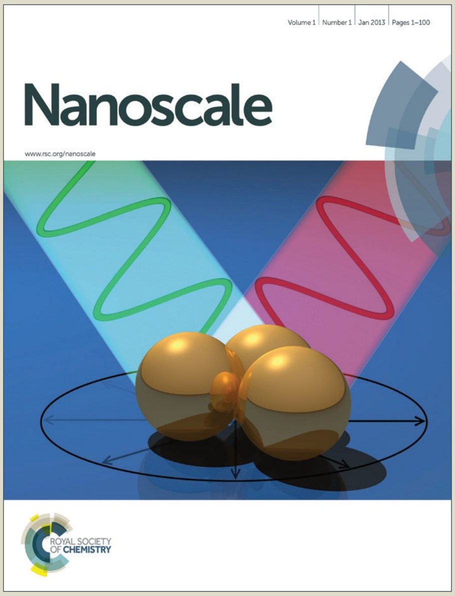

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Poly(vinylpyrrolidone) Supported Copper Nanoclusters: Glutathione Enhanced Blue Photoluminescence for Application in Phosphor Converted Light Emitting Devices

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Poly(vinylpyrrolidone) supported Cu nanoclusters were synthesized by reduction of Cu (II) ions with asorbic acid in water, and initially showed blue photoluminescence with a quantum yield of 8%. An enhancement of the emission quantum yield has been achieved by treatment of Cu clusters with different electron-rich ligands, with the most pronounced effect (photoluminescence quantum yield of 27%) achieved with glutathione. The bright blue emission of glutathione treated Cu NCs is fully preserved in the solid state powder, which has been combined with commercial green and red phosphors to fabricate down-conversion white light emitting diodes with high colour rendering index of 92.

Introduction

Noble metal nanoclusters (NCs) are tiny colloidal nanoparticles composed of a few to some hundreds of atoms, with a metal core size typically less than 3 nm.[1-7] Alongside with small size, low toxicity and biocompatibility they may exhibit reasonably strong photoluminescence (PL),[8-15] which makes them potentially interesting as bio-labels.[3] Numerous studies on luminescent Au and Ag NCs have been performed,[16-20] while it is more challenging to prepare stable Cu NCs, as they are suffering from easier oxidation in air. At the same time, copper is cheap and earth abundant element, and the fabrication of high quality luminescent Cu NCs may be important for their use in light-emitting diodes (LEDs).[21-23] Wu et al combined Cu NCs with aggregation induced PL with Au NCs,[21] while Liu et al fabricated LEDs employing Cu and Au nanosheets obtained by electrophoretic deposition of Cu and Au NCs.[23] Among the reported synthetic approaches,[24-32] polymer based method providing both binding sites (serving as a support) for Cu ions to be reduced by the suitable agents and steric hindrance to stabilize the resulting Cu NCs is an attractive approach. Polymers, proteins and DNA have all been employed to synthesize Cu NCs,[33-35] though with relatively low PL quantum yield (QY) which commonly does not exceed 10%.[36] Very recently, Pellegrino group reported Cu NCs with PL QY reaching 30% in water, employing an amphiphilic block copolymer as a suitable template.[37] Several studies have been focusing on understanding the mechanism of PL in Cu NCs, which can originate both from the metal core and the interactions between metal core and the surface ligands.[27,38,39] Wang group reported Cu NCs with dual PL emission at 420 and 600 nm, which has been ascribed to emission from singlet excited states and ligand–metal charge transfer, respectively.[27]

In this paper, we report on the aqueous synthesis of poly(vinylpyrrolidone) (PVP) supported Cu NCs, which as-prepared emit in blue region of spectrum with a PL QY of initially 8%. The PL of as-synthesized Cu NCs can be strongly enhanced to 27% QY as a result of the treatment with glutathione (GSH). To obtain more insights into the PL enhancement mechanism, a number of other short-chain water-soluble ligands all bearing a mercapto-group with combination with other polar groups (-OH, NH_2, -COOH) such as cysteine, cysteamine, 2-mercaptoethanol and 3-mercaptopropionic acid have been employed to treat the surface of as-synthesized Cu NCs. Bright blue emitting GSH treated Cu NCs were combined with commercial green and red phosphors for fabrication of down-conversion white light-emitting devices (LEDs) with a high color rendering index (CRI) of 92.

