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Stable Luminous Nanocomposite of CsPbX₃ Perovskite Nanocrystal Anchored on Silica for Multicolor Anti-counterfeit Ink and White-LED

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Inorganic perovskite (CsPbX₃, X=Cl, Br and I) nanocrystals (NCs) have received great attention for their fascinating optoelectronic properties. However, their potential applications are primarily limited by the instability arising from their mobile ionic nature. Herein, we demonstrate extremely stable CsPbX₃ nanocomposites (denoted as CsPbX₃@CA-SiO₂) using a facile and effective templated synthetic strategy, by *in-situ* anchoring of CsPbX₃ NCs onto octadecyl/propylamine capped silica particles (SiO₂ NPs). The two-step synthesis involves first the preparation of amino-group capped silica NPs from a mixed 3-aminopropyltriethoxysilane (APTES) and trimethoxy(octadecyl)silane (TMODS) precursor, which were utilized to induce nucleation and growth of CsPbX₃ nanocrystals to give CsPbX₃@CA-SiO₂ composites with monodispersed CsPbX₃ NCs (~6 nm). The emission wavelength of the resulting composite can be tuned between 400 and 650 nm by controlling the halide composition while maintaining a high photoluminescence quantum yield (PLQY=76%). The as-fabricated composites exhibit remarkable photostability and water stability, both uncommon in these materials. The CsPbX₃@CA-SiO₂ composite can also be used to create an anti-counterfeit ink and down-converting white light emitting diode (WLED). This work provides a valuable approach for the production of future optoelectronic devices, catalysts and sensors based on perovskite NCs.

Introduction

Recently, inorganic lead halide-based perovskite nanocrystals CsPbX₃ NCs (X = Cl, Br or I) have drawn broad attention from groups around the world because of their exceptional optoelectronic characteristics, such as high quantum yields (QYs > 90%), narrow emission lines, controllable bandgaps and high carrier mobility.¹⁻⁵ These prominent optoelectronic properties make them promising candidates for high-performance perovskite-based devices, such as light-emitting diodes (LED), directional lasers, solar cells, photodetectors and display backlights.⁵⁻⁸

Despite their outstanding optoelectronic properties, large-scale and practical applications are seriously limited by the materials' inherent defects and instability⁹⁻¹⁰ towards polar solvents and environmental humidity.^{1,11} In addition, exposure to heat, halides or intense light also produce surface ligands losing, structural integrity changing, severe PL quenching, energy shifting, luminescent peak broadening, and unacceptably short device lifetimes.¹²⁻¹⁵

To overcome the inherent vulnerability, many strategies have been adopted to stabilize CsPbX₃ including: regulating surface ligands (the inclusion of long-chain, branched or sterically hindered surfactant as capping ligands),¹⁶⁻²⁰ modifying crystal composition (Mn doping),²¹⁻²² incorporating NCs into a protective inorganic matrix

(SiO₂, MOF or zeolite-Y)²³⁻²⁶ or polymers (polystyrene, polymethyl methacrylate, polyvinylidene fluoride, block copolymer micelles or POSS-based polymers)²⁷⁻³⁰ etc. These treatments can dramatically enhance the NC's stability by providing a physical barrier. However, most of these approaches were either only suitable for the preparation of luminescent films or bulk materials, were not water resistant, or were not UV stable. The realization of a scalable and stable perovskite nanocomposites remains a challenge.

To generate a stable perovskite light emitter, it is essential to explore a facile and efficient method to produce monodispersed and stable NC-based composites. Silica is an ideal candidate for protecting NCs because of its excellent stability, easy surface functionalization, large surface area, nontoxic earth abundance, and ability to isolate individual NPs to prevent sintering.^{24-25, 31, 32} In this study, we apply an *in-situ* templated growth method to anchor the CsPbBr₃ NCs on amino-ligand functionalized SiO₂ particles. The capped silica particles were prepared by anisotropic deposition of the hydrolyzed APTES and TMODS with *pre*-obtained SiO₂ particles. The alkylamine chains on SiO₂ particles then serve as surface ligands, preferentially coordinating the perovskite precursors (Pb²⁺ or Cs⁺) to form nucleation points and templating the formation of homogeneous NCs composites.^{29, 33} The perovskite NCs can be separated from each other and permanently anchored onto the surface of silica spheres to create a very stable material.³¹ The photostability and the stability towards water of the resulting CsPbBr₃@CA-SiO₂ composites were evaluated by tracking the material's relative PLQY over time of exposure. As a proof of concept, we then applied these composites as an ink for counterfeit-proof signs and as a green fluorophore in a white light emitting diode (WLED) device.

