# Advanced Encryption based on fluorescence quenching of ZnO nanoparticles

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The energy dispersive x-ray spectroscopy (EDS) was used to characterize the elemental composition of the ZnO NPs, and the results of which are presented in Figure S1. One can see that the NPs are mainly composed of C, N, O, Si, Zn, and K elements. The existence of the C signal is duo to copper wire mesh supporter, Si and N signal is duo to APTES, and K is due to the residual KOH. The relative molar (At) and mass (Wt) ratio of N, O, Si, and Zn is presented in the inset of the figure. Si and N elements have been incorporated into the NPs. X-ray diffraction (XRD) pattern of the NPs has been recorded, as shown in Figure S2. The diffraction peaks are attributed to the diffraction of wurtzite ZnO.

Fourier transform infrared (FTIR) spectra of the ZnO NPs were recorded in a Bruker VERTEX-70 FTIR spectrometer using the KBr method, as indicated in Figure S3. Stretching vibration mode of Si-O at approximately 1000 $cm^{-1}$ is clearly observed, indicating that silane has been coated onto the ZnO NPs.

X-ray photoelectron spectroscopy (XPS) was used to measure the binding states of the ZnO NPs, as shown in Figure S4. Note that the binding energy has been calibrated using that of C 1s (284.5 eV), as presented in the inset of Figure S4 (a). The

Zn $2p_{3/2}$, O 1s, N 1s, Si $2p_{3/2}$ are located at 1023.8 eV, 531.1 eV, 399.7 eV and 101.6 eV, respectively. The XPS data confirm that Si has been coated onto the surface of the ZnO NPs.

The aggregation of ZnO NPs will influence the definition and resolution of the printing. To investigate whether the ZnO NPs of 0.5 mol/L induce aggregate phenomenon, the size distribution of the ZnO NPs has been measured by dynamic light scattering analysis (DLS) method, as shown in Figure S5(b). The size of the ZnO NPs shows a narrow distribution with the center of around 6 nm, which is roughly consistent with the TEM observations shown in Figure S5(a) (3- 5 nm). The above datum reveals that aggregation has not occurred in the ZnO NPs.

The fluorescence spectra and images of the ZnO NPs under different pH value have been measured, as shown in Figures S6(a) and S6(b). One can see that the fluorescence is consisted of two emission bands, one at around 525 nm, and the other at 450 nm. The intensity of the emission at around 525 nm has been quenched completely when the pH value is smaller than 6.0, indicating that the ZnO NPs have been dissolved when the pH value of the solution is less than 6.0. Nevertheless, the emission band at around 450 nm is visible in all the investigated samples, which comes from the fluorescence of the vinegar solution.

The absorption spectra of the ZnO NP solution, $CuCl_2$ solution, and ZnO NPs/$CuCl_2$ mixed solution are illustrated in Figure S7. One can see that for ZnO there is a strong absorption in the UV region, while it is almost transparent in the visible region. While the absorption spectrum of the mixed solution is very similar with that

of the ZnO NPs, indicating that the ZnO NPs have not been decomposed or degraded after the introduction of the $CuCl_2$.

