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Near-infrared-light-mediated high-throughput information encryption based on the inkjet printing of upconversion nanoparticles†

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Information security has attracted broad attention in today's information age, and information encryption on paper has been widely studied since paper is still the most important information carrier. Fluorescent inks are commonly used in information encryption on paper, but they suffer from background fluorescence interference. Herein, we develop a background-free and easy-to-perform method for information encryption based on the inkjet printing of upconversion nanoparticles (UCNPs). The UCNPs can efficiently eliminate background fluorescence interference since phosphors in paper cannot be activated by near-infrared (NIR) light. Moreover, owing to their small size, excellent dispersibility and good stability, UCNP inks can be directly applied to commercial inkjet printers for convenient and high-throughput information encryption on paper. Information was easily printed on different kinds of paper substrates and the information can only be visualized under NIR light excitation. Furthermore, a novel information encryption strategy was designed by utilizing UCNPs with different excitation wavelengths. Only excitation at the defined wavelength can obtain the correct information. This proposed information encryption strategy can completely avoid background fluorescence interference, and it also features easy operation, high throughput as well as low costs, indicating its good promise to serve as a household encryption method in our daily life.

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Introduction

In today's information age, information leakage has become a global problem, which has led to unbearable consequences, such as outbreak of war, huge casualties and serious reputation damage.[1–4] Information security has attracted broad attention and efficient encryption methods are in urgent need.[5–7] Although electronic communication has become an integral part of our lives, paper is still the most important carrier for information storage.[8–10] For instance, the global consumption of paper has increased around threefold over the past few decades, and books, magazines, or newspapers are almost always paper versions.[10] Moreover, most of the important documents are paper-based, such as banknotes, passports, cheques, and bonds.[11] Therefore, information encryption on paper still holds widespread attention.[11–14] Fluorescent inks are commonly used for information encryption on paper due to their simple operation and low cost.[15–17] However, fluorescent inks also face great challenges, most notably the background fluorescence interference.[18–20] Generally, chemical additives are added into paper to increase the whiteness, printability and opacity.[21,22] Some of the chemical additives show strong fluorescence under excitation, which can interfere with the fluorescence of inks.[21–23] As a result, the encrypted information will be seriously blurred or even completely buried by the background fluorescence. This problem significantly hinders the widespread usage of the fluorescent inks in information encryption. As a consequence, it is highly desired to develop a novel ink that can avoid background fluorescence for convenient information encryption on paper.

Upconversion nanoparticles (UCNPs) can convert near-infrared (NIR) light into UV/visible/NIR light through nonlinear optical processes.[24–27] The unique properties of UCNPs include high photochemical stability, large anti-Stokes shift and sharp-band emission, making UCNPs valuable in displays, photovoltaic devices and bioimaging.[24,25,28–30] Since chemical additives in paper cannot be excited by NIR light, UCNPs hold good promise to get rid of background fluorescence interference in information encryption.[21,22,31] Moreover, with the rapid development of thermal decomposition methods and

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solvothermal methods, UCNPs with small size, high colloidal stability and bright emission can be readily obtained.[32–36] The UCNPs can be easily loaded into commercial inkjet printers to achieve convenient and high throughput information encryption on paper. It is also worth noting that UCNPs with different excitation or emission wavelengths can be easily prepared by changing the host lattices and dopant ions.[37–42] Such tunable excitation/emission properties can further be employed to develop new encryption methods. Therefore, UCNPs are ideal candidates for information encryption on paper.

Herein, we have combined UCNPs with commercial inkjet printers to develop a general, high throughput and easy-to-perform method for background-free information encryption on paper. Specifically, UCNPs with small size, high colloid stability and bright luminescence were prepared and further loaded into an inkjet printer. Different types of information were successfully printed on paper with the UCNP inks. The high efficiency of the UCNPs in eliminating background fluorescence from paper was demonstrated, and the proposed method was further applied to information encryption on different kinds of paper substrates. Moreover, by employing UCNP inks with different excitation wavelengths, a new information encryption strategy was designed. The hidden information can be decrypted only with excitation at the defined wavelength, otherwise incomplete or even misleading information will be obtained. The developed method features free of background fluorescence, easy operation, high throughput, low cost and various potential encryption strategies, suggesting its great promise to serve as a general and household information encryption method.

