From Cu₂S nanocrystals to Cu doped CdS nanocrystals through cation exchange: controlled synthesis, optical properties and their p-type conductivity research

Jian Liu¹, Yuheng Zhao¹, Jialong Liu², Shouguo Wang³, Yan Cheng⁴, Muwei Ji¹, Yuanmin Zhou¹, Meng Xu¹, Weichang Hao² and Jiatao Zhang^{1*}

Heterovalent doping represents an effective method to control the optical and electronic properties of semiconductor nanocrystals (NCs), such as the luminescence and electronic impurities (p-, n-type doping). Considering the phase structure diversity, coordination varieties of Cu atoms in Cu₂S NCs, and complexity of Cu doping in II-VI NCs, monodisperse Cu₂S NCs with pure hexagonal phase were synthesized firstly. Then through cation exchange reaction between Cd ions and well-defined Cu₂S NCs, dominant Cu(I) doped CdS NCs were produced successfully. The substitutional Cu(I) dopants with controllable concentrations were confirmed by local atom-specific fine structure from X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS) spectroscopy, elemental analysis characterizations from X-ray photoelectron spectroscopy (XPS) and the electron spin resonance (ESR) measurement. The dominant and strong Cu(I) dopant fluorescence was verified by their absorption and photoluminescence (PL) spectra, and PL lifetime. Finally, the band positions and the p-type conductivities of the as-prepared Cu₂S and Cu(I) doped CdS NCs were identified by ultraviolet photoelectron spectroscopy (UPS) measurements. The high monodispersity of NCs enables their strong film-scale self-assembly and will hasten their subsequent applications in devices.

INTRODUCTION

Doping transition metal ions into II-VI semiconductor nanocrystals (NCs), by the intentional insertion of impurities, such as Mn, Cu and Ag ions, has garnered enormous interests in the past two decades. They have exhibited the advantages such as tunable emission, large Stoke shifts, thermal stability, and higher excited state lifetime [1–6].

Along this direction, Cu(I) and Ag (I) ions could act as heterovalent dopants and control both optical and electronic impurities properties of II-VI NCs [6–11]. However, the common problem to be encountered in the case of Cu-doped semiconductor NCs is the oxidation state of Cu ions and induced stable p-type conductivity [12,13]. Evidence from several reports showed that both Cu(I) and Cu(II) ions were stable in the oxidation state, which results in the difficulty in defining the Cu doping locations and establishing the mechanism of Cu luminescence [10–15]. For instance, some reports verified that sulfide could reduce Cu(II) to Cu(I) ions by electron paramagnetic resonance (EPR) measurement in CdS and ZnS hosts, which establish that Cu(I) can be the stable oxidation state [11,14]. Therefore, in order to get substitutional Cu(I) doping in II-VI NCs with higher purity, we chose stoichiometric Cu₂S NCs as starting materials and took advantage of cation exchange between them and Cd²⁺ ions to get Cu(I) doped CdS NCs.

Copper sulfide includes many solid phases known as CuS, Cu_{1.8}S, Cu_{1.96}S and Cu₂S, because of the common co-existence of Cu(II) and Cu(I) ions [16,17]. They have been identified as p-type semiconductor materials, because of copper vacancies in their crystal lattice [18]. The synthesis of their monodisperse NCs with high pure phase is necessary for their further optical, electronic applications. However, Cu₂S NCs are prone to form mixed phases as previous reports, which limit their electronic applications [17,19]. CdS is an important II-VI semiconductor material with bulk band gap of 2.4 eV. Due to the self-compensation ef-

¹ Beijing Key Laboratory of Construction-Tailorable Advanced Functional Materials and Green Applications, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China

² Department of Physics, Beihang University, Beijing 100191, China

³ Department of Materials Physics and Chemistry, University of Science and Technology Beijing, Beijing 100083, China

⁴ Laboratory of Chemical Biology, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

* Corresponding author (email: zhangjt@bit.edu.cn)

fect from intrinsic S vacancies that serve as donor dopants, CdS exists as n-type semiconductor naturally [20,21]. It is difficult to synthesize CdS NCs with p-type doping. However, with the advantages in band alignment and cathodic protection, p-type CdS can overcome the shortcomings of n-type CdS in photocathodes [22].