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Results and Discussion

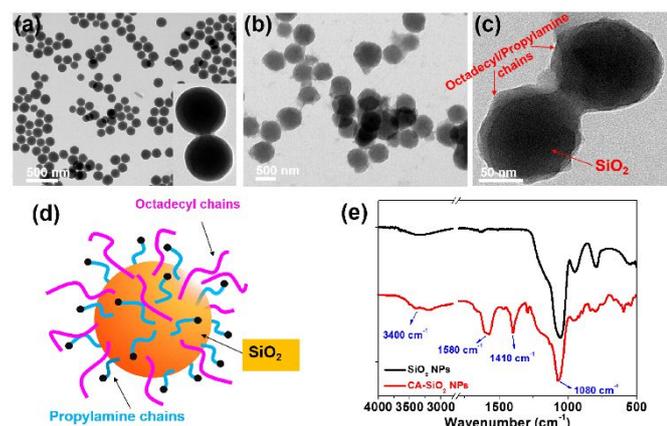


Fig. 1 Morphologies and structures of octadecyl/propylamine capped silica (CA-SiO₂) NPs. TEM images of pristine silica (a), octadecyl/propylamine capped silica NPs (b and c). (d) The schematic image of the capped silica NPs. (e) FTIR spectra of the capped (bottom) and pristine (top) silica.

We used octadecyl/propylamine capped silica spheres (SiO₂ NPs) as a substrate for the growth of CsPbBr₃ NCs. Firstly, the engineered SiO₂ NPs were synthesized by hydrolysis and condensation of *pre*-obtained SiO₂ NPs with APTES and TMOS (Supporting information Scheme S1). The capped silica (CA-SiO₂) NPs were characterized by transmission electron microscopy (TEM, Fig. 1). The functionalized silica particles present a uniform spherical morphology with a silica core and an octadecyl/propylamine shell. The particle diameter is approximately 115 nm, slightly larger than the primal silica particles (ca. 110 nm).

Functionalized silica particles were further characterized by Fourier transform infrared (FTIR) spectra and X-ray photoelectron spectroscopy (XPS). FTIR spectroscopy present strong band at 1100 cm⁻¹ and 800 cm⁻¹, assigned to the asymmetric stretching vibration, and symmetric stretching and deformation vibration of Si-O-Si (Fig. 1e). Several new peaks appear in the spectra of the functionalized silica, such as the vibrations of symmetric and asymmetric stretching vibrations of -CH₂- and -CH₃ (2850 cm⁻¹ and 2925 cm⁻¹), asymmetric deformation vibration of -CH₃ (1410 cm⁻¹) and specific deformation vibration of NH₂ (1560 cm⁻¹). XPS studies confirm the chemical element composition of CA-SiO₂ NPs (Fig. S1a) by the emerging peak at 401.88 eV for the binding energy of N1s. Thermogravimetric analysis yields a quantitative organic content about 16 wt% of CA-SiO₂, close to the amount of silane (APTES and TMOS) added (Fig. S1b). Therefore, a core-shell structural schematic drawing of the CA-SiO₂ NPs is depicted in Fig. 1d, featuring the silica core capped with octadecyl and propylamine groups.