Materials and methods

Materials

All chemicals including PVP (average molecular weight: 40,000), L-ascorbic acid (AA), copper sulfate ($CuSO_4$), L-glutathione

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Electronic Supplementary Information (ESI) available: Details including optical spectra of control experiments for Cu NC synthesis, optimization of the reaction conditions, and spectra for LEDs chips and blue LEDs. See DOI: 10.1039/x0xx00000x

(GSH) reduced, L-cysteine, cysteamine hydrochloride, 2-mercaptoethanol (ME) and 3-mercaptopropionic acid (MPA) were purchased from Sigma-Aldrich. Silicone resins OE-6551A and OE-6551B were purchased from Dow Corning Co. Phosphors VG61E and MPR635 were obtained from Mitsubishi Chemical Holdings. GaN LED chips of a surface mounted device type (UV emission centered at 380 nm) with a luminous efficiency of 0.6 lmW^{-1} were obtained from EPILED CO., ltd. Milli-Q grade water (18.2 MΩ cm) was used for all experiments.

Apparatus

Absorption and PL spectra were measured on a Varian Cary 50 UV-visible spectrophotometer and a Cary Eclipse fluorescence spectrometer, respectively. Transmission electron microscopy (TEM) measurements with the related elemental analysis were performed on a TITAN microscope with an X-FEG type emission gun, operating at 60-300 kV, and equipped with a Cs image corrector and a STEM high-angle annular dark-field detector (HAADF), providing STEM-energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB-MKII 250 photoelectron spectrometer (Thermo, USA). Time-resolved PL lifetime measurements were carried out using a time-correlated single-photon counting (TCSPC) set-up with a 320 nm laser as the excitation light source. The absolute PL QYs of both solution based and powdered samples were determined using an integrating sphere on customized fluorescence spectrometer FLS920P (Edinburgh Instruments). Luminous efficiency, correlated color temperature, CIE color coordinates, and CRI of the LEDs were measured under different forward currents in an integrating sphere with a high accuracy array rapid spectroradiometer (Haas-2000, Everfine Co., Ltd China).

Synthesis of PVP supported Cu NCs

In a typical synthesis, 0.5 g PVP was added into 10 mL of water, sonicated for 10 min, and the pH was adjusted to 6.0 with NaOH solution (1 M). 1 mL of aqueous solutions of AA (0.1 M) and 0.1 mL of $CuSO_4$ (0.1 M) were mixed with the PVP solution and left to react for 6 days at room temperature. The appearance of blue emission as observed under a UV lamp indicated formation of Cu NCs, which were dialyzed against distilled water through a dialysis membrane with a molecular weight cut off of 14000 for 48 h, and stored at 4 °C for further use.

Post preparative surface treatment of Cu NCs

Different ligands (GSH, cysteine, cysteamine, ME and MPA) were used for the surface treatment of Cu NCs. 50 mM aqueous solution of each ligand was prepared through dissolution in 10 mL of water, and pH was adjusted to 4.0 using NaOH or HCl solution (1 M). 3.6 mL of dialysed aqueous solutions of Cu NCs were mixed with 0.4 mL of the ligand solutions, pH of mixtures was adjusted to 4.0, and they were kept at room temperature for 4 days before further measurements.

Fabrication of LEDs using GSH treated Cu NCs

The aqueous solution of GSH treated Cu NCs has been evaporated under room temperature under vacuum and the remaining solid was grinded into a fine powder. 0.3 g of GSH treated Cu NC powder was mixed with 0.1 g of thermal-curable silicone resin OE-6551A. The mixture was dried at 50℃ for 1 h, and mixed with 0.2 g of the hardener OE-6551B. For fabrication of white LEDs, 3 mg of VG61E and 6 mg of MPR635 phosphors were additionally added to the mixture alongside with the Cu NC powder. The devices were constructed by applying the above mixture onto commercially available GaN LEDs chips.