Results and discussion

In this work, β-$NaYF_4$:Yb,Ho (designated as UCNPs-1) and β-$NaYF_4$:Yb,Er@$NaYF_4$:Yb@$NaNdF_4$:Yb@$NaYF_4$:Yb (designated as UCNPs-2) upconversion nanoparticles were used as the UCNP inks. The UCNPs were prepared according to previously reported protocols.[43–45] A transmission electron microscopy (TEM) image (Fig. 1a) shows that UCNPs-1 are monodisperse and have a uniform shape with an average diameter of 42 nm. The X-ray powder diffraction (XRD) pattern of UCNPs-1 (Fig. S3 in the ESI†) indicates the well-defined hexagonal structure (JCPDS No. 16-0334) of the as-synthesized UCNPs-1. The UCNPs-1 show predominantly upconversion luminescence at around 545 nm, corresponding to the transition from $^5F_4$ and $^5S_2$ levels to the $^5I_8$ ground state of Ho^{3+} (Fig. 1b). The photographs of the colloid dispersion in Fig. 1b indicate that the UCNPs-1 have excellent dispersibility and bright green luminescence. The dispersibility and stability of UCNPs-1 ink were further characterized. When dispersed in toluene, UCNPs-1 form a transparent colloidal solution without any precipitate (Fig. 1c). The bright field and the corresponding luminescence images of the colloidal solution show that UCNPs-1 ink possesses excellent dispersibility. After storage for a month, the

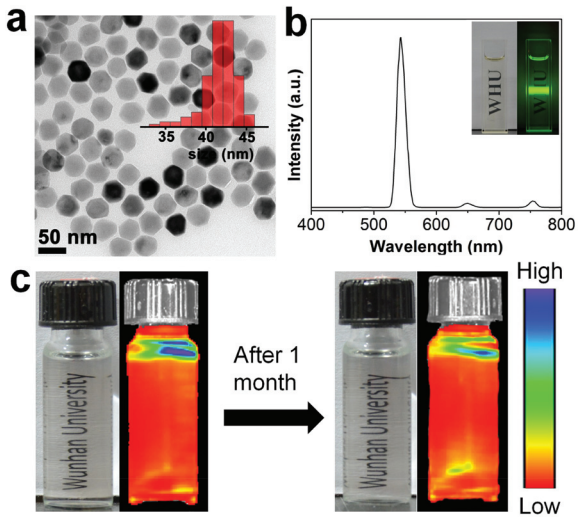


Fig. 1 TEM image (a), size distribution (inset in a), photoluminescence spectrum (b) and photograph of colloid dispersion (inset in b) of β-$NaYF_4$:Yb,Ho. (c) Bright field and the corresponding luminescence images of UCNPs-1 ink before and after storage for 1 month.

UCNPs-1 ink exhibits no apparent changes, suggesting its excellent stability (Fig. 1c).

The TEM image in Fig. 2a shows that the UCNPs-2 are also well-dispersed and display uniform size with a mean diameter of 54 nm. The XRD patterns shown in Fig. S4 in the ESI† indicate that the diffraction peaks of UCNPs-2 are all indexed as a pure hexagonal structure of $NaYF_4$ (JCPDS No. 16-0334). The UCNPs-2 show strong emission at around 550 nm (Fig. 2b), which is attributed to the transition from the $^4H_{11/2}$ and $^4S_{3/2}$ levels to the $^4I_{15/2}$ ground state of Er^{3+}. The images of the

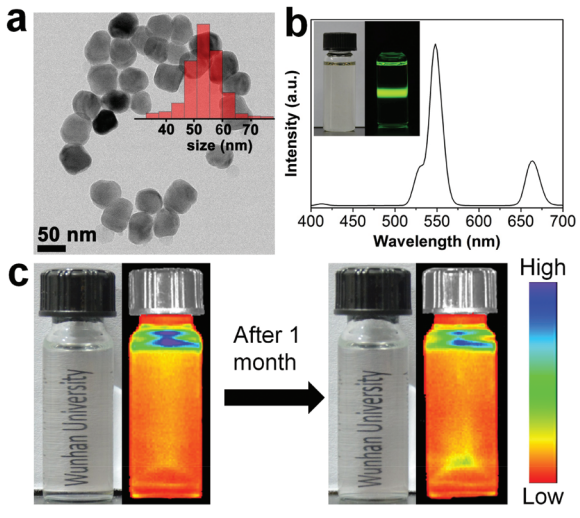


Fig. 2 TEM image (a), size distribution (inset in a), photoluminescence spectrum (b) and photograph of colloid dispersion (inset in b) of β-$NaYF_4$:Yb,Er@$NaYF_4$:Yb@$NaNdF_4$:Yb@$NaYF_4$:Yb. (c) Bright field and the corresponding luminescence images of UCNPs-2 ink before and after storage for 1 month.