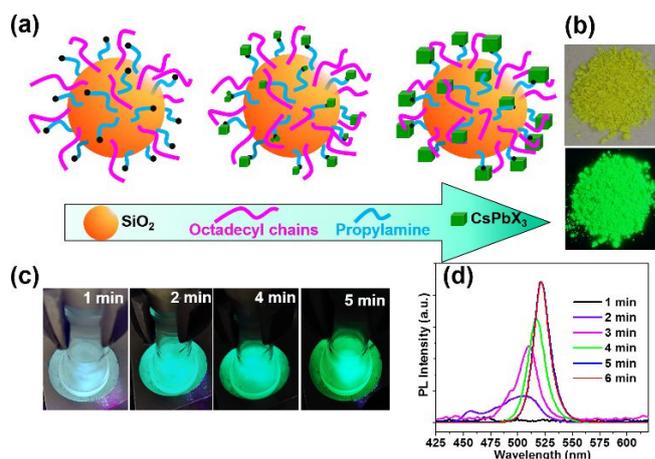


Fig. 2 (a) Schematic illustration of the synthesis of CsPbBr₃@CA-SiO₂. (b) Digital images of the composites under daylight and UV light. (c) Digital images of the reaction as a function of reaction time (0-5 min). (d) Photoluminescence spectra of the CsPbBr₃@CA-SiO₂ composites as a function of reaction time.

Generally, amino or carboxyl end groups coordinate precursors (Pb²⁺ and Cs⁺) to form nucleation points at which the perovskite NCs grow.^{29, 32} Herein, an *in-situ* growing mechanism for fabricating nanocomposite by anchoring CsPbX₃ spatially on SiO₂ particles is proposed in Fig. 2a. During the initial reaction system, nucleation can take place on the capped silica NPs' surface. Then, the precursors will further attach on the capped silica spheres surface over time, yielding CsPbBr₃@CA-SiO₂ composites with high luminescence.

As the reaction progresses, the transparent solution changes to glaucous and purple-blue emission under UV light, subsequently to blue and green (Fig. 2c). To gain insight into the reaction process, *in-situ* PL spectra as a function of reaction time were measured with an interval of 1 min in Fig. 2d. Initially no emission was detected. After 2 min, a weak and broad blue emission at 460-520 nm was observed, deriving from the nucleation and preliminary growth of NCs. After 3 and 5 min, cyan and bright green emission can be observed (Fig. 2d). With the prolongation of reaction time to 5 min, the PL spectra exhibited a continuous redshift and the PL intensity increased gradually. PL studies indicated that the *in-situ* growth can be quenched within 5 min by ice bath. The dried powder of CsPbBr₃@CA-SiO₂ also exhibits strong luminescence under UV light, which can be used as high performance solid-state emitters (Fig. 2b).

TEM show spherical shaped composites with fairly uniformly distributed NCs adhering on the surface of silica sphere (Fig. 3a and b). No obvious large particles are observed. High resolution TEM (HR-TEM) shows the crystallinity of CsPbBr₃ NCs and an average size of 6 nm (Fig. 3c-d). The decorative perovskite NCs on SiO₂ NPs surrounded with compact organic layers are notoriously sensitive to electron beam damage, so the HR-TEM images were taken quickly in order to minimize the exposure time.^{15, 29} In comparison, SEM images of the blend of silica NPs and *pre*-obtained perovskite particles (to serve as a control) exhibit obvious phase separation with randomly distributed CA-SiO₂ NPs and CsPbBr₃ NCs (Fig. S4).

