# Metal oxide hybridization enhances room temperature phosphorescence of carbon dots-$SiO_2$ matrix for information encryption and anti-counterfeiting

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## Experimental section

### Materials

Ammonium critrate ($C_6H_5O_7(NH_4)_3$), ammonia solution($NH_3.H_2O$, 25%) and tetraethyl orthosilicate (TEOS) were obtained from Tianjing Damao chemical reagent Co., Ltd. Zinc chloride ($ZnCl_2$), magnesium chloride ($MgCl_2$) and aluminum chloride hexahydrate ($AlCl_3.6H_2O$) were purchased from Aladdin Chemical Co., Ltd. Deionzed water was got from a milipore purification system.

### Synthesis of CDs@$SiO_2$

$C_6H_5O_7(NH_4)_3$ (1 mmol), $NH_3.H_2O$ (1ml) and TEOS (1 ml) were mixed in deionized water (10 ml). After stirring for 4 h, the gel solids were obtained by centrifugation at 9000 rpm for 10 min. Finally, the collectd gel solids were added to an alumina crucible and placed in muffle furnace at 500℃ for 60 min ( the heating rate was 2 ℃/min)

**Synthesis of CDs@$SiO_2$-MO**

The synthesis of CDs@$SiO_2$-MO is similar to that of CDs@$SiO_2$, except that CDs@$SiO_2$-MgO and CDs@$SiO_2$-ZnO require the addition of 2 mmol $MgCl_2$ and 2 mmol $ZnCl_2$ to the precursor solution, respectively. CDs@$SiO_2$-$Al_2O_3$ requires the addition of 2 mmol $AlCl_3.6H_2O$ to the precursor solution, and heating temperature is 600℃.

**Characterization**

The X-ray diffraction (XRD) patterns were obtained using the DB-ADVANCE X-ray diffraction analyzer diffractometer. The morphology and EDS spectra of samples were investigated by field emission scanning electron microscopy (SEM, FEI Quatan FEG 250) equipped with an energy dispersive spectrometer (EDS). The microstructure of samples was performed on a high-resolution transmission electron microscope (TEM, JEOL JEM-F200). The X-ray photoelectron spectroscopy (XPS) of the samples was measured using a Thermo Fisher ESCALAB Xi and the surface functional groups were investigated using Fourier transform infrared spectroscopy (FT-IR) on a Thermofisher Nicolet iS10 spectrophotometer. The photoluminescence (PL) spectra and time-resolved PL spectra were recorded on an Edinburgh Instruments FLS 1000 spectrometer. The ultraviolet-visible (UV-Vis) absorbance spectra were recorded by PE Lambda 950.

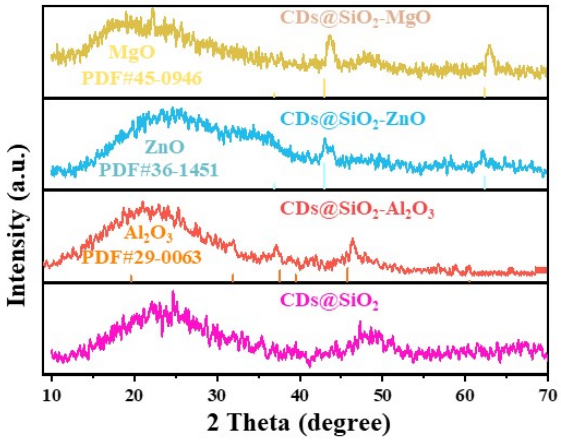


Figure S1. XRD patterns of $CDs@SiO_2$ and $CDs@SiO_2$-MO.