Results and Discussion

Fig. 1a illustrates the formation process of Cu NCs. PVP contains an amide group in each monomer, and has been widely employed as a stabilizer of metal nanoparticles.[12, 38] Copper ions are bonded to nitrogen by interaction of lone electron pairs of N atoms with empty orbitals of Cu^{2+}, resulting in zones of their high concentration. AA is a mild reduction reagent, able to reduce Cu ions preferably at such sites. After completion of the reduction, the resultant product was dialyzed in order to remove unreacted precursors and small molecular weight by-products, while leaving behind Cu NCs immobilized (supported) on PVP template. No emission was detected in dialyzing water, confirming that all luminescent clusters formed are linked to PVP support.

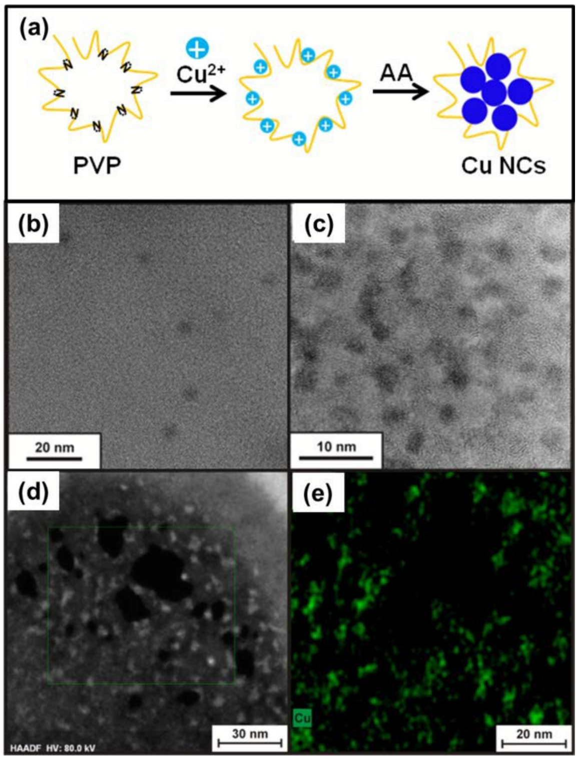

Figure 1. (a) Schematic illustration for the Cu NCs formation on PVP support; (b, c) HRTEM images of Cu NCs at different magnifications; (d) HAADF TEM image of Cu NCs, and (e) EDS elemental mapping of Cu from the selected area of c.

HRTEM images (Fig. 1b and c) show Cu NCs which are quasi-spherical in shape with a diameter around 3 nm. The presence of the PVP template makes it difficult to achieve high TEM image contrast and to resolve the cluster's crystallinity. To further verify the presence of Cu NCs, element-sensitive HAADF TEM images were obtained (Figure 1d), with bright spots identifying the presence of metallic copper. EDS elemental mapping further proved that these spots contain copper (Fig. 1e).

XPS analysis was carried out to study the oxidation states of Cu as shown in Fig. 2a. Reduction of copper (II) ions is confirmed by the absence of satellite features around 942 eV. Two peaks at 932 and 952 eV were assigning to $2p_{3/2}$ and $2p_{1/2}$ binding energies of Cu atom. We note that the difference between $2p_{3/2}$ peaks of Cu and Cu^+ species is only 0.1 eV.[27] Therefore, the valence state of the Cu in Cu NCs most likely lies between zero and one, which is consent with previous reports.[14, 27, 40]

Fig. 2b shows the UV–visible absorption spectrum of as-synthesized Cu NCs, with two peaks at 380 and 443 nm. Considering that control reactant mixtures containing PVP/Cu^{2+} or AA/Cu^{2+} do not exhibit similar absorption peaks (Fig. S1), these absorption peaks are ascribed to the inter-band electronic transitions of the Cu NCs formed in the presence of PVP.[32] Furthermore, no surface plasmon resonance absorption band around 560–600 nm was observed, indicating the absence of large copper particles.[27, 36] Well pronounced peak at 380 nm was observed in the PL excitation (PLE) spectrum of Cu NCs, which is consistent with literature.[41, 42] The PL emission spectrum of Cu NCs showed a peak at 423 nm, also in agreement with previous reports.[43, 44] Chen group prepared blue emitting Cu NCs (PL peak centered at 430 nm) using reduction of Cu^{2+} by AA on polyethyleneimine. [43] Cao and co-workers reported Cu NCs stabilized by tannic acid with a PL peak at 430 nm.[44] We note that neither PVP/Cu^{2+} nor AA/Cu^{2+} mixtures showed PL signals (Fig. S2), suggesting that the formation of Cu clusters indeed requires the combination of all the three reaction ingredients – copper (II) ions as a copper source, AA as a reducing agent and PVP as a supporting template. The as-synthesized Cu NCs were stable for over one month when stored at 4°C, without any detectable changes of their absorption and PL spectra.