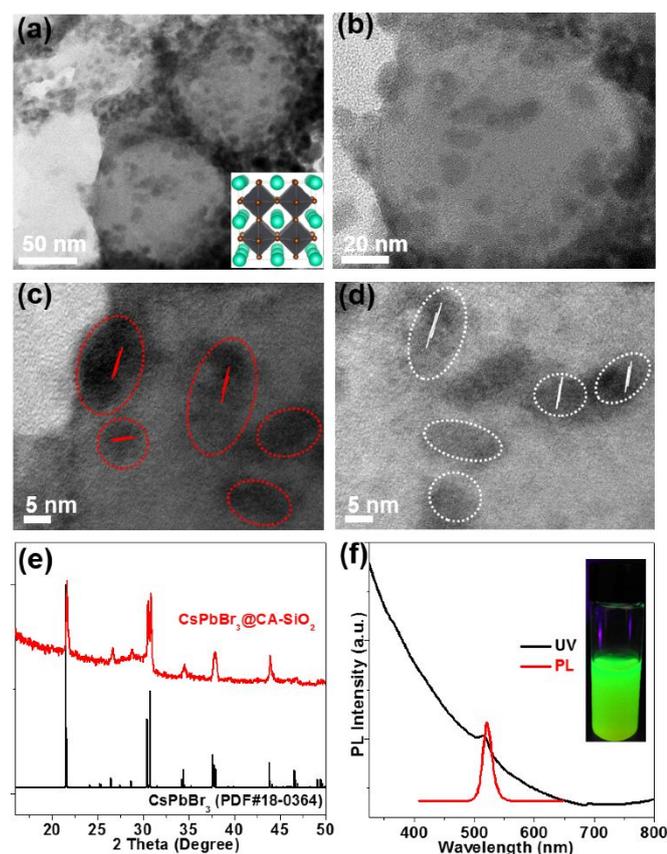


Fig. 3 Morphologies, chemical structures and optical properties of the CsPbBr₃@CA-SiO₂ composite. TEM (a), high-magnification TEM (b and d) and high resolution TEM (HR-TEM) images (c and e). The inset in (a) is a schematic image of the crystal structure of CsPbBr₃. (e) XRD pattern with the standard orthorhombic crystal structure of CsPbBr₃. (f) Optical absorption and PL emission spectra. Inset in (f) is a photograph of the colloidal solution of the composites under UV light.

Chemical structure of CsPbBr₃@CA-SiO₂ composites was analyzed with powder X-ray diffraction pattern (XRD), XPS and energy dispersive spectrometer (SEM-EDS) analysis. Powder XRD of the CsPbBr₃@CA-SiO₂ yielded peaks at $2\theta=17.6, 25.1, 35.6, 39.6, 43.5, 50.2, 53.2$ and 56.2° in the diffractogram, corresponding well to the orthorhombic CsPbBr₃ crystal phase (JCPDF #01-072-7929) (Fig. 3e).^{1, 2, 28} XPS analyses (Fig. S5a) further indicate that the elemental composition of the CsPbBr₃@CA-SiO₂ powder contains all the elements expected from the CsPbBr₃ NCs (Cs, Br and Pb) and capped SiO₂ (Si, C, N and O). The elemental ratio of Cs:Pb:Br measured by XPS is about 1:1.1:3.2, matching well with the expected ratio of CsPbBr₃.²⁸ SEM-EDS image further confirm the presence of Si, Cs, Pb and Br in the CsPbBr₃@CA-SiO₂ composite (Fig. S5b).

The UV-Vis absorption and photoluminescence (PL) spectra of the CsPbBr₃@CA-SiO₂ composite were shown in Fig. 3f. It was found that the absorption onset and PL emission peak of the CsPbBr₃@CA-SiO₂ composite are 518 nm and 520 nm, respectively (Fig. 3f), with a PLQY value of around 76%, higher than that of previously reported encapsulated NCs.³⁴⁻³⁶