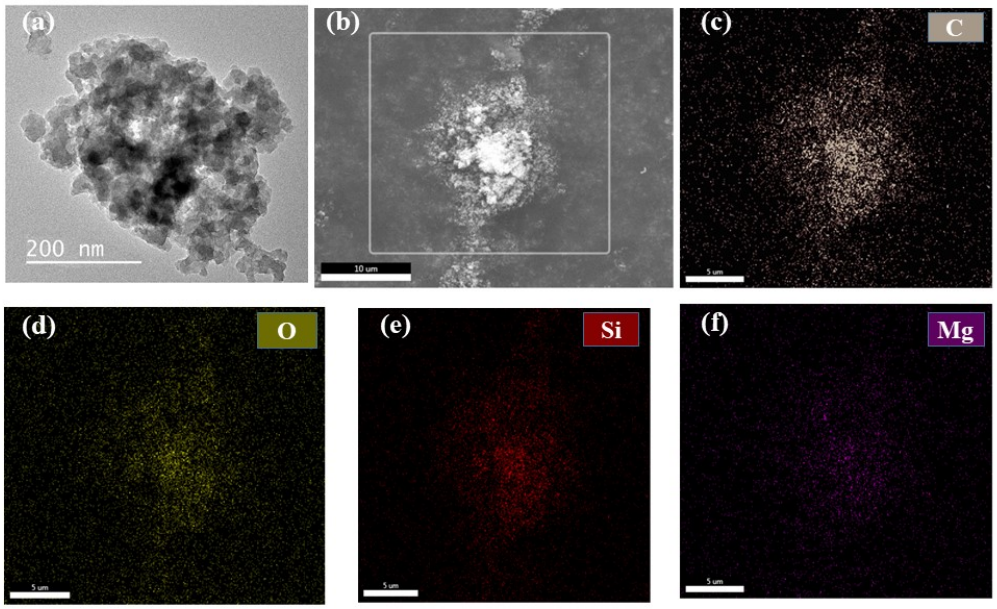


Figure S2. a-b) TEM and SEM image of $CDs@SiO_2$-MgO. c-f) The elemental mapping (C, O, Si and Mg) of EDS spectrum.

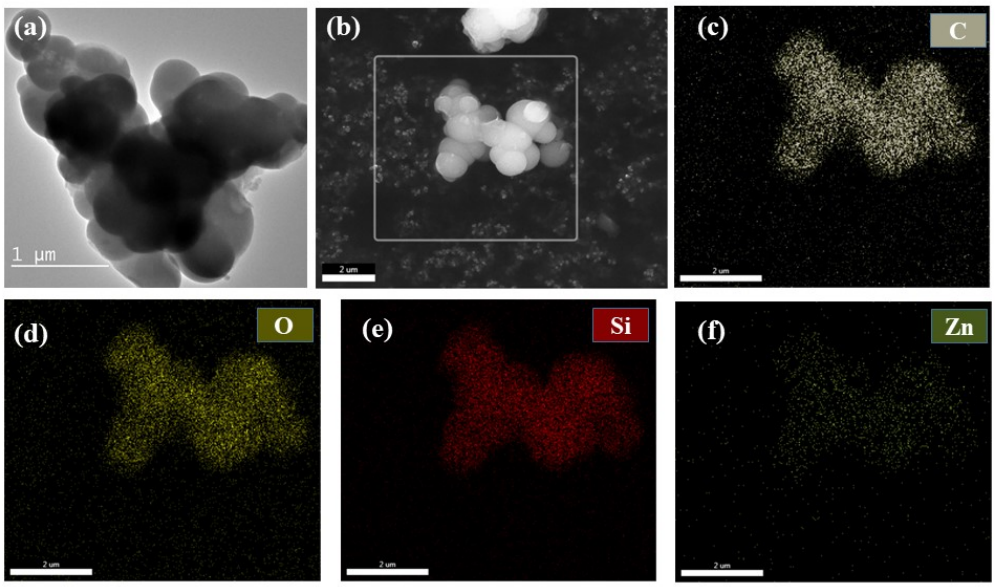


Figure S3. a-b) TEM and SEM image of CDs@$SiO_2$-ZnO. c-f) The elemental mapping (C, O, Si and Zn) of EDS spectrum.

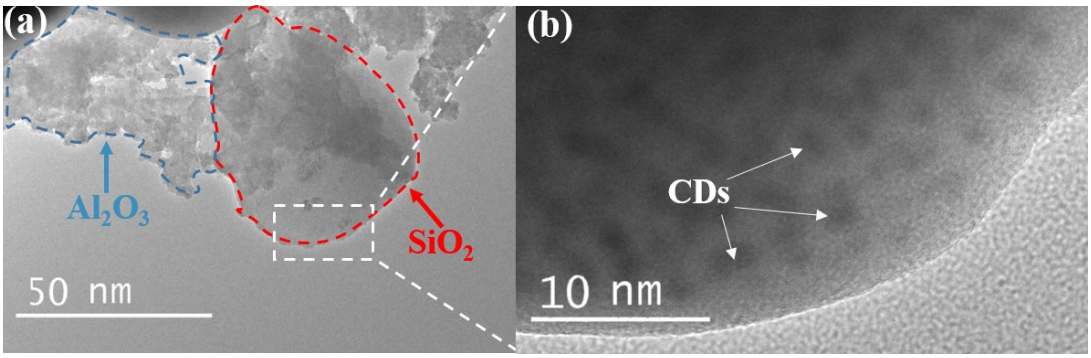


Figure S4. a-b) TEM images of CDs@$SiO_2$- $Al_2O_3$.