Due to intrinsic self-purification effect of dopants [1], in order to get stable p-type or n-type doped level in semiconductor NCs, the acquirement of effective heterovalent substitutional doping is the very first step. Cation exchange has been demonstrated as a synthetic strategy to obtain monodisperse semiconductor NCs with preserving original size, shape and tunable composition and dopants of semiconductor NCs [23–27]. Several research groups have achieved the electronic impurities through the cation exchange between II–VI NCs matrix and dopant ions [4,28,29]. In order to get deep-position location of Cu(I) dopants in CdS matrix, we took a special cation exchange process (Fig. 1a) between Cu^+ ions in stoichiometric Cu_2S NCs and Cd^{2+} in solution. From exterior to interior, trace tributylphosphine (TBP) initiates cation exchange and generates single crystalline CdS NCs with trace Cu(I) residue deep inside. Therefore, we synthesized monodisperse stoichiometric Cu_2S NCs with pure hexagonal phase firstly. Then through cation exchange reactions of Fig. 1a, dominant Cu(I) doping in CdS NCs was obtained. The Cu(I) doping with controllable concentrations in produced CdS NCs lattice matrix and dominantly substitution of Cd ions were confirmed by X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) analysis and the electron spin resonance (ESR) measurement. Cu(I) dopant induced stable luminescence was demonstrated by the room-temperature steady photoluminescence (PL) spectra and luminescence lifetime. The p-type conductivities and band structures of the as-prepared Cu_2S and Cu(I) doped CdS NCs were identified by ultraviolet photoelectron spectroscopy (UPS) analysis.

EXPERIMENTAL SECTION

Materials

All chemicals were used without further processing. Cupric chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, #10125-13-0, >99% purity) and sodium stearate ($\text{C}_{18}\text{H}_{35}\text{NaO}_2$, #822-16-2, >96% purity) were purchased from Beijing Chemical Works. Dodecanethiol (DDT, #122-55-0, >98% purity) was purchased from Sinopharm Chemical Reagent Co., Ltd. TBP (#998-40-3, >95% purity) and cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, #10022-68-1, >99% purity) were purchased from Aladdin. Oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$, #112-80-1,

>99% purity) were purchased from Aladdin and oleymanine ($\text{C}_{18}\text{H}_{37}\text{N}$, #112-90-3, 80%–90% purity) was purchased from Beijing InnoChem Science & Technology Co., Ltd.

Monodisperse Cu_2S NCs preparation

The copper stearate ($\text{Cu}(\text{St})_2$) was synthesized according to the reference [30]. Then, 0.25 mmol (157.7 mg) $\text{Cu}(\text{St})_2$ and 0.25 mL DDT were mixed in a Teflon autoclave, followed by adding 5 mL oleic acid and 3 mL oleymanine. After stirring for 3 min, the mixture was heated at 200°C for 2.5 h. The resulting products were precipitated by ethanol and dispersed in toluene.

Cu(I) doped CdS NCs preparation

Typically, 0.25 mmol Cu_2S NCs dispersed in 8 mL toluene were mixed with 1 mL $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ methanol solution (0.1 g/mL). Then, 0.1 mL TBP was added, and the mixture was reacted at 56°C for 2 h under magnetic stirring. The resulting products were precipitated by ethanol and dispersed in toluene. 2.2% concentration of Cu dopants in CdS NCs can be obtained.

To achieve different concentrations of Cu dopants, the addition of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ methanol solution and the reaction temperature should be altered. For 4% concentration of Cu dopants in CdS NCs, for instance, 0.1 mL $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 g/mL) methanol solution should be added to the Cu_2S colloid solution and the reaction temperature should be changed from 56°C to 25°C. Also, to get 0.5% Cu dopants, 3 mL $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 g/mL) methanol solution was needed and the reaction temperature should be kept at 65–70°C for 3 h. When 4 mL $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 g/mL) methanol solution was added and kept at 65–70°C for 5 h, similarly, the more complete cation exchange would happen. In this case, the Cu dopant concentration was almost close to 0%.

