

## Electronic Supplementary Information

### Dual-donor ( $Zn_i$ and $V_O$ ) mediated ferromagnetism in copper-doped ZnO nanocrystalline films: a thermally driven defect modulation process

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**Fig. S1** Etching experimental result by ICP-AES.

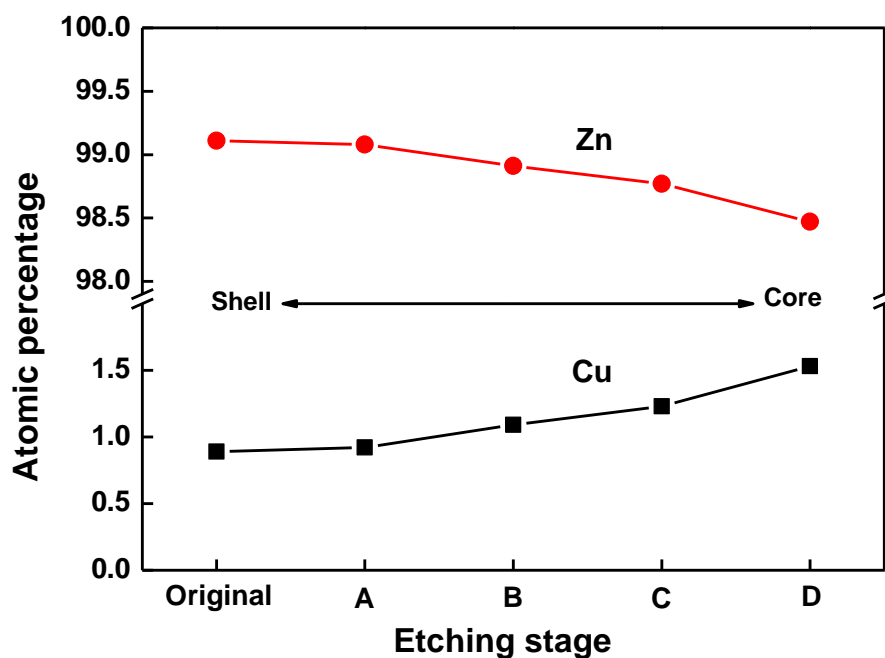
**Fig. S2** Room-temperature PL decay curves of different annealed samples monitored at the peak of GB (a) and YB (b).

**Fig. S3** The comparison of PL and PLE (14.6 K) including its 1<sup>st</sup> derivative spectrum for 900 °C vacuum annealed ZnO:Cu film.

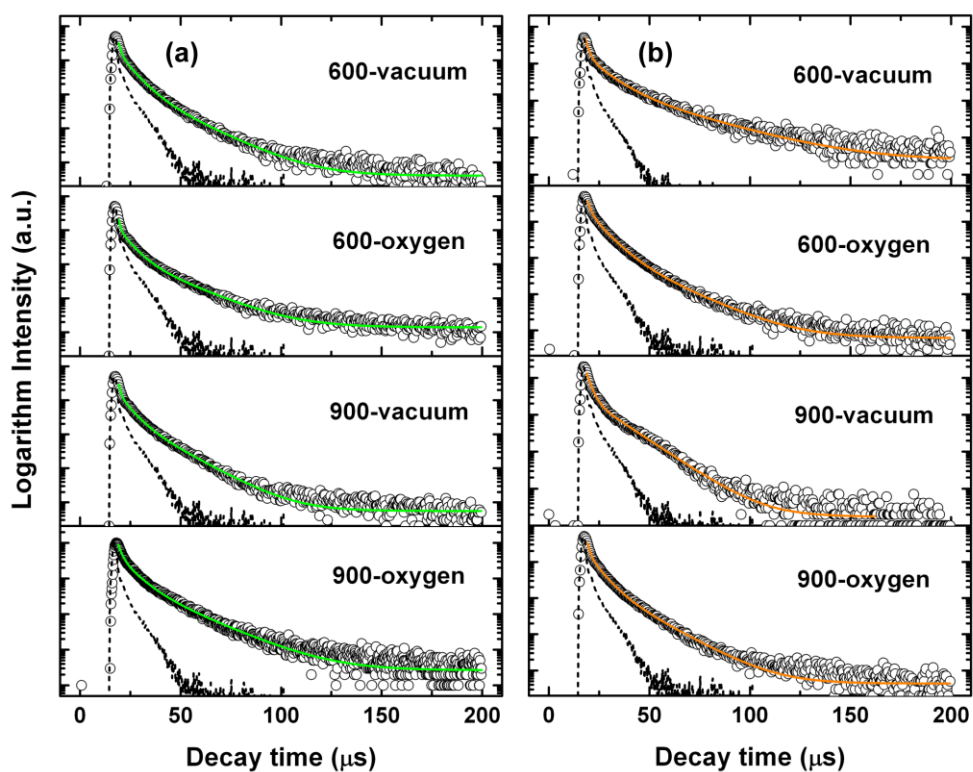
**Fig. S4** C 1s XPS spectrum in 900 °C vacuum annealed ZnO:Cu film with surface etched ca. 10 nm.