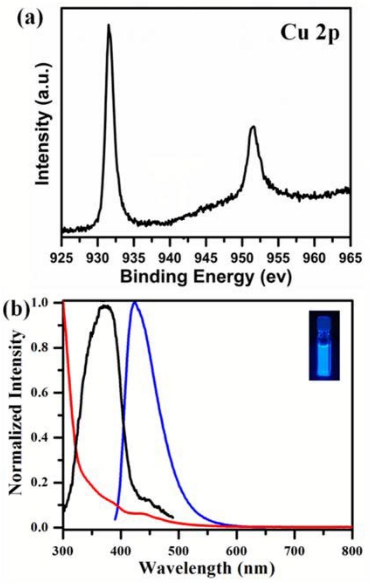

Figure 2. (a) XPS spectrum of Cu 2p electrons in Cu NCs. (b) Absorption (red line), PLE (black line, detection wavelength 430 nm) and PL (blue line, excitation wavelength 380 nm) spectra of as-synthesized Cu NCs (photograph of the blue emitting solution shown in inset).

The PL intensity of Cu NCs varied with the varying PVP concentration and pH of the PVP solution, reaching the maximum for 1.25 mM PVP at pH 6.0 (Fig. S3 and S4). Cu NCs synthesized at these conditions had PL QY of 8%, which is comparable to the previously reported methods.[30, 45, 46] PL of noble metal NCs may originate from the metal core or from the interactions between metal core and the surface ligands.[17, 47] The effect of surface ligands on PL of Au and Ag NCs has been widely studied, and it was found that ligands with electron-rich atoms or chemical groups improve the PL QY.[48-50] For Cu NCs, the ligand effect on PL has not been systematically explored so far. As a result of GSH treatment of as-synthesized Cu NCs, their absorption peak at 380 nm increased 5-fold (Fig. 3a) and the PL intensity of Cu NCs 9-fold, without changing the peak position (Fig 3b). The formation of new species as a result of GSH treatment can be ruled out by comparison of PLE spectra of as-synthesized Cu NCs and GSH treated ones (Fig. 3b), which confirms the same nature of the emitting species in both cases. The optimum PL enhancement for GSH treatment has been achieved at pH 4.0 (Fig. S5), where PL QY of Cu NCs reached 27%, the value comparable with the highest previously reported by Pellegrino et al.,[31] under employment of specifically designed amphiphilic block copolymer. The PL decay curves of as-synthesized and GSH-treated Cu NCs are presented in Fig. 3c, and do not change much as a result of the treatment. These curves can be fitted by three-exponential functions. For as-prepared Cu NCs, three components of 0.8 ns (41%), 3.6 ns (54%) and 9.2 ns (5%) were obtained. An average PL lifetime of 2.7 ns was calculated, which attributes to emission from the singlet excited state, as has been observed in the PL decays of previously reported Cu NCs.[27, 39] After GSH treatment, three components of 1.2 ns (42%), 3.0 ns (54%) and 8.6 ns (4%) with an average PL lifetime of 2.5 ns were obtained, which were almost the same as for the as-synthesized Cu NCs.

The strong PL enhancement observed for Cu NCs as a result of GSH treatment points out that their emission cannot solely be attributed to the metal core, but is rather related to its interaction with surface ligands. GSH possesses a thiol group, which has a strong metal-chelating ability, alongside with amino and carboxyl groups, which are electron-rich groups as well. To clarify the influence of external electron-rich ligands on the emission of Cu NCs, we tested different water-soluble ligands, such as cysteine, cysteamine, ME and MPA which all have -SH group at the one end linked by two -CH_2- to other electron rich group(s). As a result of the treatment,