Low resolution and high resolution transmission electron microscopy

Samples for transmission electron microscopy (TEM) characterizations were prepared by placing one drop of toluene colloid onto a 300 mesh copper grid with a carbon support film. A JEOL JEM 1200EX working at 100 kV and a high-resolution TEM (FEI Tecnai G2 F20 S-Twin working at 200 kV) were utilized to characterize the morphology, crystal lattice details, energy dispersive spectra (EDS) elemental mapping and line scan elemental analysis. The HRTEM image intensity was analyzed by DigitalMicrograph (Gatan Co. LTD.).

To investigate the location and extent of lattice distortion of the as-prepared CdS NCs induced by Cu doping, in-

Figure 1 (a) Schematic illustration of the preparation process to achieve deep monovalent Cu doping in CdS NCs. (b) XRD patterns of the as-prepared Cu₂S and CdS NCs. (c and d) HRTEM images of Cu₂S NCs (c) and Cu doped CdS NCs (d), inset: single particle of CdS NCs and line profile analysis by digital micrograph. (e) Typical HRTEM image of Cu doped CdS NC along <0001> and corresponding strain mappings for Dxx, Dyy, Rxy and Sxy by GPA analysis.

plane strain was calculated by STEM_CELL software based on the developed theory, geometric phase analysis (GPA), which enables us to construct false colour strain maps of fringe deformation in two reference directions (D_{xx} and D_{yy}), fringe rotation (R_{xy}) and shear strain (S_{xy}).

Inductive coupled plasma–optical emission spectroscopy analysis

100 mg/mL Cu doped CdS NCs in hexane were evaporated to powders for the Cu dopants concentration analysis using inductive coupled plasma–optical emission spectroscopy (ICP-OES) from ICP-OES iCAP6300. The measurement parameters were: plasma power 1150 W; atomized gas velocity 0.6 L/min; auxiliary flow 0.5 L/min; pump rate 50 rpm.

XPS analysis

The XPS spectra were obtained from a PHI Quantera II X-ray photoelectron spectrometer using Al K α non-monochromatic radiation. The colloidal nanocrystals were dip-coated on glass substrate for XPS characterization. The measurement parameters were: light spot size 100 μ m; power 100 W; voltage 20 kV. An energy correction was made to account for sample charging based on the C 1s peak at 284.8 eV. The elemental concentrations were reported relative to carbon, calculated from the XPS spectra based on the area of the characteristic photoelectron peaks after correcting for atomic sensitivity.

XANES and EXAFS characterizations

The Cd k -edge and Cu k -edge XANES and EXAFS (extended X-ray absorption fine structure) spectra of CdS NCs doped with Cu were collected in fluorescence mode due to the lower concentration, and the Cu k -edge of CuS and Cu₂S were collected in transmission mode on beamline BL14W1 at Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics (SINAP), China. The electron beam energy was 3.5 GeV, and the maximum stored current was 300 mA. The raw data analysis was performed by using the FEFF6 software package according to the standard data analysis procedures.

ESR measurement

EPR measurements were performed with powder samples at room temperature in an electron spin resonance spectrometer (JEOL ESR FA-200) at X-band (9.0 GHz).

UV-Vis-NIR absorption and photoluminescence spectroscopy

The UV-Vis-NIR absorption spectra of the as prepared

CdS QDs toluene colloids were recorded on a Shimadzu UV3600 UV-Vis-NIR spectrophotometer at room temperature (RT). The steady state luminescence spectra of colloidal samples were collected on a Hitachi F-4500 fluorescence spectrophotometer at RT.