**Fig. S5** XPS core-level spectra in 2p area for 600 °C (a) and 900 °C (b) oxygen annealed ZnO:Cu films.

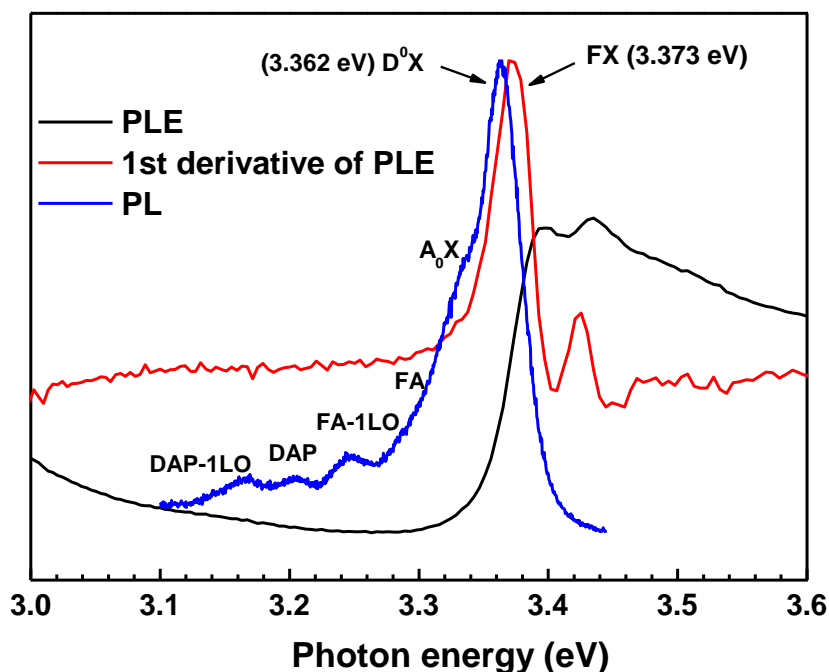
**Fig. S6** Magnetic response from pure ZnO films annealed at 900 °C vacuum and 900°C oxygen.



**Fig. S1** Etching experimental result by ICP-AES. Cu atoms tend to be distributed in inner part of NC. Detailed experimental description about quantitative etching experiments is as follows. Four groups of 10 $\mu$ L purified NC colloidal solution (containing 0.5 mg NCs) were diluted in 1 mL chloroform solvent, respectively. Here, acetic acid was used as etchant. Here, acetic acid was used as etchant. Prior to the addition, a series of etchant solutions with different concentrations ( $3.0 \times 10^{-6}$  mM,  $6.0 \times 10^{-6}$  mM,  $9.0 \times 10^{-6}$  mM, and  $1.2 \times 10^{-5}$  mM) with the same volume (0.5 mL) were prepared and denoted as solution A, B, C, and D, respectively. The etchant solutions were added into the NC solutions within 5 min under stirring and then the reactions were lasted for 90 min. After fully complete etching processes, all samples underwent extensive methanol and *n*-octylamine washing to remove the residuals from the etchant and the ions etched away from NCs. The obtained etched NC species could be further suspended in chloroform for the TEM observation and elemental analysis.