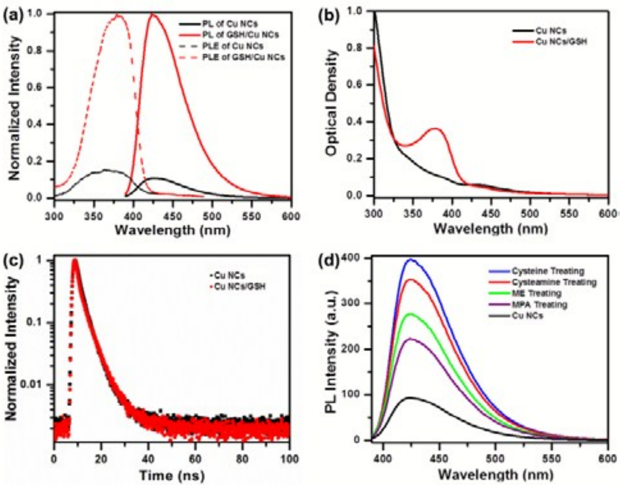

Figure 3. (a) Absorption spectrum and (b,c) PLE (detection wavelength 500 nm) and PL (excitation wavelength 380 nm) spectra of as-synthesized Cu NCs and GSH treated Cu NCs. (c) PL decays of Cu NCs and GSH treated Cu NCs (excitation wavelength 320 nm). (d) PL spectra (excitation wavelength 380 nm) of Cu NCs, as-synthesized and treated by different ligands listed in the frame.

enhancement of PL of Cu NCs has been observed indeed (Fig. 3d) without any changes in the emission peak position, alongside with an increase of the absorption peak at 380 nm (Fig. S6). The PL QY of Cu NCs treated with these ligands followed the order: cysteine (33%) > cysteamine (31%) > ME (29%) > MPA (22%) which well correlates with the inductive effect of the functional groups -COOH>-OH>-NH$_2$>-SH changing from their electron withdrawal to electron donation ability. This supports our hypothesis that the electron-rich groups of the ligands can improve the PL of Cu NCs. For comparison, Arakawa group synthesized Cu NCs without using any protective ligands, which showed a very low PL QY of 0.65%.[29] Jia et al. obtained Cu NCs using D-penicillamine (containing –SH, -NH$_2$, -COOH groups) as a ligand, with a PL QY reaching 17%.[39] Ghosh et al. prepared Cu NCs in the presence of lysozyme which contains -OH and –NH groups, with PL QY of 18%.[36] The highest reported value of PL QY for Cu NC was so far 30%, which was achieved by Pellegrino group using an amphiphilic block copolymer, containing poly(ethylene glycol) and sulfur atoms chains.[37] Chen group has found that the PL of dihydrolipoic acid-stabilized Cu NCs can be enhanced after addition of PVP.[51] Gosh et al. showed the pH sensitivity of PL of Cu NC with the mixed PVP/dihydrolipoic acid stabilizers[38]; protonation/deprotonation of -SH/S$^-$ and -COOH/-COO$^-$ groups of dihydrolipoic acid led to an increase of PL signal at pH >5,where the electron donating ability of those groups becomes higher. We note that Cu NC samples treated by different ligands differed in stability as the PL signal was concerned. GSH-treated Cu NCs were most stable and kept 50% of PL intensity after 5 days; for MPA and cysteamine treated NCs a decrease by 50% happened already after 1 day of storage at room temperature, and for cysteine and ME treated Cu NCs it happened after 2 days. The highest stability of GSH-treated Cu NCs can be attributed to both the longer carbon chain and the existence of oppositely charged functional groups (-COOH and -NH$_2$) on this particular ligand. The longer carbon chain of GSH has larger flexibility, which can diminish the diffusion possibility of subversive species (ions, dissolved oxygen) towards the Cu core. The oppositely charged functional groups could coordinate together via inter-ligand electrostatic interaction, and amplify the steric hindrance for the subversive species. This is consistent with previous studies by Xie group on Au NCs stabilized by ligands with different length and functional groups.[13]

PVP supported, GSH treated Cu NCs can be easily processed into the powder form in a rather large scale (>2 g), simply by drying the mother solution under vacuum. The obtained composite PVP/Cu NCs powder preserved optical properties of the solution-based samples, as demonstrated by its PLE and PL spectra shown in Fig. 4a. Notably, there was no change in PL QY after forming the powder, which remained as high as 27% in the solid state. The obtained NC powder has been employed as the color conversion layer of the blue and white LEDs, which were fabricated by applying the down-conversion mixtures onto commercial UV GaN chips. An efficient down conversion of the narrow emission spectrum of the GaN chip (centered at 380 nm) to the broader spectrum of Cu NC with a peak at 430 nm has been achieved, as shown in Fig. S7. Photograph of a blue LED fabricated by using Cu NCs powder as a down-conversion layer is presented in Fig. 4b, with a CIE chromaticity coordinates of (0.194. 0.175) (Fig. S7) and a CRI of 57.