colloid dispersion of UCNPs-2 in Fig. 2c indicate that UCNPs-2 are well-dispersed and produce bright green luminescence under 808 nm excitation. Similarly, the UCNPs-2 ink shows excellent dispersibility and stability, as evidenced by the bright field and the corresponding luminescence images (Fig. 2c). The above results clearly demonstrate the small size, good monodispersibility, excellent stability and bright emission of the UCNPs, indicating their good potential in information encryption on paper with inkjet printing.

The schematic representation of the background-free information encryption is outlined in Scheme 1. The UCNP ink is directly added into the cartridges of a commercial inkjet printer, and information is printed on office paper by the inkjet printer loaded with the UCNP ink. For comparison, a commercial green UV ink is also employed. The information printed with UV ink and UCNP ink is invisible under ambient light because both inks show little absorption in the visible region. Under UV lamp excitation, the chemical additives in paper emit strong blue fluorescence and this background fluorescence seriously interferes with the green fluorescence of the UV ink, resulting in buried information. However, under NIR light excitation, the paper does not exhibit any background fluorescence and the UCNP ink displays bright emission, leading to the appearance of the encrypted information.

The performance of the UCNP inks in eliminating background fluorescence from paper was further investigated. The Einstein's famous saying, "To raise new questions, new possibilities, to regard old problems from a new angle, requires creative imagination and marks real advance in science", was printed on paper with a commercially available green fluorescent ink and the UCNPs-1 ink. As shown in Fig. 3a, the paper encrypted with the UV ink displays strong blue fluorescence under UV excitation, and the fluorescence of the ink is completely buried by the background fluorescence, leading to serious loss of the encrypted information. Such a phenomenon is usually encountered in information encryption on paper with commercial fluorescent inks. As for the paper bearing information encrypted with UCNPs-1 ink (Fig. 3b), no background fluorescence shows up under NIR light excitation

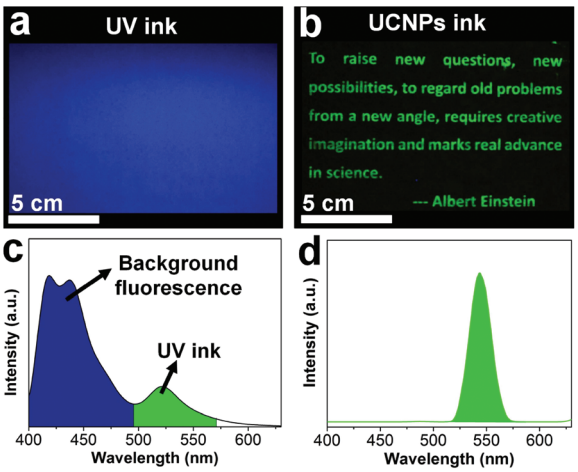
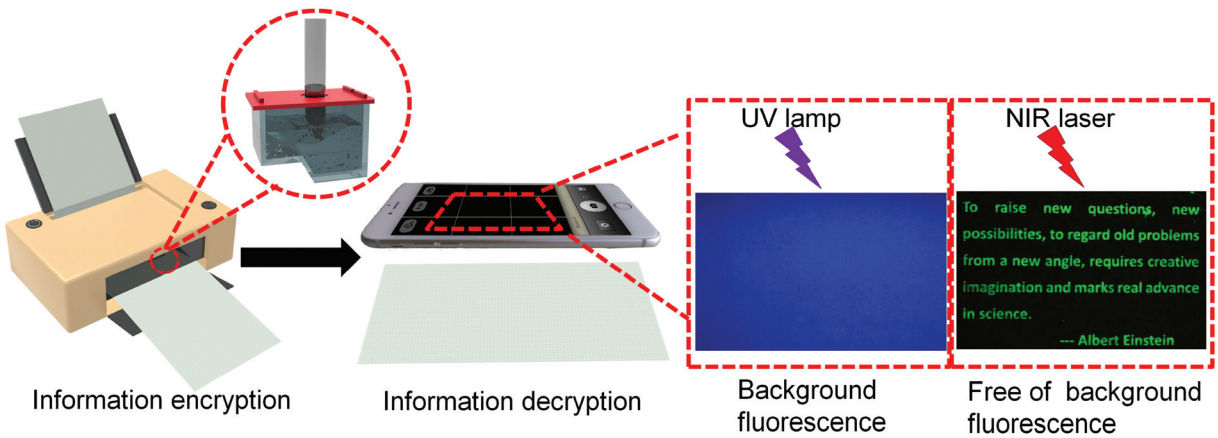