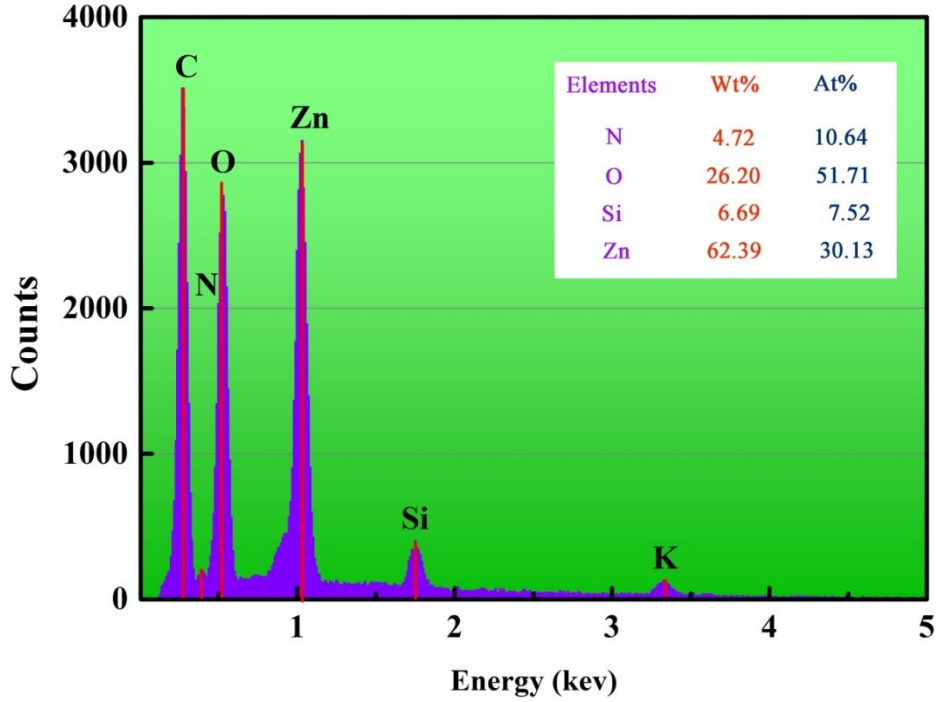


Figure S1. The EDS spectrum of the ZnO NPs, the inset shows the elemental composition of the ZnO NPs.

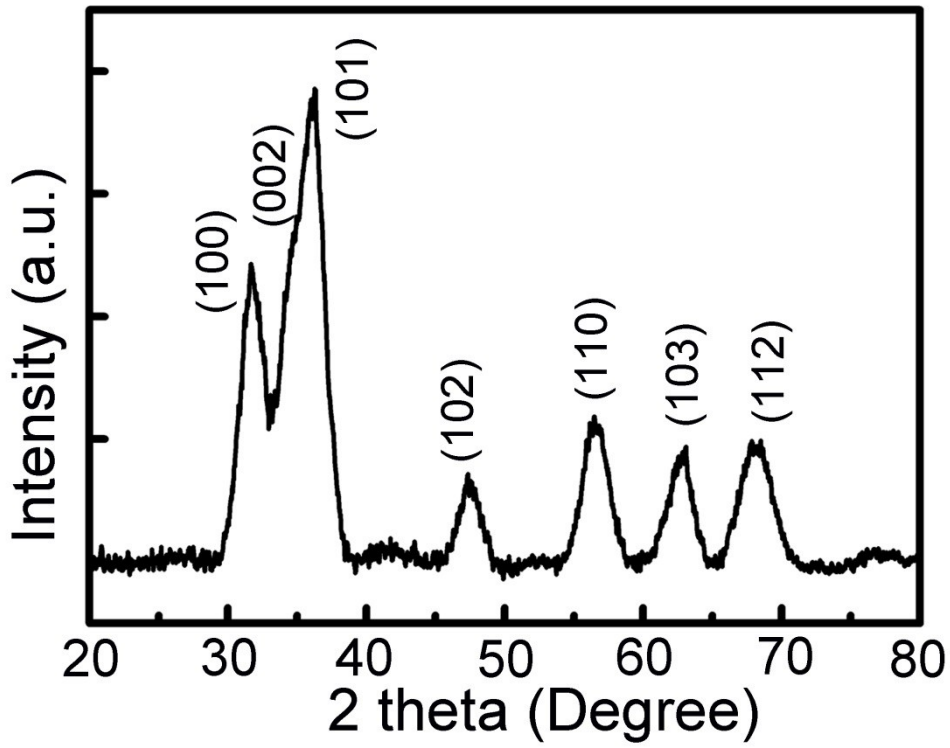


Figure S2. XRD pattern of the ZnO NPs.