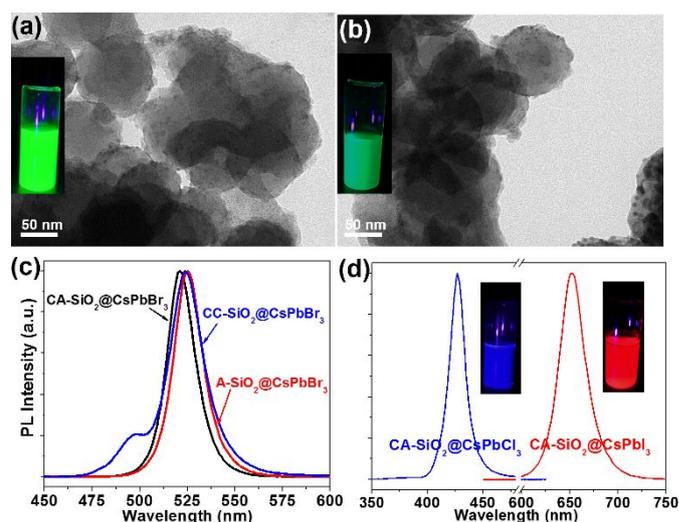


Fig. 4 Morphology and optical properties of CsPbBr₃@A-SiO₂ and CsPbBr₃@CC-SiO₂ spheres. TEM images of the typical CsPbBr₃@A-SiO₂ (a) and CsPbBr₃@CC-SiO₂ (b). Insets in (a) and (b) are photographs of the corresponding colloidal solutions under UV light. PL emission spectra of CsPbBr₃@CA-SiO₂, CsPbBr₃@A-SiO₂ and CsPbBr₃@CC-SiO₂ (c), and CsPbCl₃@CA-SiO₂ and CsPbI₃@CA-SiO₂ (d).

By virtue of the facile synthetic process, we can also prepare CsPbBr₃@A-SiO₂ (CsPbBr₃ NCs anchored on propylamine-capped silica NPs) and CsPbBr₃@CC-SiO₂ (CsPbBr₃ NCs anchored on octadecyl/carboxyl-capped silica NPs) composites. TEM analysis indicated the corresponding morphology in Fig. 4a and b. The anchored NCs distribute uniformly on SiO₂ particles, with average diameters between 6-14 nm. The crystallinity and elemental composition of CsPbBr₃@A-SiO₂ and CsPbBr₃@CC-SiO₂ were further confirmed by PXRD and XPS analysis (Fig. S6). As expected, the CsPbBr₃@A-SiO₂ composite presents stronger PL emission than CsPbBr₃@CC-SiO₂, and similar PL emission with CsPbBr₃@CA-SiO₂ (Fig. 4c). Compared with CsPbBr₃@CA-SiO₂, the emission spectra of CsPbBr₃@A-SiO₂ and CsPbBr₃@CC-SiO₂ exhibits a slight red shift, with an emission maximum at 523 nm. A small shoulder at 495 nm can be detected for CsPbBr₃@CC-SiO₂, possibly attributable to the polar environment imposed by carboxylation.²⁹

It is worthwhile to mention that halide perovskites feature flexible tunability of band gap via modulation of halide anion.²⁻³ We prepared the CsPbX₃@CA-SiO₂ composites with various emission colors by using different lead halide precursors (from pure PbCl₂, and PbI₂ instead of PbBr₂) in the nanocrystal synthesis. Fig. 4d shows the optical results of CsPbCl₃@CA-SiO₂ and CsPbI₃@CA-SiO₂. Compared with the pure bromide-based sample of green emission (520 nm), CsPbCl₃@CA-SiO₂ and CsPbI₃@CA-SiO₂ composites show blue (427 nm) and red (650 nm) emissive fluorescence, yielding PLQYs of 28% and 67%, respectively (Fig. 4d and Table S1).

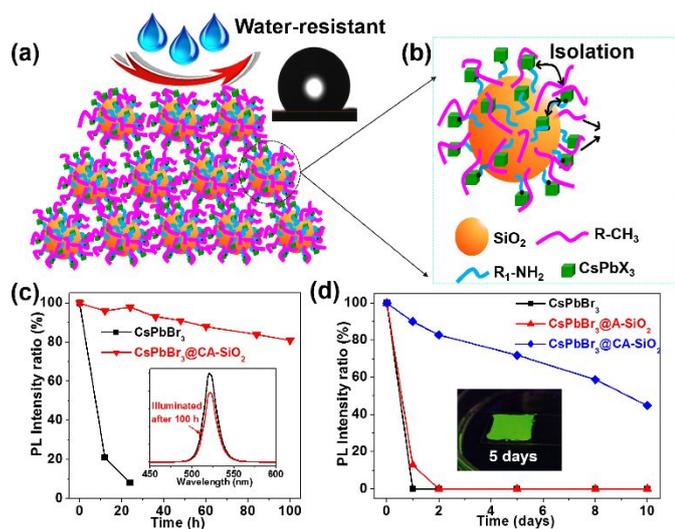


Fig. 5 (a) Schematic illustration of the film surface of CsPbBr₃@CA-SiO₂ composites with dewetting property. Inset in (a) is the photo showing the hydrophobicity of the WCAs. (b) Schematic illustration of CsPbBr₃@CA-SiO₂. (c) The relative PLQY plots against different UV irradiation times. Inset in (c) is the PL intensity before and after illuminated by UV light. (d) The relative PLQY plots of CsPbBr₃, CsPbBr₃@A-SiO₂ and CsPbBr₃@CA-SiO₂ films upon immersing in water over time. Inset in (d) is the photograph of the CsPbBr₃@CA-SiO₂ film taken under UV irradiation after immersion in water for 5 days.