Fig. 3 (a) Image of paper encrypted with commercial fluorescence ink under UV lamp excitation. (b) Image of paper encrypted with UCNPs-1 ink under 980 nm light excitation. The emission spectrum of paper encrypted with UV ink (c) and paper encrypted with UCNPs-1 ink (d).

and a legible image of the information appears. Moreover, the emission spectra of the above two encrypted papers were measured. As shown in Fig. 3c, the fluorescent ink encrypted paper displays a strong band at around 425 nm, which can be ascribed to the background fluorescence of paper. It is also noted that the intensity of the background fluorescence is much stronger than that of UV ink (at around 520 nm), which leads to the loss of encrypted information under excitation. The spectrum in Fig. 3d shows that the UCNPs-1 ink encrypted paper displays a strong emission band at around 545 nm and no background fluorescence band is observed, which is in good agreement with the image shown in Fig. 3b. The above results clearly demonstrate that the UCNP ink can completely eliminate background fluorescence interference, making it valuable in information encryption on paper.

Furthermore, the feasibility of UCNP inks for complicated pattern encryption on different kinds of substrates was tested. An architectural drawing was printed on office paper with

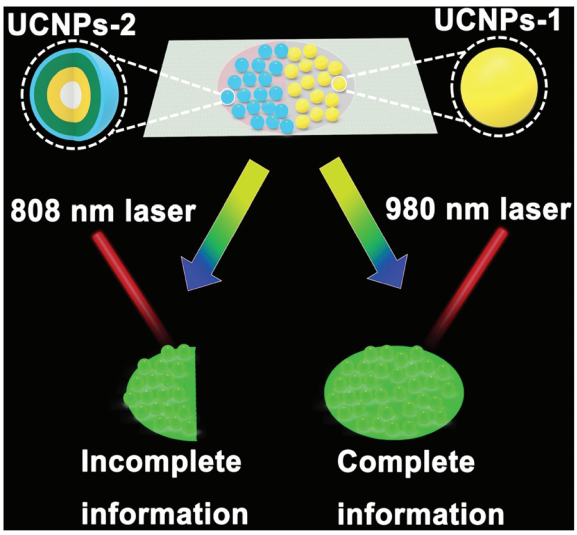


Scheme 1 Schematic illustration of information encryption on paper with the UCNP ink.

UCNPs-1 ink and was further decrypted with a NIR laser. As shown in Fig. 4a, the hidden architectural drawing is clearly visualized without any significant loss of details. In addition to office paper, the UCNP ink is also applicable to other kinds of paper substrates. The images in Fig. 4b–d demonstrate that information can be readily printed on banknotes, envelopes and postcards with the UCNPs-1 ink. The images of the above patterns printed on these substrates are all clearly observed without any background fluorescence interference. Similar results were also obtained in information encryption tests with the UCNPs-2 ink (Fig. S7 and S8 in the ESI†). The above results thus clearly demonstrate that the UCNP inks are free of background fluorescence and are highly compatible with inkjet printing to realize high throughput information encryption on different kinds of paper substrates.

As mentioned above, the excitation wavelength of UCNPs can be easily tuned. Based on this unique property, a new information encryption strategy was further designed. As shown in Scheme 2, the information to be encrypted is divided into two parts. One part is printed with UCNPs-1 ink and the other part is printed with UCNPs-2 ink. Because only UCNPs-2 ink can be excited with an 808 nm laser, incomplete information will be obtained under 808 nm excitation. In contrast, complete information can be obtained under 980 nm excitation since both of the UCNP inks can be excited by a 980 nm laser.

The feasibility of the proposed information encryption strategy was further tested by printing the code "8888" and the word "UCNPs-INK" onto office paper. As shown in Fig. 5a, an incorrect code "0512" is obtained under 808 nm excitation, which is attributed to the activation of UCNPs-2 ink. Such an incorrect code may seriously mislead the reader. In contrast, the correct code "8888" is visualized only with 980 nm light irradiation (Fig. 5a). Similarly, the word "UCNPs" is obtained with the 808 nm laser while the encrypted word "UCNPs-INK" is recorded with 980 nm excitation (Fig. 5b). Based on the above results, one can clearly see that UCNP inks possess great flexibility in information encryption due to their tunable optical properties.