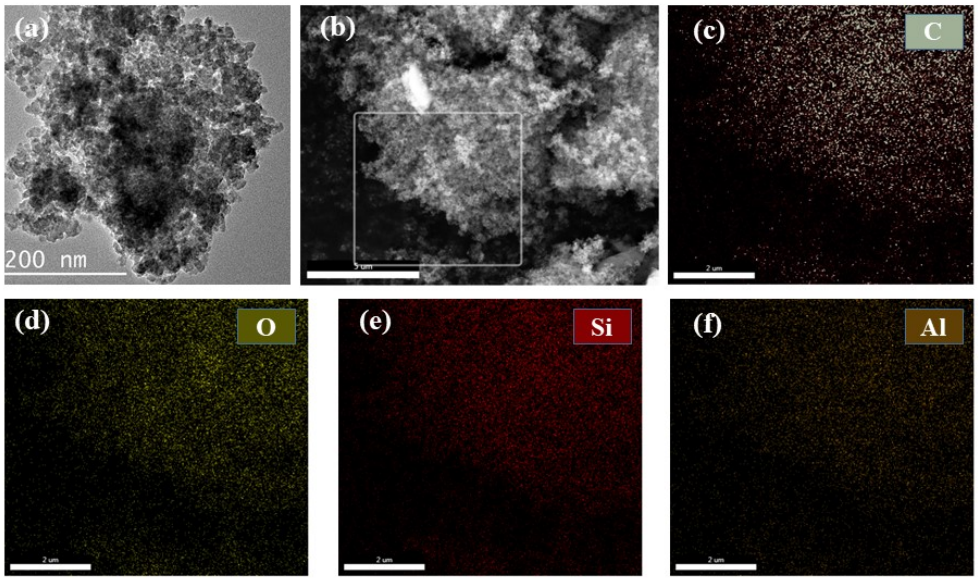


Figure S5. a-b) TEM and SEM image of CDs@$SiO_2$- $Al_2O_3$. c-f) The elemental mapping (C, O, Si and Al) of EDS spectrum.

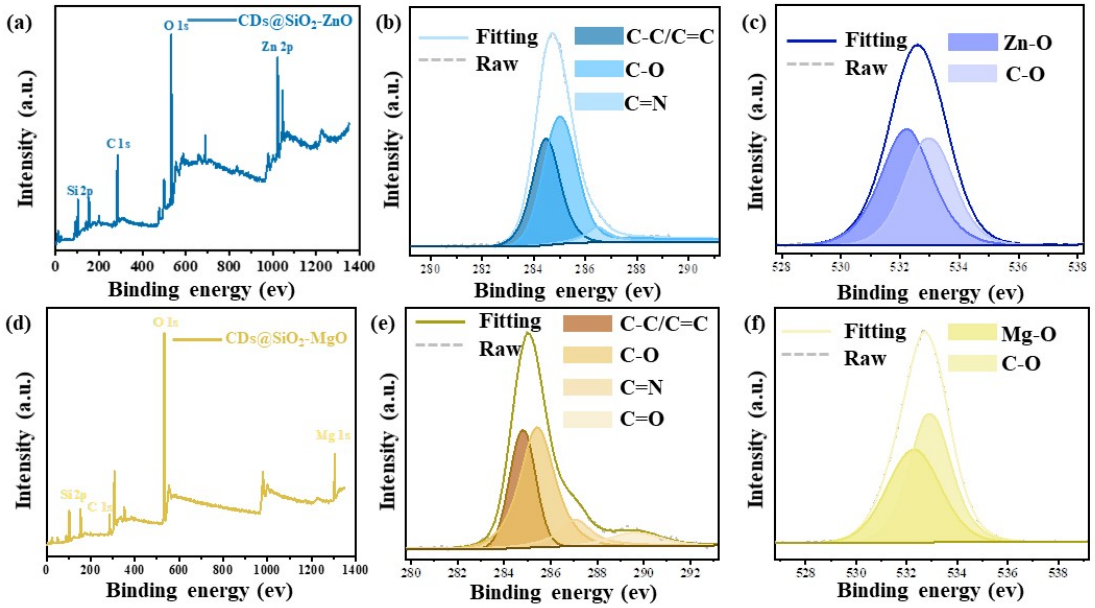


Figure S6 a,b) XPS spectra of CDs@$SiO_2$-ZnO and CDs@$SiO_2$-MgO; and b–c, e-f) high-resolution XPS spectra of C 1s, O 1s.