The thus formed CsPbBr₃@CA-SiO₂ composite is expected to provide excellent dewetting properties and enhanced photostability. The photostability of CsPbBr₃@CA-SiO₂ composite was investigated by illuminating continuously under UV lamps (365 nm). The CsPbBr₃@CA-SiO₂ composite presents outstanding photostability, with no measurable PL intensity decrease after 24 hours of constant illumination. Even after 100 h, ~82% of the initial PL intensity was still maintained with no PL peak shift (Fig. 5c). In contrast, the pure CsPbBr₃ film degraded from green to yellow upon illumination, and the PL intensity decreases dramatically over 24 h (Fig. 5c). Clearly, although there are no discrete barrier layers, the NCs on the CsPbBr₃@CA-SiO₂ composite are spatially isolated, which inhibits fusion, aggregation, and other proximity related degradation pathways.^{28, 35, 37}

To measure the composite's water resistance, we immersed solid films on glass slides into deionized water (Fig. 5d). The relative PL of the CsPbBr₃@A-SiO₂ film decayed to 13% after 1 day and was fully quenched after 2 days. The pure perovskite films are completely quenched after 1 hour of water immersion. However, CsPbBr₃@CA-SiO₂ films present much higher stability, retaining 72% and 59% PLQY after immersing in water for 5 and 8 days (Fig. 5d). Besides, the surface is hydrophobic, as suggested by a static water contact angle of 132° (inset in Fig. 5a). The excellent dewetting property possibly results from the surface alkyl chains and micro/nano structural features (Fig. 5a), surpassing previously reported encapsulated NCs.^{32, 38-39} Photographs inserted in Fig. 5d further confirm that the CsPbBr₃@CA-SiO₂ film remain highly fluorescent after immersing in water for 5 days. Compared with single SiO₂ particle-coated CsPbX₃ NCs that have exhibited enhanced stability,^{24, 40} the *in-situ* growth method to anchor the CsPbBr₃ NCs on amino-ligand functionalized SiO₂ particles is superior in stabilizing the NCs by better spatial

isolation of NCs and providing an excellent dewetting barrier to shield environmental agents.

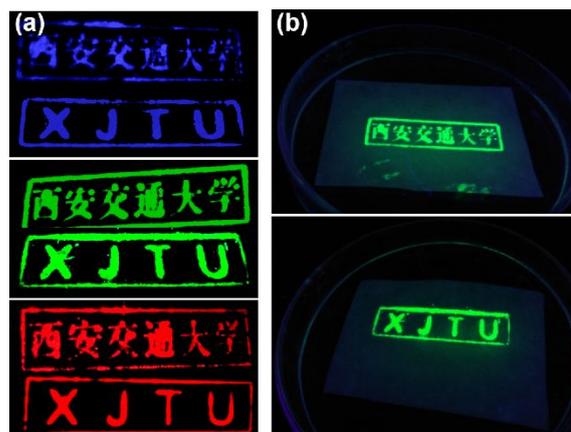


Fig. 6 (a) Photograph of customized patterns containing CsPbCl₃@CA-SiO₂ (blue), CsPbBr₃@CA-SiO₂ (green) and CsPbI₃@CA-SiO₂ (red) under UV light. (b) Photograph of the patterns containing CsPbBr₃@CA-SiO₂ after immersion in water for 5h.