Scheme 2 Schematic illustration of the information encryption strategy based on UCNPs-1 and UCNPs-2 inks.

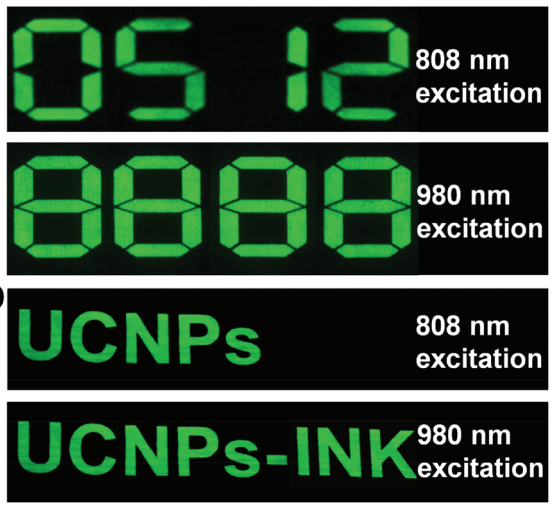


Fig. 5 (a) Images of the encrypted information "8888" under 808 nm excitation and 980 nm excitation. (b) Images of the encrypted information "UCNPs-INK" under 808 nm excitation and 980 nm excitation.

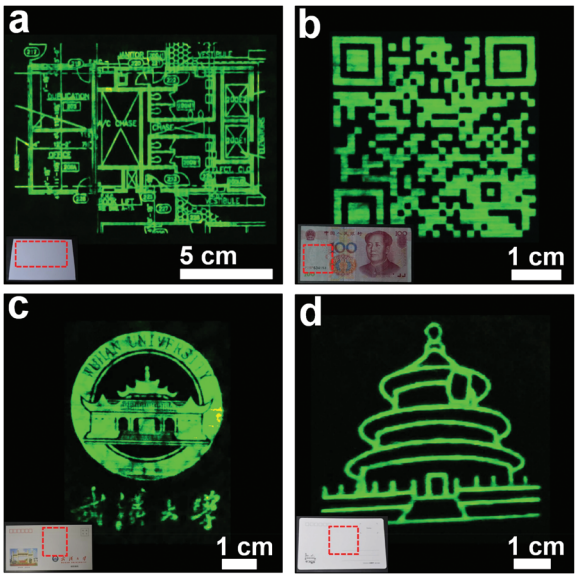


Fig. 4 (a) Image of architectural drawing encrypted on paper. (b) Image of the QR code encrypted on a banknote. (c) Image of the university logo encrypted on an envelope. (d) Image of the temple of heaven encrypted on a postcard.

Conclusions

In summary, we have highlighted the special advantages of UCNPs in eliminating background fluorescence and their ver-

satility in information encryption on paper. The prepared UCNPs display small size, good dispersibility, excellent stability and bright emission. By combining UCNP inks with commercial inkjet printers, easy-to-perform and high throughput information encryption has been achieved on different kinds of paper substrates. The hidden information can be readily decrypted without any loss of the details due to the completely suppressed background fluorescence. Moreover, the UCNP inks show great flexibility in information encryption since the excitation and emission wavelengths can be fine-tuned. To conclude, the developed method can serve as a general approach for information encryption on paper and we anticipate that this method will find widespread usage in our daily life.

Experimental section

Chemicals and materials

Holmium oxide (Ho_2O_3, 99.99%), erbium oxide (Er_2O_3, 99.99%), ytterbium oxide (Yb_2O_3, 99.99%), neodymium acetate (III) hydrate ($C_6H_9O_6Nd{\cdot}xH_2O$, 99.9%), trifluoroacetic acid (CF_3COOH, AR), sodium trifluoroacetate (CF_3COONa, 98%), oleic acid (OA), and 1-octadecene (ODE) were purchased from Aladdin. Yttrium oxide (Y_2O_3, 99.99%), acetic acid (CH_3COOH, AR), ethanol (AR), cyclohexane (AR), chloroform (AR), toluene (AR), sodium hydroxide (NaOH, AR), and ammonium fluoride (NH_4F, AR) were purchased from Sinopharm Chemical Reagent Co. (China).