Fluorescence lifetime characterization

The ps time-resolved fluorescence apparatus supplied with the excitation laser pulses (450 nm) by an optical parametric amplifier (OPA-800CF, Spectra Physics) was used and the measurements were carried out at RT. The excitation energy at the sample was 50 nJ/pulse. Fluorescence collected with the 90°-geometry was dispersed by a polychromator (250is, Chromex) and detected by a streak camera (C5680, Hamamatsu Photonics). Analysis of the kinetic traces derived from time-resolved spectra was performed individually using nonlinear least-squares fitting to a general sum-of-exponentials function after deconvolution of the instrument response function (IRF). The absolute quantum yields of 2.2% Cu doped CdS NCs was analyzed on Hamamatsu absolute quantum yield spectrometer C11347 with the excitation laser pulses (360 nm).

UPS characterizations

Samples were analyzed on Thermo Scientific ESCALab 250Xi using UPS. The gas discharge lamp was used for UPS, with helium gas admitted and the He I (21.22 eV) emission line employed. The helium pressure in the analysis chamber during analysis was about 2×10^{-8} mbar. The data were acquired with -10 V bias.

RESULTS AND DISCUSSION

Many reports indicated that colloidal Cu₂S NCs were prone to form as the hexagonal and cubic phase mixtures [19,31]. Herein, hexagonal phase chalcocite Cu₂S NCs (JCPDS # 26-1116) with good purity and crystallization were synthesized successfully, as confirmed by XRD pattern and the indexed lattice spacing in Figs 1b and c. Then based on cation exchange process shown in Fig. 1a, hexagonal structured CdS NCs (JCPDS # 41-1049) were produced (see also XRD patterns in Fig. 1b). The cation exchange scheme in Fig. 1a hints the possibility that little of Cu⁺ remains in the NCs. The presence of Cu residue was confirmed by ICP-OES elemental analysis and could reach to the concentration of 2.2% typically (Table S1 in the supplementary information). It is difficult to identify Cu atoms in CdS lattice matrix directly by TEM imaging because of the adjacent atomic numbers of Cu to Cd. Herein, based on the correction with HRTEM image of CdS without defects (Fig. S1), line profile analysis by digital micrograph (Fig. 1d) and the

strain mapping by GPA of HRTEM images were applied to characterize the Cu doping induced lattice strain. The inserted intensity line profiles along the rectangles in Fig. 1d show intensity changes from the substitution by Cu^+ for Cd^{2+} in the lattice matrix. The binding force of S–Cd differs with that of S–Cu in Cu doped CdS NCs, leading to lattice distortion and thus contrast variation pixel by pixel. From GPA analysis (see the details of GPA analysis in SI-1), it is indicated that Cu(I) ions are in the deep position of CdS matrix.

The large-scale TEM images in Figs 2a and b confirm the high monodispersity of as-prepared Cu_2S and Cu doped CdS NCs with the average diameter of 4.1 nm. The high monodispersity of NCs and the appropriate van der Waal forces provided by the capping ligands enable the self-assembly of NCs into superlattice [19,32]. As a result, large-scale multilayer superlattices of Cu_2S and Cu doped CdS

NCs with hexagonal close packing order can be easily established (Figs 2c and d). This effective bottom-up self-assembly has laid the foundation for their use in large-area film applications (see also the insert pictures of their films). When prolonging the reaction time of Cu_2S NCs to 3 h, the average size of Cu_2S NCs could be tailored to be 5.9 nm and then similarly sized Cu doped CdS NCs could be obtained via cation exchange (see Fig. S2).

To characterize the Cu dopant concentration and locations via cation exchange, XPS, XANES and EXAFS spectroscopy of Cu doped CdS NCs were carried out. XPS analysis of the as-prepared CdS NCs are shown in Figs 3a, 3b and S3. The Cd 3d peak is split into $3d_{5/2}$ (403.5 eV) and $3d_{3/2}$ (410.3 eV) peaks and the peaks at 160.5 and 161.5 eV correspond to S 2p transitions (Fig. S3). These observed binding energy values are in agreement with the reported data on CdS NCs [33,34]. The Cu dopant XPS spectra

Figure 2 HRTEM images of (a) Cu_2S and (b) Cu doped CdS NCs. (c and d) NCs and their initiative large-scale self-assembly into superlattice, with the inset showing their bulk sized film on glass substrate.