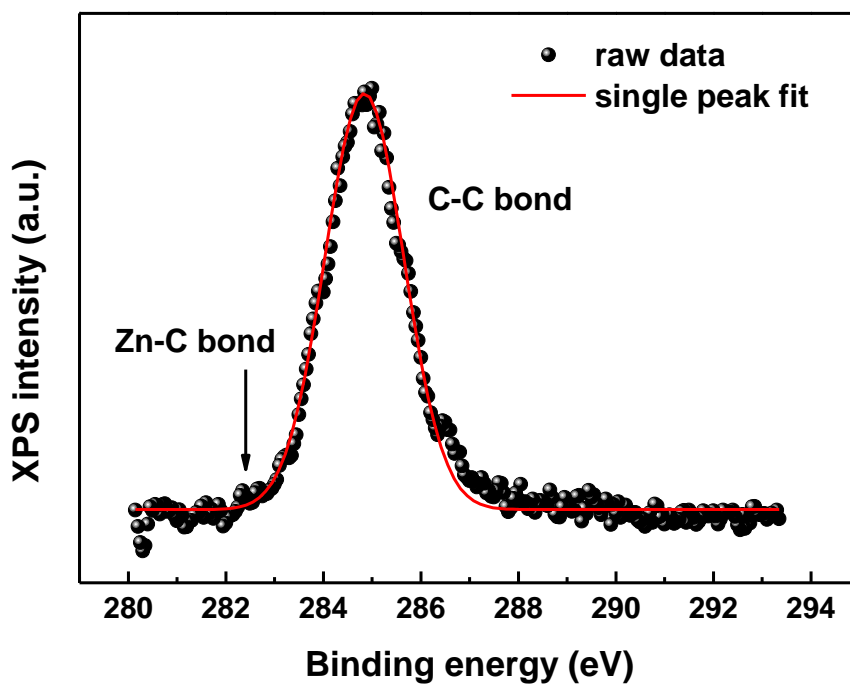


**Fig. S2** Room-temperature PL decay curves of different annealed samples monitored at the peak of GB (a) and YB (b). Dashed lines represent IRF (instruments response function) signals and solid ones fitted curves via multiexponential fitting method.



**Fig. S3** The comparison of PL and PLE (14.6 K) including its 1<sup>st</sup> derivative spectrum for 900 °C vacuum annealed ZnO:Cu film. The dip of 1<sup>st</sup> derivative of PLE spectrum clearly shows the energy level position of free exciton (FX). According to the definition, localization energy  $E_{loc} = E_{FX} - E_{D^0X} = 11$  meV. And  $E_{loc}$  is given by more generally by  $E_{loc} = A + B \cdot E_D = -3.8 + 0.365 \cdot E_D$ , where  $E_D$  is the donor ionization energy. Hence,  $E_D$  can be estimated to be 40 meV.

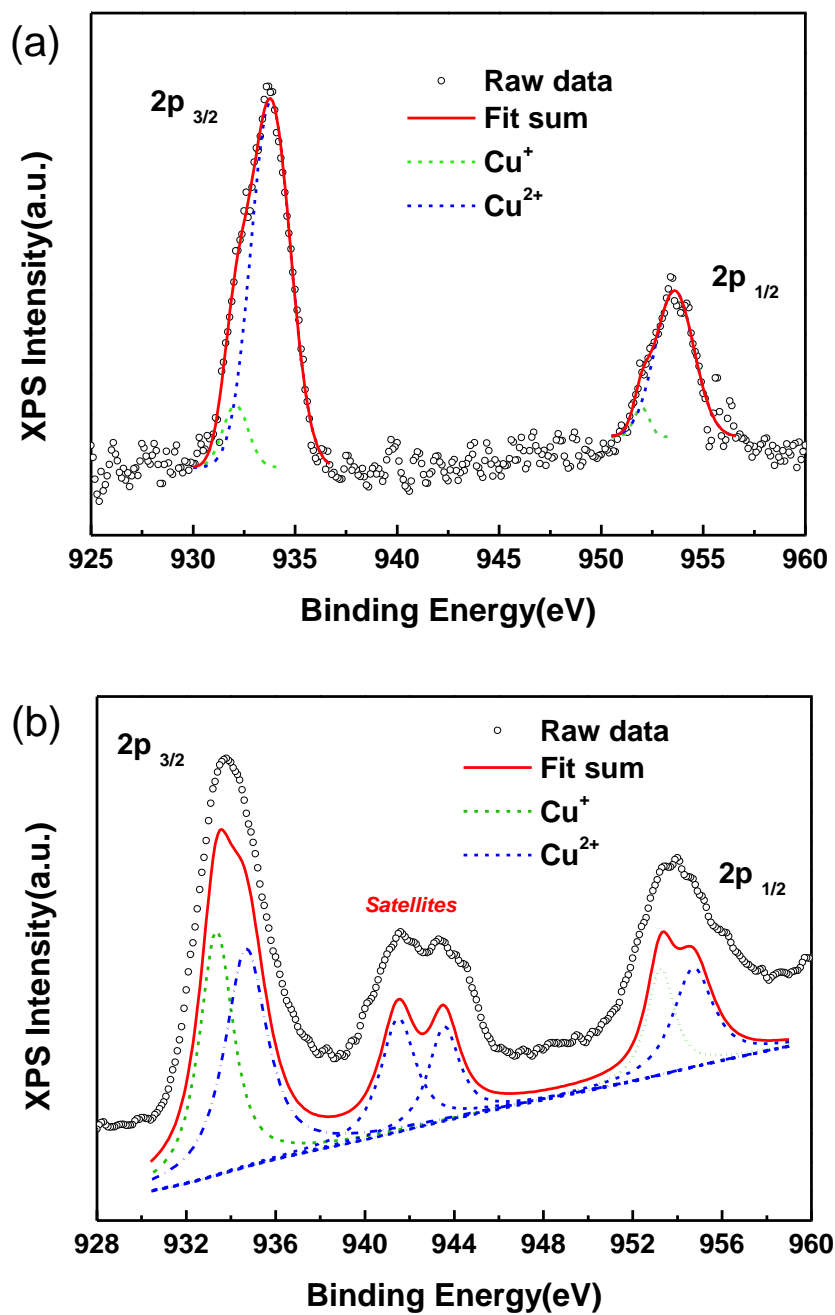
**Ref:** He, H. P. et al. *J. Appl. Phys.* **2007**, *102*, 013511.