Preparation of $RE(CF_3COO)_3$

The synthesis of $Y(CF_3OO)_3$ is taken as an example. Typically, Y_2O_3 (10 mmol) was added into a three-neck flask. Then 120 mL deionized water and 80 mmol trifluoroacetic acid were added under vigorous stirring. The mixture was kept refluxing at 140 °C for 6 h and a transparent solution was obtained. Then the solution was filtered and transferred into an evaporating basin. With the evaporation of water, a white powder of $Y(CF_3COO)_3$ was obtained. The powder was washed three times with deionized water. The remaining $RE(CF_3COO)_3$ were synthesized with the corresponding amounts of RE_2O_3 according to the above procedure.

Preparation of $NaYF_4$:Yb,Ho UCNPs (UCNPs-1). Hexagonal phase OA-coated $NaYF_4$:20%Yb,2%Ho nanoparticles were synthesized with a previously reported protocol.[43] Typically, 0.3770 g $Y(CF_3COO)_3$, 0.1124 g $Yb(CF_3COO)_3$, 0.0101 g $Ho(CF_3COO)_3$, and 0.2720 g $NaCF_3COO$ were added into a 100 mL three-neck flask with 5 mL of ODE and OA. A solution of ODE (15 mL) and OA (10 mL) was added in another three-neck flask. Both solutions were heated to 125 °C for 30 minutes under vacuum with magnetic stirring to remove residual water and oxygen. The ODE and OA solution was then heated to 320 °C under an Ar atmosphere and maintained at 320 °C. The lanthanide trifluoroacetate solution was then dropwise injected into the ODE and OA solution within 15 minutes. After that, the reaction was kept at 320 °C for 1 h under an Ar atmosphere. After cooling to room temperature, the UCNPs-1 were collected by centrifugation and washed several times with ethanol and cyclohexane (v/v, 1 : 1).

Preparation of $NaYF_4$:Yb,Er@$NaYF_4$:Yb@$NaNdF_4$:Yb@$NaYF_4$:Yb core–shell nanoparticles (UCNPs-2). The core–shell UCNPs-2 were synthesized according to a previously reported protocol.[44,45] Hexagonal phase OA-coated $NaYF_4$:18% Yb,2%Er core nanoparticles were prepared firstly. Briefly, 1 mmol $Y(CF_3COO)_3$, 0.18 mmol $Yb(CF_3COO)_3$, 0.02 mmol $Er(CF_3COO)_3$ and 1 mmol $NaCF_3COO$ were added into a 100 mL three-neck flask with 20 mmol ODE and 20 mmol OA. Then the solution was heated to 125 °C for 30 minutes under vacuum with magnetic stirring. Next, the solution was heated to 320 °C under an Ar atmosphere and maintained at 320 °C for 30 min with stirring. After cooling to room temperature, the nanoparticles were collected by centrifugation and washed several times with ethanol and cyclohexane (v/v, 1 : 1). After that, the nanoparticles were dried in air. The epitaxial growth of the shell layer was as follows. The prepared core nanoparticles were dispersed in 20 mL solution of OA and ODE (v/v, 1 : 1) in a 100 mL three necked flask. The mixture was then heated to 125 °C for 30 minutes under vacuum with magnetic stirring. Next the mixture was heated to 320 °C under an Ar atmosphere and maintained at 320 °C. At the same time, a mixture containing 0.45 mmol $Y(CF_3COO)_3$, 0.05 mmol $Yb(CF_3COO)_3$, 0.5 mmol $NaCF_3COO$ and 4 mL solution of OA and ODE (v/v, 1 : 1) was dropwise injected into the above solution. The resulting mixture was maintained at 310 °C for 1 h with stirring. The hot injection step was repeated to maintain the growth of the multi-layer nanoparticles by changing the components of $RE(CF_3COO)_3$ (0.45 mmol $Nd(CF_3COO)_3$, 0.05 mmol $Yb(CF_3COO)_3$ or 0.45 mmol $Y(CF_3COO)_3$, 0.05 mmol $Yb(CF_3COO)_3$). Finally, when cooling to room temperature, excess ethanol was added into the mixture and the UCNPs-2 were obtained by centrifugation and washed several times with ethanol and cyclohexane (v/v, 1 : 1).

Preparation of UCNP inks

Briefly, 20 mg upconversion nanoparticles were dispersed in 10 mL toluene by sonication. The colloid dispersion was then rotated for 30 min followed by centrifuging at 200 rpm for 3 min. Finally, the UCNP ink can be obtained by filtering the colloid dispersion through a pore filter with 200 nm pore size.