Figure 3 XPS spectra of Cd 3d (a) and Cu 2p (b) in the as-prepared CdS NCs. (c) Cu k -edge XANES spectra of CuS, Cu₂S, and 2.2% Cu dopant in CdS NCs. (d) Magnitude of the Fourier transforms of k^3 -weighted Cu k -edge and Cd k -edge EXAFS functions in 2.2% Cu doped CdS NCs, Cu₂S NCs, and CuS.

with different concentrations (4%, 2.2% and 0.5%) in Fig. 3b show two symmetric peaks at 931.8 and 951.5 eV with a peak splitting of 19.8 eV, characteristic of monovalent copper [35]. XANES and EXAFS analysis are useful to determine the oxidation states of the Cu dopants and the nearest neighbor coordination profiles of Cu atoms [36–38]. The k -edge XANES spectra of 2.2% Cu dopants is shown in Fig. 3c, compared with CuS and Cu₂S. As shown, Cu(I) compound Cu₂S exhibits a lower energy absorption edge at about 8982 eV, while the Cu(II) compound CuS shows higher energy at 8985 eV, as indicated by the dash lines. The absorption edge of CdS: 2.2% Cu (at 8982 eV) is more close to that of Cu₂S, suggesting the valence of Cu in CdS: 2.2% Cu is +1 dominantly. It is consistent with the XPS results. Fig. 3d shows the Cu k -edge Fourier transform of k^3 -weighted functions without phase correction for Cu₂S, CuS, and CdS: 2.2% Cu. For comparison, Cd k -edge EXAFS spectrum for CdS is also presented. Compared with Cu₂S and CuS, the coordination environment of Cu in CdS:

2.2% Cu is similar to that of Cu₂S. It is because that there are two coordination peaks in CuS while only one in Cu₂S and CdS: 2.2% Cu. In addition, the bond length of Cu–S in CdS: 2.2% Cu is shorter than Cd–S bond length in CdS due to the smaller ionic radius of Cu⁺ than Cd²⁺. These features support the dominance of substitutional Cu⁺ doping. Furthermore, the similar tetrahedral location of Cu in Cu₂S to that of Cd in the CdS matrix and the same hexagonal-close-packed matrix of sulfur atoms in chalcocite Cu₂S and CdS are the prerequisites for substitutional Cu⁺ doping. The analysis of Cu XPS spectra in CdS NCs verifies that the oxidation state of Cu dopant here is mainly Cu⁺. This is also consistent with the experimental fact that Cu₂S NCs precursor with good phase purity is chosen as a starting material in cation exchange process.

To further confirm Cu⁺ doping, the ESR measurement was performed on the Cu-doped CdS NCs with 2.2% concentrations of Cu and no optical excitation was observed. Since the electron configuration of Cu⁺ is 3d¹⁰, it should be

diamagnetic. If Cu exists as Cu^0 or Cu^{2+} in CdS NCs, it will give an obvious paramagnetic signal [11]. The results of ESR measurement are shown in Fig. S4 in Supplementary information. The data were normalized by the magnification and Cu mass amounts in doped CdS samples, CuCl_2 and $\text{Cu}(\text{NO}_3)_2$ which were calculated as 2%, 47.4%, 34%, respectively. It clearly shows that ESR spectra from CuCl_2 (red circles) and $\text{Cu}(\text{NO}_3)_2$ (blue diamonds) as reference samples exhibit strong signals with magnetic fields from 250 to 350 mT. This paramagnetic behavior comes from d^9 electron configuration of Cu^{2+} in CuCl_2 and $\text{Cu}(\text{NO}_3)_2$ respectively. However, no obvious paramagnetic signals are observed in this region of magnetic fields for Cu doped CdS samples, indicating that the samples are diamagnetic. The ESR measurements confirm the Cu^+ in Cu doped CdS samples, in good agreement with the analysis of XPS and XANES.