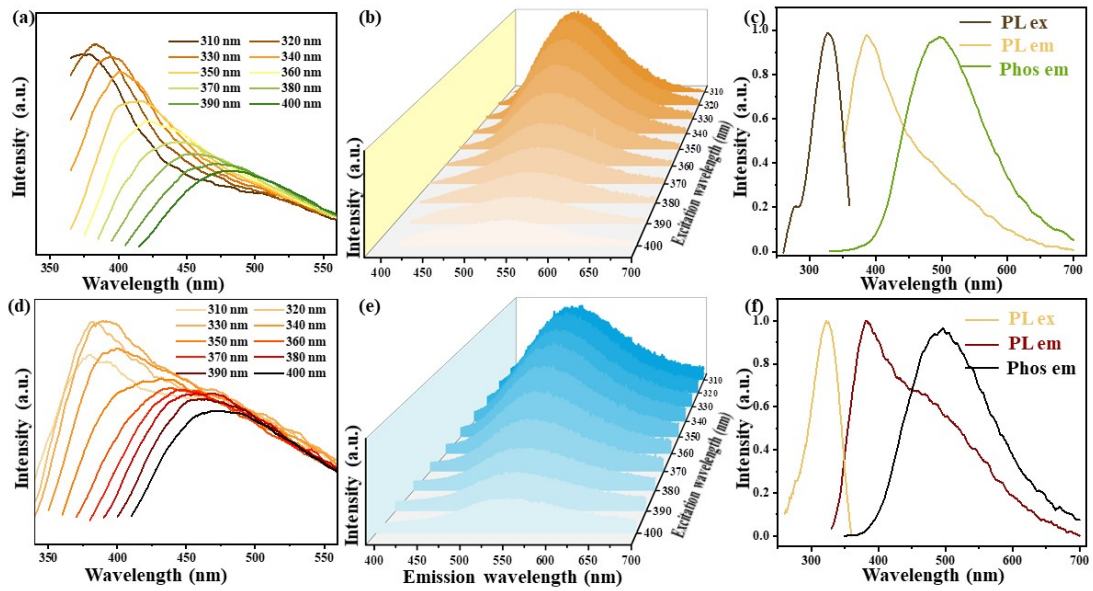


Figure S7. a-b, d-e) Fluorescence and phosphorescence emission spectra of CDs@$SiO_2$-MgO and CDs@$SiO_2$-ZnO at different excitation wavelengths . c,f) Optimal excitation, fluorescence and phosphorescence emission spectra of CDs@$SiO_2$-MgO and CDs@$SiO_2$-ZnO.