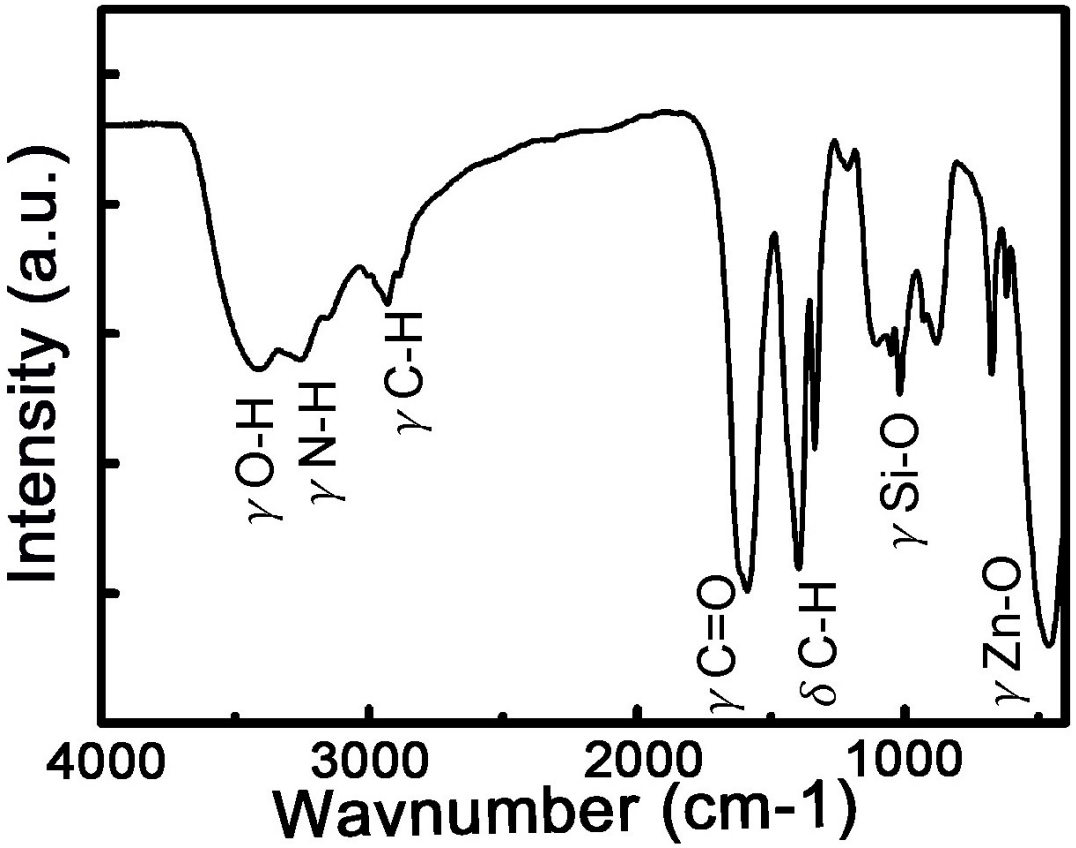


Figure S3. FTIR spectra of the ZnO NPs.