Fig. 4a shows the UV-Vis-NIR absorption spectrum of the as-synthesized Cu_2S NCs toluene colloid. Different from the nonstoichiometric Cu_{2-x}S NCs, there are no localized surface plasmon resonance (LSPR) induced absorp-

tion peaks in NIR region [17]. The absorption spectrum in Fig. 4a only shows the Cu_2S band gap induced absorption edge feature. This stoichiometric composition of Cu_2S precursor is helpful to get dominant Cu(I) substitutional doping in CdS NCs after cation exchange. UV-Vis absorption and RT steady PL spectra of the as-prepared CdS NCs colloid with different Cu dopant concentrations are shown in Figs 4b and c. The quantum confinement induced exciton absorption features in Fig. 4b confirm the CdS nanocrystal formation. Interestingly, exciton recombination induced emission in PL spectra can hardly be observed. However, with optimal Cu dopant concentration (2.2%), the defect-related red fluorescence peak at about 620 nm is strong and dominant at room temperature. The absolute quantum yields of 2.2% Cu doped CdS NCs reached to 28.9%. The higher and lower concentrations of Cu doping (see 4% and 0.5% Cu doping in Figs 4b and c) both lead to weaker dopant PL because they are not good for stable dopant level formation. Consistent with the reported complete cation exchange by Alivisatos group [23], the 0% Cu doping in CdS NCs here would lead to the coexistence of exciton re-

Figure 4 (a) UV-Vis-NIR absorption spectra of Cu_2S NCs. (b) Cu doped CdS NCs: UV-Vis absorption spectra with different Cu dopant concentrations. (c) Cu doped CdS NCs: RT steady state fluorescence spectra with different Cu dopant concentrations ($\lambda_{\text{ex}} = 400$ nm). (d) Dopant emission dynamics monitored at the peaks of 620 nm by time-resolved fluorescence lifetime (τ) measurements, inset: schematic diagram of electronic structure responsible for dominant 2.2% Cu dopant PL.

combination induced emission and wide weak surface trap emission at ~ 600 nm (see Fig. S5). As shown in Fig. 4d, the dominant fluorescence peak at ~ 620 nm exhibits ultra-long lifetime decay behavior. The 620-nm kinetic curve can be well fitted with a two-exponential model, resulting in two lifetimes of 0.2 μ s and 1.3 μ s, respectively. This long-lived fluorescence further supports the dominance of Cu dopant related emission. It is confirmed that this peak is not due to the surface states but because of the weak spatial overlap between the conduction band electron wave function and the localized copper state [39]. Though the nature of the Cu-related center in the CdS is not fully understood, it is generally agreed that the center is related to Cu T_2 state [40], which results from the split of Cu d levels and stay above the valence band. One possible origin for this only dopant-related peak is the recombination of carriers that are bound to the impurity with those that are optically excited into the lowest quantum-confined level [7]. When Cu is in the +1 state, activation of the impurity band occurs via nonradiative capture of a hole from the valence band, thus the Cu dopant emission results from the recombination of

electrons from the conduction band and Cu-bound holes in the Cu T_2 states [12]. The schematic diagram of electronic structure responsible for dominant Cu dopant PL is summarized in the insert schematic diagram in Fig. 4d. As a result, the self-quenching problem is solved here due to the large Stokes shift of 0.88 eV (Fig. S6), with benefits for their potential applications in luminescent solar concentrators (LSCs) and bio-imaging [41,42].

UPS is a convincing way to determine the valence band and Fermi level positions of semiconductors [43,44]. The energy band diagrams of the as-prepared Cu_2S and Cu doped CdS NC films were determined by UPS and UV-Vis absorption measurements (Figs 5 and 6). Calculated from UPS analysis (Figs 5a and b), the work function of the as-prepared Cu_2S NCs is 4.67 eV and the valence band maximum is 4.93 eV (detailed calculations can be found in supplementary information SI-2). Based on the valence band maximum and the band gap of the Cu_2S NCs film (1.08 eV) determined by UV-Vis absorption spectrum (Fig. 5c), the schematic representation of calculated band level positions of Cu_2S NCs film can be obtained in Fig. 5d. Similar

Figure 5 (a and b) UPS spectra of Cu_2S NC film; (c) UV-Vis absorption spectrum for the Cu_2S NC film. (d) Energy band diagrams of Cu_2S NC film determined from UPS and UV-Vis absorption measurements demonstrating calculation of work function and schematic representation of calculated band level positions.