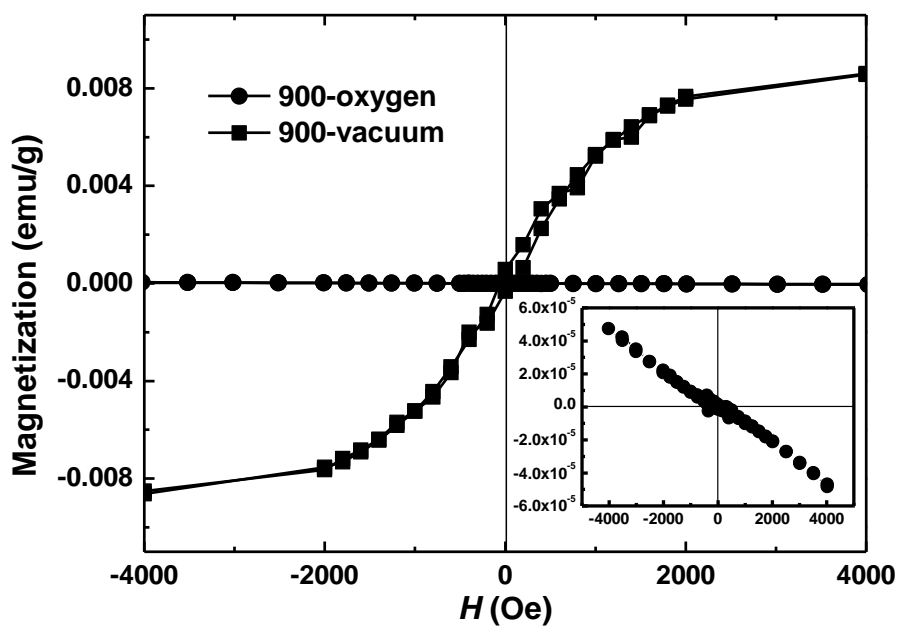
**Fig. S4** C 1s XPS spectrum in 900 °C vacuum annealed ZnO:Cu film with surface etched ca. 10 nm. The peak at 284.6 eV can be attributed to free carbon (carbon from contamination). The absence of carbon atoms in the carbide between 280 and 284 eV, i.e. Zn-C bond, indicates that carbon substitution for oxygen is not present in our samples.

**Ref:** Pan, H. et al. *Phys. Rev. Lett.* **2007**, *99*, 127201.

Meyer, B. K. et al. *Phys. Rev. B*, **2007**, *76*, 184120.



**Fig. S5** XPS core-level spectra in 2p area for 600 °C (a) and 900 °C (b) oxygen annealed ZnO:Cu films. The presence of satellite peak indicates the segregation of CuO due to the multiplet splitting in the  $2p^53d^9$  final state.



**Fig. S6** Magnetic response from pure ZnO films annealed at 900 °C vacuum and 900 °C oxygen. Oxygen annealing induced a diamagnetic feature (inset) and vacuum annealing corresponds to a weak FM loop.