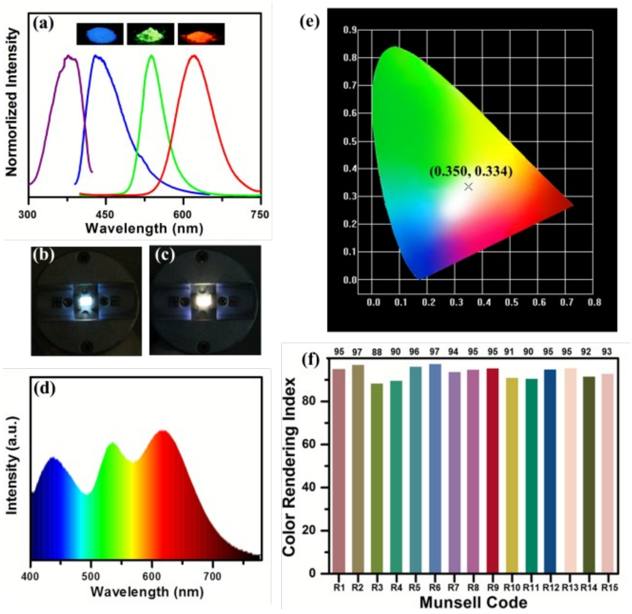

Figure 4. (a) PLE spectrum (detection wavelength 435 nm) of powdered GSH treated Cu NCs (purple line); PL spectra (excitation wavelength 380 nm) of powdered GSH treated Cu NCs (blue line), VG61E (green line) and MPR635 (red line) phosphors, with the photographs of the respective powders. Photographs of (b) blue LED and (c) white LED. (d) Emission spectrum, (e) CIE chromaticity coordinate and (f) CRI at various Munsell codes of white LED.

In order to fabricate white light LEDs, two commercially available green and red phosphors (see Materials and Methods for details) were mixed with Cu NCs powder. The emission spectra of the Cu NCs powder, and green and red phosphors excited at 380 nm are presented in Fig. 4a, together with the respective photographs. PL peaks are located at 434, 538 and 620 nm, respectively. Photograph of the white LEDs device and its three-component emission spectrum are shown in Fig. 4c and Fig. 4d. The white light has CIE chromaticity coordinate of (0.350, 0.334), which is close to that of sun light, [52] with a high CRI value of 92, color temperature of 4742 and a luminous efficiency of 9.8 lmW^{-1}. The CRI was obtained by calculating the average color rendering of each Munsell code (Fig. 4f). The CRI for each Munsell code was above 88 and a high value of 95 was observed for R12, which corresponds to the color rendering of blue reign. It demonstrates that Cu NCs employed in the down-conversion white LED provide high contribution towards the overall CRI. Table S1 shows the performance comparison of our devices with previously reported[21,23] metal NC-based white LEDs. A warmer white light with a higher CRI has been achieved, useful as an indoor lighting source.

Conclusions

In summary, we employed HRTEM, HAADF TEM, EDX mapping and XPS measurements to confirm the formation of Cu NCs supported on PVP template. The PL of as-synthesized Cu NCs has been strongly enhanced as a result of surface treatment with GSH, increasing from 8% to 27%. The observed trends in the PL enhancement using cysteine, cysteamine, MCH and MPA demonstrate that it originates from the interactions between Cu NCs and the electron-rich functional groups of these ligands. Strong blue emission of GSH treated Cu NCs has been fully preserved in the powdered state, allowing us to fabricate both blue and white LEDs (CRI 92) when combining Cu NCs with green and red-emitting phosphors. This study has provided a facile synthetic pathway towards strongly emitting, reasonably stable Cu NCs and demonstrated a convenient way to enhance their PL QY.

Acknowledgements. This work was supported by the Research Grant Council of Hong Kong S.A.R. (T23-713/11) and by the Ministry of Education, Youth and Sports of the Czech Republic (LO1305).

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