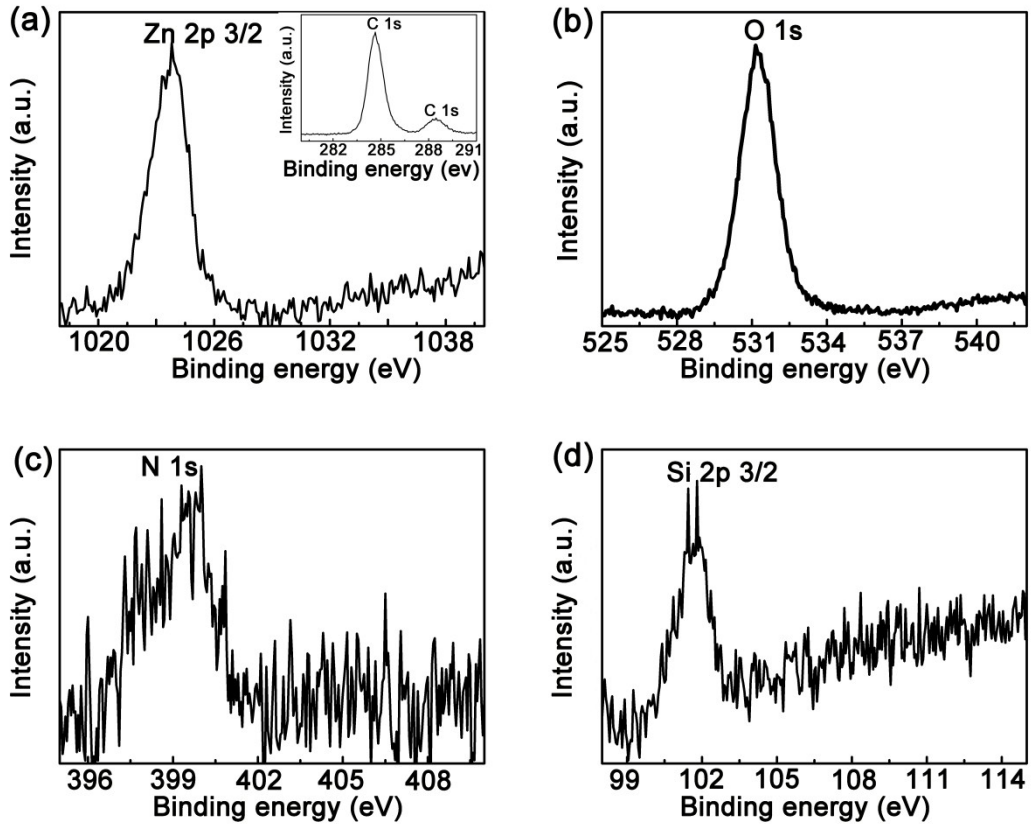


Figure S4. Zn 2p (a), O 1s (b), N 1s (c) and Si (2p) XPS pattern of ZnO NPs.

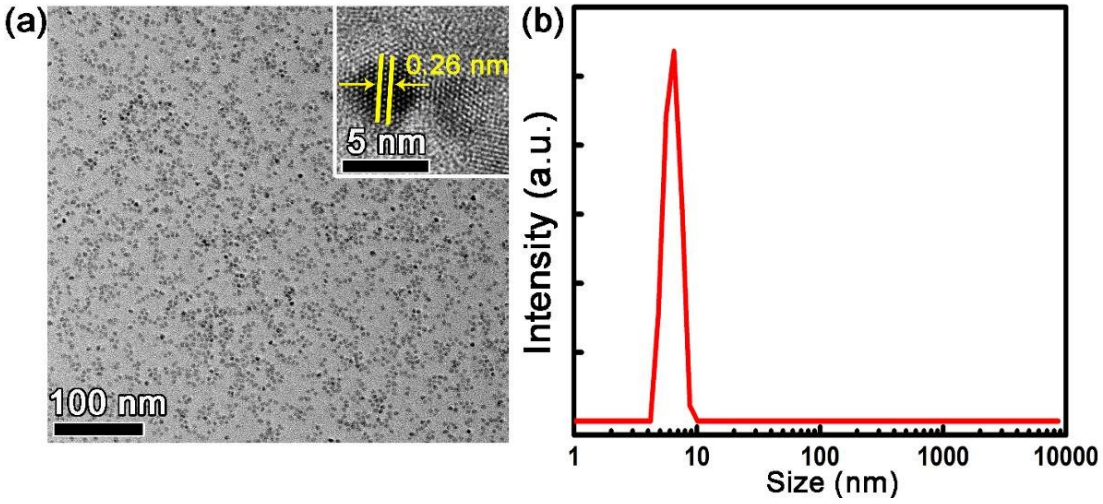


Figure S5. (a) TEM image of the ZnO NPs with concentration of 0.5 mol/L, and the inset shows the high resolution TEM image of the NPs. (b) The DLS spectrum of ZnO NPs with concentration of 0.5 mol/L, revealing the size of the ZnO NPs is around 6.0 nm.