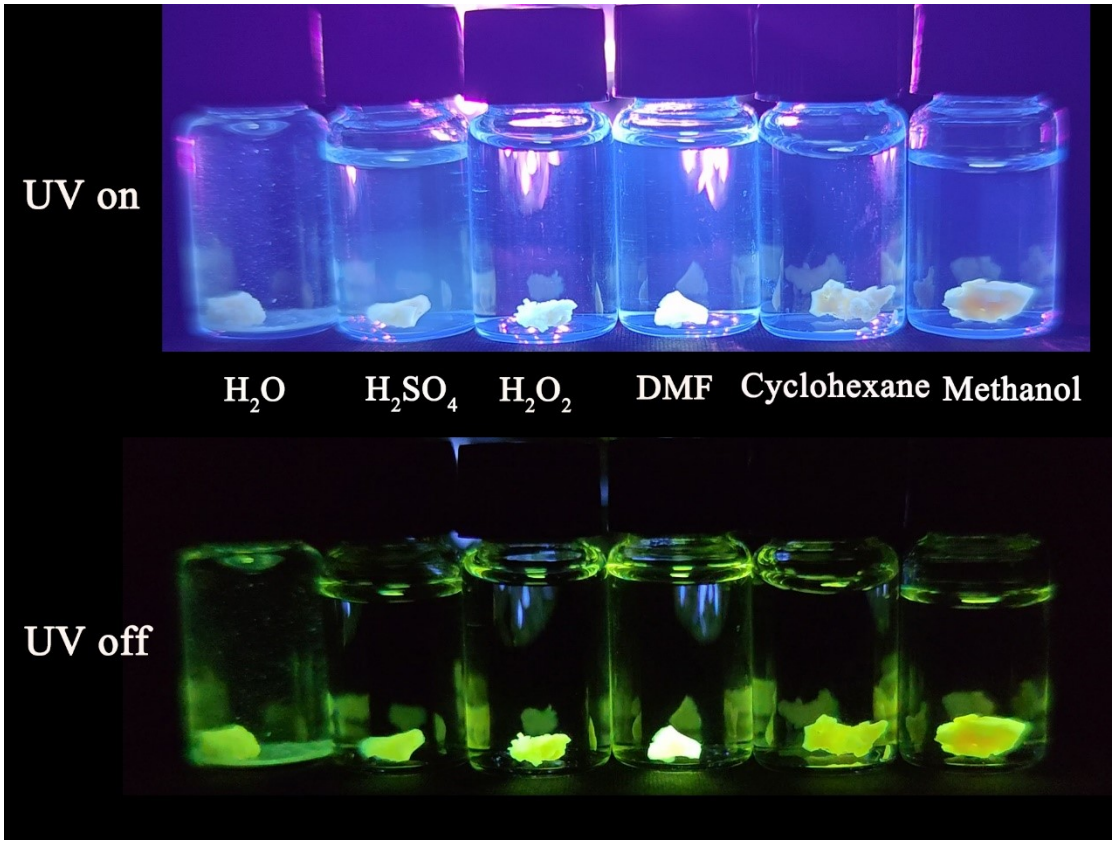


Figure S8. Photographs of the CDs@$SiO_2$- $Al_2O_3$ powder in water, strong oxidizing agents ($H_2O_2$,

$H_2SO_4$) and polar solvents (DMF, cyclohexane, methanol ) excited with a 365 nm UV lamp, and after turning off UV.

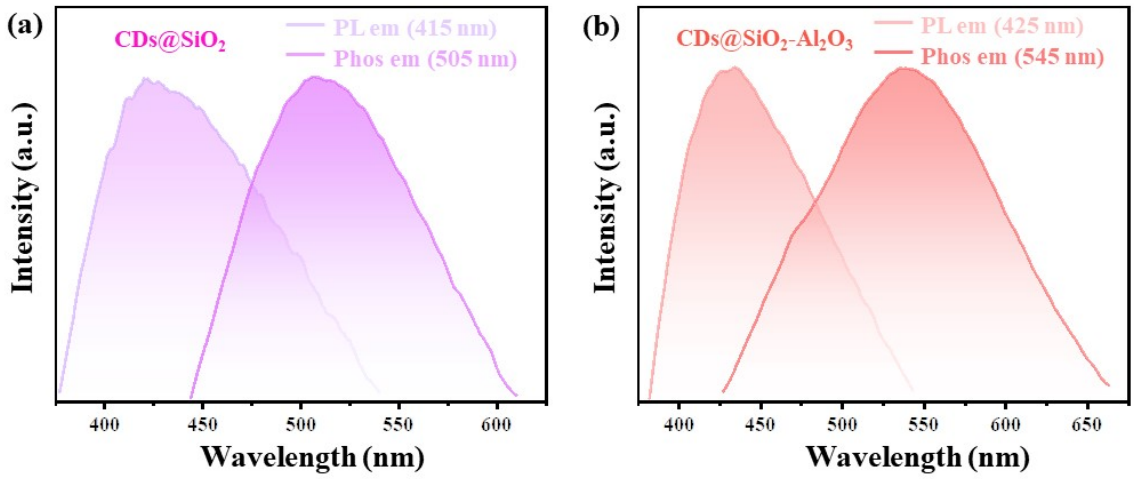


Figure S9. a,b) Fluorescence and phosphorescence emission spectra of CDs@$SiO_2$ and CDs@$SiO_2$-$Al_2O_3$ at 365 nm excitation.

Table S1 Phosphorescent properties of RTP CDs in various matrices

| name | $\lambda_{em}$ (nm) | lifetime (S) | QY (%) | Ref. |
|---|---|---|---|---|
| WSP-CNDs@silica | 520 | 1.86 | 11.6 | [1] |
| CDs@$SiO_2$-600 | 464 | 5.72 | 26.36 | [2] |
| CNDs-RhB@silica | 600 | 0.91 | 3.56 | [3] |
| CNDs@silica | 520 | 1.57 | 12.6 | [4] |
| GCDs@$SiO_2$-OCDs | 580 | 0.376 | 11.6 | [5] |
| B,N,P-$CDs_{280}$@$SiO_2$ | 502 | 1.97 | 3.15 | [6] |
| g-CDs@$Al_2O_3$ | 510 | 0.0007 | 42.6 | [7] |
| CDs@$Al_2O_3$-700 | 500 | 0.911 | 41.7 | [8] |
| CDs@$SiO_2$-$Al_2O_3$ | 520 | 0.689 | 40.1 | This work |

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