Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2021

## **Supporting Information**

## Dual Information Encryption of Carbon Dots Endowed with Recoverable Functions after Interception

Chen Yang,<sup>a,†</sup> Ru Li,<sup>a,†</sup>, Jun Zhang, <sup>\*,a</sup> Zhi-Kai Cao,<sup>a</sup> Chun-Li Liu,<sup>a</sup> Meng Zhang,<sup>a</sup> Wen-Peng Han,<sup>a</sup> Seeram Ramakrishna,<sup>b</sup> Yun-Ze Long<sup>\*,a</sup>

<sup>a</sup> Collaborative Innovation Center for Nanomaterials & Devices, College of Physics, Qingdao

University, Qingdao 266071, China

<sup>b</sup> Center for Nanofibers & Nanotechnology, Department of Mechanical Engineering, National

University of Singapore, Singapore 117574, Singapore

\*Address correspondence to iamjunzhang@163.com and yunze.long@163.com.

<sup>†</sup>These two authors contributed equally to this work.

Materials	Encryption	Decryption	Encryption	Security	Ref.
	regents	regents	categories		
g-C3N4 QDs	$H_2C_2O_4$	NaHCO <sub>3</sub>	single	low	[S1]
Perovskite	butyl amine	CH <sub>3</sub> COOH	single	low	[S2]
QDs					
Graphene	Cu <sup>2+</sup> and CA	Cys	multiple	high	[S3]
QDs and					
Eu <sup>3+</sup> DP					
CDs	Cu <sup>2+</sup> and Fe <sup>3+</sup>	EDTA and AA	multiple	high	This
					work

**Table S1** Information encryption in this work compared to other materials.



Fig. S1 PL spectra of CDs excited by different excitation wavelengths.



Fig. S2 The PL spectra of CDs quenched by different metal ions.



Fig. S3 The encryption and decryption mechanisms.



Fig. S4 PL intensity of CDs after adding different encrypting and decrypting reagents.



Fig. S5 At pH=1, (a) the fluorescence of CDs can be quenched by  $Cu^{2+}$ , (b) EDTA cannot recover CDs PL. At pH=5, (c) the fluorescence of CDs can be quenched by  $Cu^{2+}$ , (d) and EDTA can recover CDs PL.

As shown in Fig. S5, when CDs at pH=1, EDTA cannot recover the fluorescence of CDs-Cu<sup>2+</sup>. When CDs at pH=5, EDTA can recover the fluorescence of CDs-Cu<sup>2+</sup>. The reason is that the strong acid environment may destroy the process, namely EDTA replacing Cu<sup>2+</sup> out of the CDs-Cu<sup>2+</sup>, so that fluorescence of CDs-Cu<sup>2+</sup> cannot be recovered.

## The reason for AA could recover fluorescence of CDs-Fe<sup>3+</sup>, but EDTA cannot recover:

The reason for AA can recover fluorescence of CDs-Fe<sup>3+</sup> but EDTA cannot is that AA is based on redox mechanism and EDTA is based on complex mechanism. When AA is added to the CDs-Fe<sup>3+</sup>, due to that reduction reaction can happen from Fe<sup>3+</sup> to Fe<sup>2+</sup>, and Fe<sup>3+</sup> is better than Fe<sup>2+</sup> for the strong oxidability of Fe<sup>3+</sup> in electron acquisition, so that the fluorescence recovers.<sup>S4, S5</sup> When EDTA is added to the CDs-Fe<sup>3+</sup>, due to that the pH ranges from 1.5 to 2.5 is the complexation formation conditions of Fe<sup>3+</sup> and EDTA,<sup>S6</sup> the complex reaction cannot happen between EDTA and Fe<sup>3+</sup>, so that the EDTA cannot recover fluorescence of CDs-Fe<sup>3+</sup>.



Fig. S6 The red circle only adds encryption reagent of  $Fe^{3+}$ , the yellow circle only adds encryption reagent of  $Cu^{2+}$ .

As shown in Fig. S6, adding only one decryption reagent (key-1 or key-2) will result in different information. That is, the information encrypts of yellow circle part can only be decrypted by key-1 but cannot by key-2, the information encrypts of red circle part can only be decrypted by key-2 but cannot by key-1.



Fig. S7 Designed template pattern for Figure S8.



**Fig. S8** Deluded information application. (a) Encryption pattern under UV light. (b-e) The obtained information after using the key on the encrypted pattern: (b) key-2, (c) key-1, (d) key-3, (e) key-4. Only key-4 can obtain the real information, and others are deluded fake information.

To achieve the subtraction rule, we additional introduced a pH-sensitive CDs,<sup>S7</sup> which will quench at pH larger than 5. The pattern is designed according to Fig. S7, and the fluorescent ink is sprayed on the specific position with two kind of CDs followed by adding  $Fe^{3+}$  and  $Cu^{2+}$  at the specific position. Under UV light, the document shows nothing information in Fig. S8a. Whatever using key-1 (EDTA) or key-2 (AA) or key-3 (EDTA+AA), it will get " $\pm$ " (means soldier) or " $\square$ " (means mouth) or " $\ddagger$ " (means lucky) that are all fake information (Fig. S8b-d). The fake information here is readable and not messy code. Only using key-4 (NaOH) in Fig. S8d can get the correct information of " $\ddagger$ " (means ancient).



Fig. S9 Photograph of letter "H" is not visible under (a) natural light, but shows blue handwriting under (b) UV light.



Fig. S10 Designed template pattern for Figure 4.



**Fig. S11** (a) Encryption pattern under UV light. (b-d) The obtained information after using different keys on the encrypted pattern: (b) key-1, (c) key-2, (d) key-3. Only key-3 can obtain the real information, and the designed overlap pattern can save storage space.

As shown in Fig. S11a, the encrypted information cannot be seen under the UV light. Using key-1, key-2 and key-3 on encrypted information can see "HELP" (Fig. S11b), "5690" (Fig. S11c) and "8888" (Fig. S11d), respectively. The advantage of this encryption method is that the fake information obtained by using incorrect decryption method is still readable, so that it will mislead others to think that it is useful information thus giving up further decrypt.

## **Supporting References**

- S1. Z. Song, T. Lin, L. Lin, S. Lin, F. Fu, X. Wang and L. Guo, Angew. Chem. Int. Ed. Engl., 2016, 55, 2773-2777.
- S2. C. Sun, S. Su, Z. Gao, H. Liu, H. Wu, X. Shen and W. Bi, ACS Appl. Mater. Interfaces, 2019, 11, 8210-8216.
- S3. J. Zhao, Y. Zheng, Y. Pang, J. Chen, Z. Zhang, F. Xi and P. Chen, J. Colloid Interface Sci., 2020, **579**, 307-314.
- S4. R. Bandi, N. P. Devulapalli, R. Dadigala, B. R. Gangapuram and V. Guttena, ACS Omega, 2018, 3, 13454-13466.
- S5. J. F. Y. Fong, S. F. Chin and S. M. Ng, *Biosens. Bioelectron.*, 2016, **85**, 844-852.
- S6. Y. Zhang, D. Dreisinger, T.-A. Zhang, G. Lv, W. Zhang and F. Xie, *Hydrometallurgy*, 2019, 188, 54-63.
- S7. P. Yang, L. G. Zhou, S. L. Zhang, N. Wan, W. Pan and W. Z. Sheng. J. Appl. Phys., 2014, 116, 244306.