The information encryption with green fluorescent UV ink

The designed information was printed on office paper with an HP Deskjet 1010 printer loaded with commercially available green color UV ink and then the photograph of the paper under UV light excitation was recorded with the Nikon camera.

The information encryption with UCNPs-1 ink or UCNPs-2 ink

The designed information was printed with the HP Deskjet 1010 printer equipped with a UCNP ink-loaded cartridge on office paper. Then the information was decrypted under 980 nm light excitation or 808 nm light excitation.

The information encryption with UCNPs-1 ink and UCNPs-2 ink

The designed information was divided into two parts. One part of the designed information was printed onto office paper with UCNPs-1 ink and the other part was printed with UCNPs-2 ink *via* inkjet printing. Then, the information encrypted on paper was captured under 808 nm light excitation or 980 nm light excitation. A short wave pass filter was used to filter the background light of the laser source throughout the recording process.

Acknowledgements

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Notes and references

1 M. T. Dlamini, J. H. P. Eloff and M. M. Eloff, *Comput. Secur.*, 2009, **28**, 189–198.
2 Y. Cui, R. S. Hegde, I. Y. Phang, H. K. Lee and X. Y. Ling, *Nanoscale*, 2013, **6**, 282–288.
3 K. Kotani, *Japanese intelligence in World War II*, Osprey, Oxford, UK, 2009.
4 E. Zielińska, W. Mazurczyk and K. Szczypiorski, *Commun. ACM*, 2014, **57**, 86–95.
5 B. Yoon, J. Lee, I. Park, S. Jeon, J. Lee and J. M. Kim, *J. Mater. Chem. C*, 2013, **1**, 2388–2403.
6 E. L. Prime and D. H. Solomon, *Angew. Chem., Int. Ed.*, 2010, **49**, 3726–3736.
7 X. Li, Y. J. Xie, B. Song, H. L. Zhang, H. Chen, H. J. Cai, W. S. Liu and Y. Tang, *Angew. Chem., Int. Ed.*, 2017, **56**, 2689–2693.
8 W. Jeong, M. I. Khazi, D. H. Park, Y. S. Jung and J. M. Kim, *Adv. Funct. Mater.*, 2016, **26**, 5230–5238.
9 W. Wang, N. Xie, L. He and Y. Yin, *Nat. Commun.*, 2014, **5**, 5459.
10 RISI, World pulp annual historical data- excerpt, http://www.risiinfo.com/Marketing/ahd/Excerpts/world_pulp.pdf (accessed: September, 2013).
11 R. L. V. Renesse, presented in part at the European Conference on Security and Detection, London, UK, Apr. 28–30, 1997.
12 J. Andres, R. D. Hersch, J. E. Moser and A. S. Chauvin, *Adv. Funct. Mater.*, 2014, **32**, 5029–5036.
13 W. Yao, Q. Tian, J. Liu, Z. Wu, S. Cui, J. Ding, Z. Dai and W. Wu, *J. Mater. Chem. C*, 2016, **4**, 6327–6335.
14 B. Yoon, D. Ham, O. Yarimaga, H. An, C. Lee and J. Kim, *Adv. Mater.*, 2011, **23**, 5492–5497.
15 Q. Lou, S. Qu, P. Jing, W. Ji, D. Li, J. Cao, H. Zhang, L. Liu, J. Zhao and D. Shen, *Adv. Mater.*, 2015, **27**, 1389–1394.
16 X. Hou, C. Ke, C. J. Bruns, P. R. Mcgonigal, R. B. Pettman and J. F. Stoddart, *Nat. Commun.*, 2015, **6**, 6884.
17 K. Jiang, L. Zhang, J. Lu, C. Xu, C. Cai and H. Lin, *Angew. Chem., Int. Ed.*, 2016, **55**, 7231–7235.
18 Y. Lu, J. Zhao, R. Zhang, Y. Liu, D. Liu, E. M. Goldys, X. Yang, P. Xi, A. Sunna and J. Lu, *Nat. Photonics*, 2013, **8**, 32–36.
