NCs. A possible explanation is that the electromagnetic energy interacts with the NCs at the molecular level, where the electromagnetic energy is transferred and converted to heat through the motion of the molecules.<sup>[8]</sup> This results in rapid and uniform heating of the aqueous semiconductor NCs and therefore high quality NCs

(QY~60%).<sup>[9]</sup> In contrast, the refluxing only transfers heat from the surfaces of the solution and the process is dependent on several parameters: diffusion of heat and conductivity of solution.

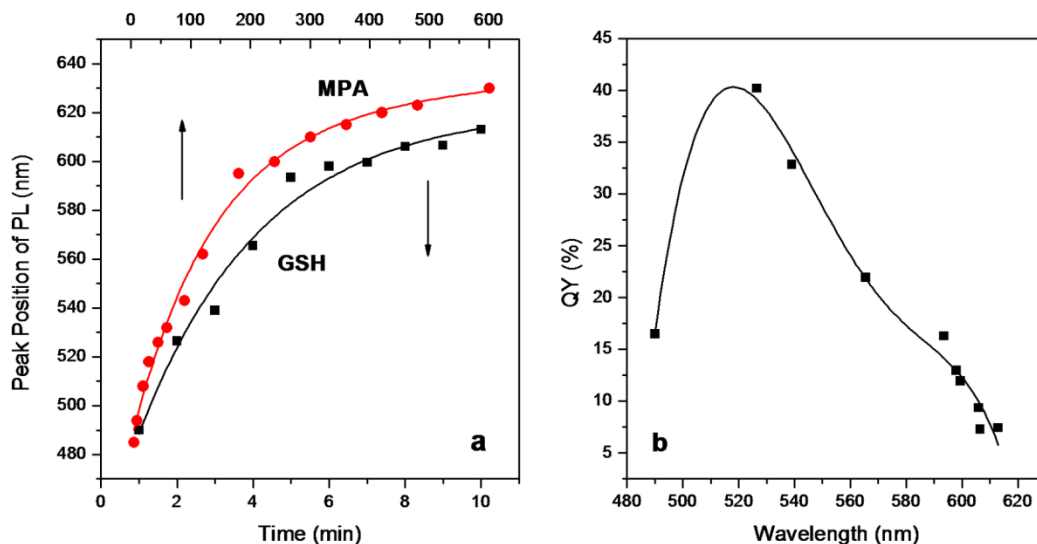


Figure S7 (a) Temporal evolution of PL peak position of doped NCs with MPA (●) and GSH (■); (b) PL QY curve of doped NCs with GSH.

Moreover, the evolution of optical properties is also related to the ratio of silver ions to cadmium ions in precursor solutions. With the decline of ratio, the PL emission scope goes from 480~630 nm to 480~550 nm, and their FWHM of excitation change from 150 nm to 85 nm, as shown in Fig.S4. This indicates that the doping level increases gradually by increasing the  $\text{Ag}^+$  ratio in precursor from 2.5 to 10%. In the Williams-Prener model, the more impurities NCs are doped, the longer wavelengths emission peaks shifts due to the shortening of the distance between conduction band and valence band.<sup>[10]</sup> Interestingly, the sharpness of absorption peak is about three times higher than others, when the ratio of silver impurity to host is 2.5%, which is similar to the absorption spectra of N-NCs. It is confirmed indirectly that the concentration of impurity doped in core of N-NCs is not more than 0.05 mM and the PL emission of doped NCs greatly depends on the concentration of impurity in central position. Fig.S5 is PL QY curves of  $\text{Ag}^+$ -doped CdS NCs with different ratio of  $\text{Ag}^+$  to  $\text{Cd}^{2+}$  in precursors solution synthesized

through core/shell-doping strategy. This indicates higher level of  $\text{Ag}^+$  is good for improving PL QY of doped NCs, but if the ratio is more than 10%, the stability of colloidal solution would be influenced greatly.

The effect of mercapto-ligands on the PL properties of doped NCs is also studied. Some mercapto-ligands used for growing NCs are selected as capping reagent, such as, GSH, Cys and TGA. However, all of them are not fit for the synthesis of doped NCs but GSH. Serious precipitation is observed for the resulting NCs within 2 hours. Fig.S6 presents temporal evolution of the absorption spectra and emission spectra of C-NCs (ratio=1:20) with GSH. Within 10 minutes, the position of emission peak shifts from 490 nm to 610 nm and their corresponding PL QY (~40%), as shown in Fig.S7. Consequently, the thiol capping-molecules with amino group are propitious to growth of doped NCs, but it is not crucial to improve the PL QY of doped NCs.

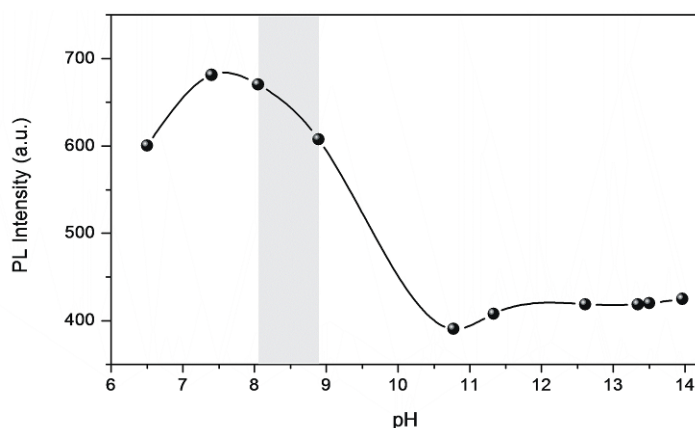


Figure S8 Influences of pH value on the PL intensity of NCs solution.  $1 \text{ mol}\cdot\text{L}^{-1}$  NaOH or HCl solution is used to adjust the pH of NCs solution to between 6 and 14.

Finally, the pH value of the solution influenced the PL intensity and stability of doped-NCs. As shown in Fig.S8, PL intensity of doped NCs was highest when the pH value was around 7.5. And the PL intensity of doped NCs was lowest when the pH value was from 10.5 to 14. However, their stability increased gradually (from several days to months) as the value of pH shifted from 6.5 to 8. And when the pH value is more than 8, the stability of doped NCs was good enough for months. To keep the well stability and PL intensity of doped NCs, the optimum of pH value is

from 8 to 9.

## References

1. G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991.
2. J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, 2<sup>nd</sup> ed., 1992.
3. J. Han, H. Zhang, Y. Tang, Y. Liu, X. Yao and B. Yang, *J. Phys. Chem. C*, 2009, **113**, 7503.
4. S. F. Wuister, C. M. Donegá and A. Meijerink, *J. Phys. Chem. B*, 2004, **108**, 17393.
5. A. Hässelbarth, A. Eychmüller and H. Weller, *Chem. Phys. Lett.*, 1993, **203**, 271.
6. C. Wang, Y. E. L. Fan, S. Yang and Y. Li, *J. Mater. Chem.*, 2009, **19**, 3841.
7. N. Pradhan, D. Goorskey, J. Thessing and X. Peng, *J. Am. Chem. Soc.*, 2005, **127**, 17586.
8. J. R. Lill, E. S. Ingle, P. S. Liu, V. Pham and W. N. Sandoval, *Mass Spectrom. Rev.*, 2007, **26**, 657.
9. L. Li, H. Qian and J. Ren, *Chem. Commun.*, 2005, 528.
10. (a) E. F. Apple and F. E. Williams, *J. Electrochem. Soc.*, 1959, **106**, 224; (b) J. S. Prener and D. J. Weil, *J. Electrochem. Soc.*, 1959, **106**, 409.