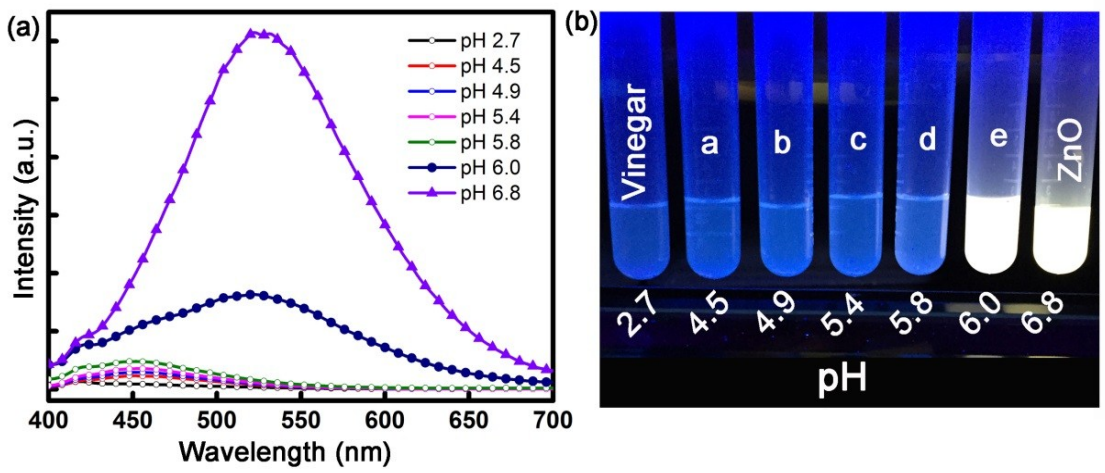


Figure S6. The fluorescence spectra (a) and images (b) of the ZnO NP solution with pH of 2.7, 4.5, 4.9, 5.4, 5.8, 6.0, 6.8, respectively.

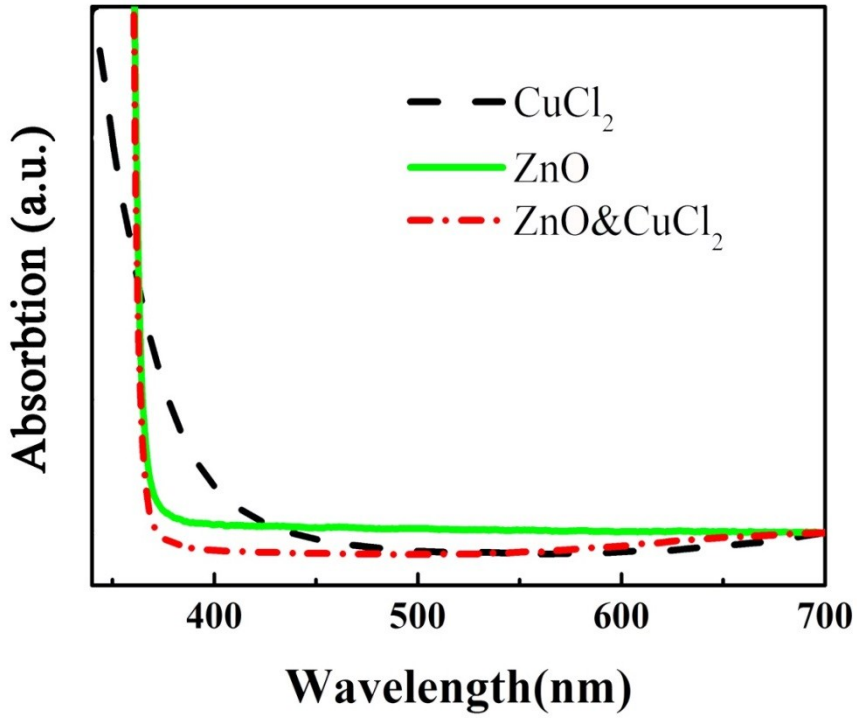


Figure S7. UV-Vis absorption spectra of the ZnO NPs, $CuCl_2$, and ZnO NPs/$CuCl_2$ mixed solution.