19 Y. Zhang and J. He, *Phys. Chem. Chem. Phys.*, 2015, **17**, 20154–20159.
20 X. Chen, X. Jin, J. Tan, W. Li, M. Chen, L. Yao and H. Yang, *J. Colloid Interface Sci.*, 2016, **468**, 300–306.
21 S. G. Murray, in *The Chemistry of Paper*, ed. J. C. Roberts, Springer, Netherlands, 1991, ch. 9, pp. 132–161.
22 A. Ginebreda, D. Guillén, D. Barceló and R. M. Darbra, in *Global Risk-Based Management of Chemical Additives I: Production, Usage and Environmental Occurrence*, ed. B. Bilitewski, R. M. Darbra and D. Barceló, Springer, Heidelberg, Germany, 2012, ch. 2, vol. 18, pp. 11–34.
23 R. D. Hersch, *Appl. Opt.*, 2008, **47**, 6710–6722.
24 H. Dong, L. D. Sun and C. H. Yan, *Chem. Soc. Rev.*, 2015, **44**, 1608–1634.
25 W. Zheng, P. Huang, D. Tu, E. Ma, H. Zhu and X. Chen, *Chem. Soc. Rev.*, 2015, **44**, 1379–1415.
26 F. Wang, R. Deng and X. Liu, *Nat. Protoc.*, 2014, **9**, 1634–1644.
27 X. M. Li, F. Zhang and D. Y. Zhao, *Chem. Soc. Rev.*, 2015, **44**, 1346–1378.
28 R. Deng, F. Qin, R. Chen, W. Huang, M. Hong and X. Liu, *Nat. Nanotechnol.*, 2015, **10**, 237–242.
29 Y. W. Zhang, L. Huang, Z. J. Li, G. L. Ma, Y. B. Zhou and G. Han, *ACS Nano*, 2016, **10**, 3881–3885.
30 S. H. Xu, X. R. Zhang, H. W. Xu, B. Dong, X. S. Qu, B. T. Chen, S. Zhang, T. X. Zhang, Y. Cheng, S. Xu and H. W. Song, *Sci. Rep.*, 2016, **6**, 22350.
31 J. Wang, T. Wei, X. Li, B. Zhang, J. Wang, C. Huang and Q. Yuan, *Angew. Chem., Int. Ed.*, 2014, **53**, 1616–1620.
32 H. X. Mai, Y. W. Zhang, R. Si, Z. G. Yan, L. D. Sun, L. P. You and C. H. Yan, *J. Am. Chem. Soc.*, 2006, **128**, 6426–6436.
33 F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong and X. Liu, *Nature*, 2010, **463**, 1061–1065.
34 X. Chen, D. Peng, Q. Ju and F. Wang, *Chem. Soc. Rev.*, 2015, **44**, 1318–1330.
35 M. You, M. Lin, S. Wang, X. Wang, G. Zhang, Y. Hong, Y. Dong, G. Jin and F. Xu, *Nanoscale*, 2016, **8**, 10096–10104.
36 M. Pang, X. S. Zhai, J. Feng, Y. Song, R. P. Deng, Z. Wang, S. Yao, X. Gea and H. J. Zhang, *Dalton Trans.*, 2014, **43**, 10202–10207.
37 F. Wang and X. Liu, *J. Am. Chem. Soc.*, 2008, **130**, 5642–5643.
38 S. Han, Q. Xian, Z. An, Y. Zhu, L. Liang, H. Yu, H. Wei and X. Liu, *Nat. Commun.*, 2016, **7**, 13059.
39 X. Xie, N. Gao, R. Deng, Q. Sun, Q. H. Xu and X. Liu, *J. Am. Chem. Soc.*, 2013, **135**, 12608–12611.
40 Y. F. Wang, G. Y. Liu, L. D. Sun, J. W. Xiao, J. C. Zhou and C. H. Yan, *ACS Nano*, 2013, **7**, 7200–7206.

41 Y. Zhong, G. Tian, Z. Gu, Y. Yang, L. Gu, Y. Zhao, Y. Ma and J. Yao, *Adv. Mater.*, 2014, **26**, 2831–2837.
42 X. Y. Li, X. W. Liu, D. M. Chevrier, X. Qin, X. J. Xie, S. Y. Song, H. J. Zhang, P. Zhang and X. G. Liu, *Angew. Chem., Int. Ed.*, 2015, **54**, 13312–13317.
43 R. Naccache, F. Vetrone, V. Mahalingam, L. A. Cuccia and J. A. Capobianco, *Chem. Mater.*, 2009, **21**, 717–723.
44 X. Hu, Y. Wang, H. Liu, J. Wang, Y. Tan, F. Wang, Q. Yuan and W. Tan, *Chem. Sci.*, 2017, **8**, 466–472.
45 B. Liu, Y. Chen, C. Li, F. He, Z. Hou, S. Huang, H. Zhu, X. Chen and J. Lin, *Adv. Funct. Mater.*, 2015, **25**, 4717–4729.