Figure 6 (a and b) UPS spectra of 2.2% Cu doped CdS NCs film; (c) UV-Vis absorption spectrum for 2.2% Cu doped CdS NCs film. (d) Energy band diagrams of 2.2% Cu doped CdS NCs film determined from UPS and UV-Vis absorption measurements demonstrating calculation of work function and schematic representation of calculated band level positions.

to the calculations of Cu_2S NCs film, Cu doped CdS NCs can also be figured out. Obviously, both the Fermi levels of Cu_2S film and Cu doped CdS film are closer to the valence band, which confirms that Cu_2S is a p-type semiconductor material and verifies that heterovalent Cu(I) impurities in CdS NCs can produce p-type electronic impurity. Consistent with the reported p-type CdS films created by ion-implantation of Cu acceptors [21], a large proportion of the Cu dopants here have substituted into Cd sites and acted as acceptors. They are compensated with electrons from Vs centers and accommodated on Cd sites as Cu^+ ions. This is the origin of the p-type conduction in CdS NCs.

CONCLUSION

In summary, the hexagonal phase Cu_2S NCs and their topotactic conversion to be Cu(I) doped CdS NCs by cation exchange were synthesized successfully. The dominant substitutional Cu(I) dopant leads to the effective dopant luminescence and p-type conductivity in CdS NCs. The UPS characterizations figured out their band structures and the p-type conductivity. This study will enhance the understanding about fundamental mechanism of Cu do-

pants. The bottom-up assembly to be large-scale films will find wider potential applications in devices.

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- Author contributions** Zhang J initiated and guided the whole project.

Liu J, Zhao Y, Ji M, Zhou Y and Xu M conceived the study and wrote the manuscript. Liu J and Wang S executed the high resolution TEM study and ESR measurement. Cheng Y and Hao W acquired and analyzed the XANES spectra. All authors contributed to the discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Jian Liu was born in Jiangsu, China, in 1991. He received his BSc degree in 2013 from the University of Shanghai for Science and Technology, and is now studying at Beijing institute of technology for his MSc degree. His research interest includes doping semiconductor nanocrystals.

Jiatao Zhang was born in 1975. He received his PhD degree in 2006 from the Department of Chemistry, Tsinghua University, China. Currently he is Xu Teli Professor in the School of Materials and Engineering, Beijing Institute of Technology. He was awarded Excellent Young Scientist foundation of NSFC in 2013. He also serves as the director of Beijing Key Laboratory of Construction-Tailorable Advanced Functional Materials and Green Applications. His current research interest is inorganic chemistry of semiconductor based hybrid nanostructures to possess novel optical, electronic properties for applications in energy conversion and storage, catalysis, optoelectronics and biology.

中文摘要 异价掺杂, 能有效调控半导体纳米晶的电学及光学性能, 实现高效掺杂发光及n型、p型导电类型的调控. 因为Cu₂S晶型多变、Cu原子配位繁杂以及Cu掺杂II-VI纳米晶的体系复杂等问题, 本文提出一种全新的方法, 首先可控制备了单分散的高纯度六方相Cu₂S纳米晶, 然后通过可控的离子交换反应, 合成了单分散Cu(I)掺杂的CdS纳米晶. 通过X射线近边吸收谱(XANES)、扩展X射线吸收精细结构(EXAFS)、X射线光电子能谱(XPS)及电子顺磁共振波谱(EPR)等精确表征手段证实了可控浓度的取代型的异价Cu掺杂. 其紫外-可见吸收光谱、荧光光谱、荧光寿命光谱等表征证实了以Cu(I)掺杂为主导的掺杂发光, 绝对量子产率可达28.9%. 紫外光电子能谱(UPS)确认了Cu(I)掺杂的CdS为p型半导体. 高度单分散的CdS掺杂纳米晶可以形成大规模的自组装, 将会加速其在光电器件上的应用.