CsPbBr₃@CA-SiO₂ composite demonstrated excellent optical properties and high stability as the green fluorophore, which can be used in a proof of concept multicolor anti-counterfeiting security ink. As a demonstration, Fig. 6a exhibited the customized patterns on a piece of filter paper under the 365 nm UV light by CsPbCl₃@CA-SiO₂, CsPbBr₃@CA-SiO₂ and CsPbI₃@CA-SiO₂ composite inks with hand carved seals, respectively. The ink is nearly colorless under room light, but exhibits excellent uniformity and strong PL emission under UV light, emitting bright red, green and blue colors (Fig. 6a). Besides, the high PL emission can be preserved even under immersion in water for 5 h, implying its excellent water stability (Fig. 6b), which is superior than the other anti-counterfeiting security ink based on non-emissive Cs₄PbX₆ NCs.⁴¹

Besides, we also fabricated a down-converting white light emitting device (WLED).^{25, 28, 40} Fig. 7a illustrates the typical WLED device structure, in which YAG powder and CsPbBr₃@CA-SiO₂ are used as the red and green sources. Each layer is sequentially deposited onto a blue-emitting GaN chip.²⁸ The electroluminescence (EL) spectrum of the prepared WLED device presents a narrow green emission peak at 525 nm attributed to the CsPbBr₃@CA-SiO₂ and a broad red emission peak at 660 nm originating from the YAG phosphor, excited by the 460 nm GaN LED.

Saturated and bright white emission can be clearly observed when the device is operated at a current of 20 mA (Fig. 7b), featuring a CIE color coordinate (0.3225, 0.3468), very close to balanced white light emission (0.33, 0.33), indicating its high color purity. The WLED device exhibits an acceptable luminous efficacy (LE) of 26.3 lm/W. The WLED device was highly stable at currents up to 140 mA (Fig. 7c) and operating for 20 min at 20 mA (Fig. S7), implying that the composite is a valuable light emitter even at high current densities. Therefore, these results indicate the great potential of the CsPbBr₃@CA-SiO₂ composite as a promising fluorophore for anti-counterfeiting and wide-color gamut lighting and display devices.

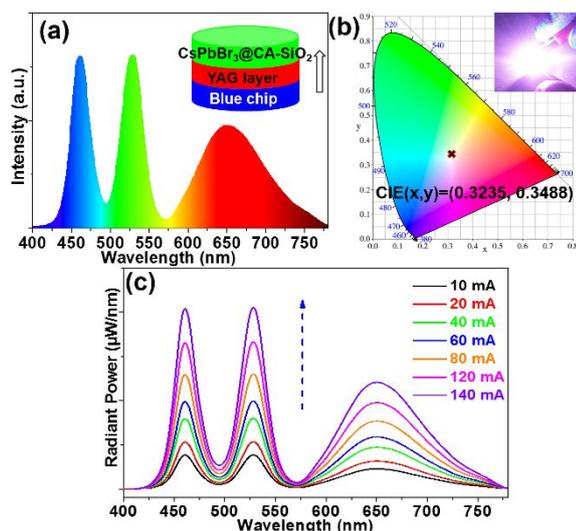


Fig. 7 (a) EL emission spectra of the WLED. Inset in (a) is the schematics of the WLED, composed of GaN blue (460 nm) LED chips, CsPbBr₃@CA-SiO₂ films and YAG powder mixed with silicone resin as the blue, green and red light source. (b) CIE color coordinates of the fabricated devices with composite films. Inset in (b) is a photograph of a working device with an applied current of 20 mA. (c) EL spectra of fabricated WLED under various operation currents.

Conclusion

In summary, we report a facile synthesis of highly luminescent and stable CsPbX₃@CA-SiO₂ nanocomposites. The silica NPs capped with octadecyl and propylamine groups (appr. 120 nm) were employed as templates for perovskite NCs growth, yielding monodisperse NCs (~6 nm) anchored onto SiO₂ NPs. The resulting composites exhibit a high photoluminescence quantum yield (76%), tunable anion-dependent emission wavelength, enhanced photostability and remarkable water stability compared to free NCs and previously reported encapsulated NCs. The CsPbX₃@CA-SiO₂ composite can be used as an anti-counterfeit ink and a fluorophore for WLED, indicating their promising potentials in solid-state optoelectronics. We believe this work will open the door for future research into multifunctional perovskite-based composites for real-world optoelectronic applications.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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