Supporting Information

Unexpected Surface Superparamagnetism in Antiferromagnetic Cr_2O_3 Nanoparticles

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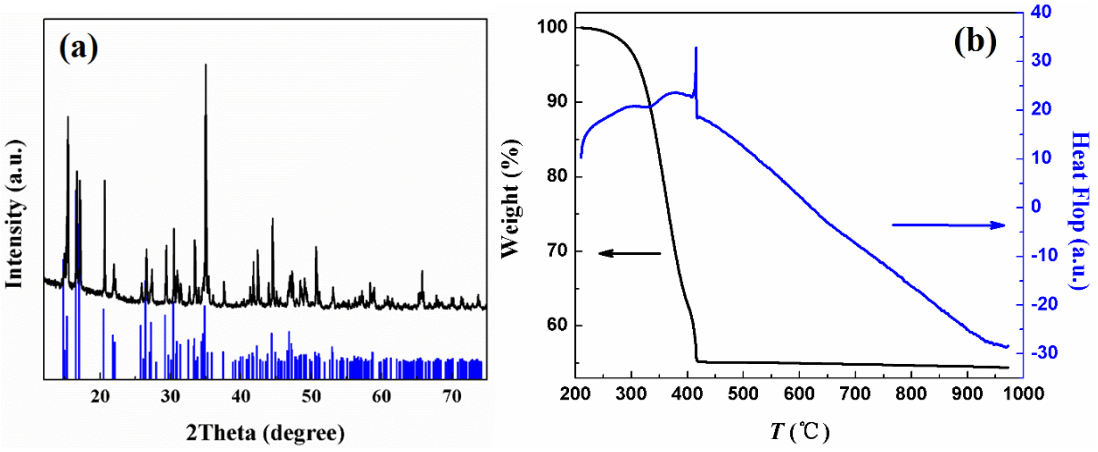


Fig. S1 (a) XRD pattern of $CrCl_3 \cdot 6H_2O$ precursor (JCPDS No. 71-2121). (b) TG-DTA curves of $CrCl_3 \cdot 6H_2O$ precursor which were performed in the air under a heating rate of 10 ºC/min.

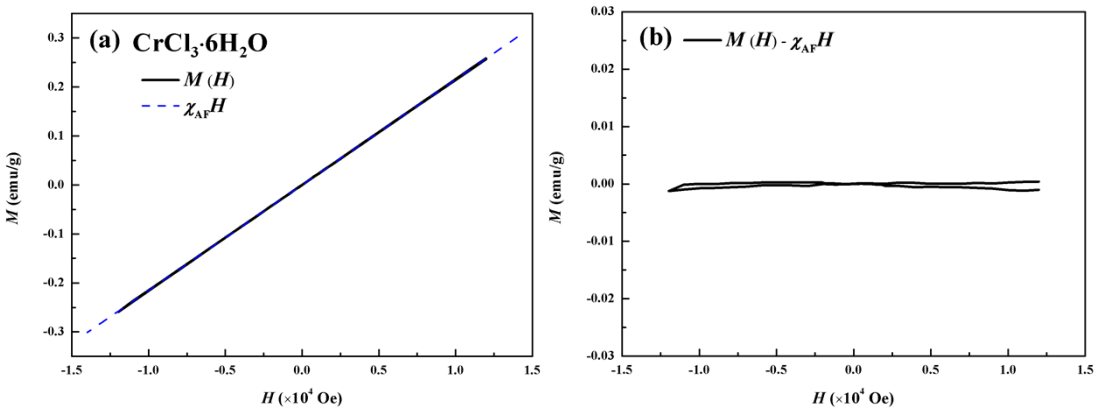
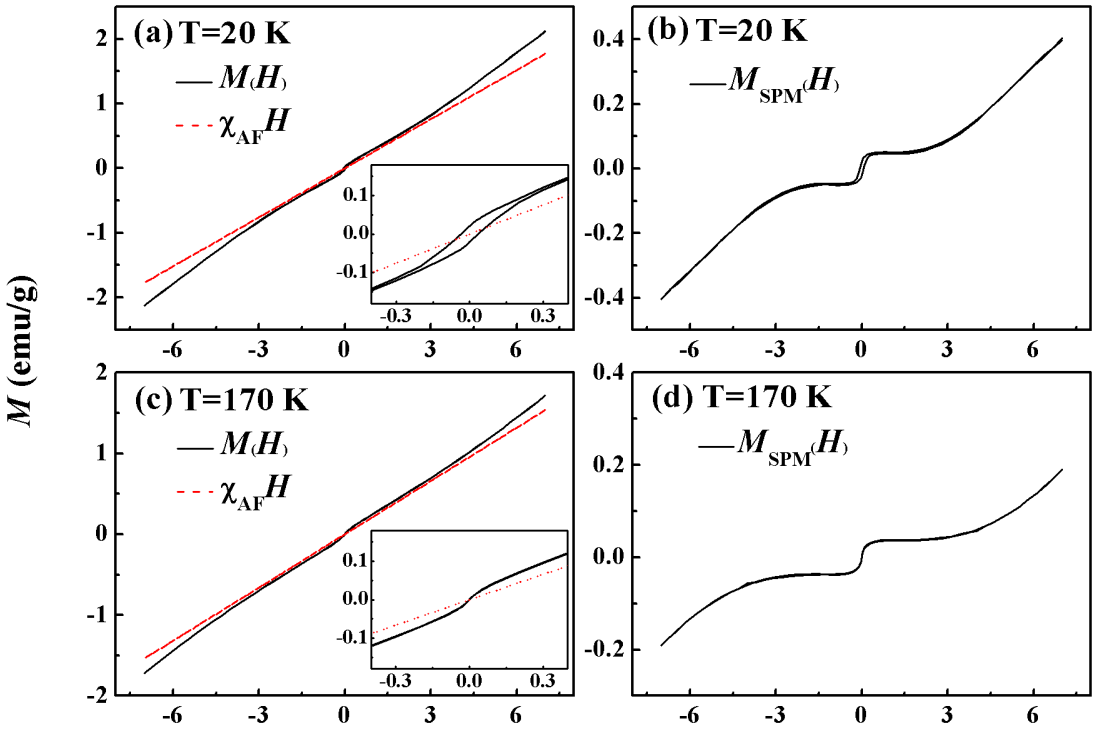


Fig. S2 (a) *M-H* curve of $CrCl_3 \cdot 6H_2O$ precursor and the fitted AF signal (χ_{AF}**H*). (b) The signal after subtracting AF contribution from the raw *M-H* curve.

For clarity, the raw signals and AF magnetization (χ_{AF}*H) are shown in Fig. S3. The SPM signals were described by the equation M (H) = M_{SPM} (H) + χ_{AF}*H.[1, 2] The AF susceptibility (χ_{AF}) was obtained by linear fitting the M (H) curve in high field. However, in our sample, the χ_{AF} increases obviously in high field (> 2 T), which is attributed to the occurrence of SF and the moments in AF core reverse from parallel to perpendicular to the applied field. In that case, the χ_{AF} cannot be approximated as a constant. So we fitted the slope using the data before SF transition (< 2 T) and after the saturation of S-shape SPM signal (> 0.5 T).

The nonlinear M (H) curves originate from two reasons: 1. S-shape SPM signal in lower field is attributed to the presence of Cr^{4+} in particle surface, and this could exist above T_N of Cr_2O_3; 2. another nonlinear signal in higher field (> 2 T) is due to the SF transition of AF core and only present below T_N.



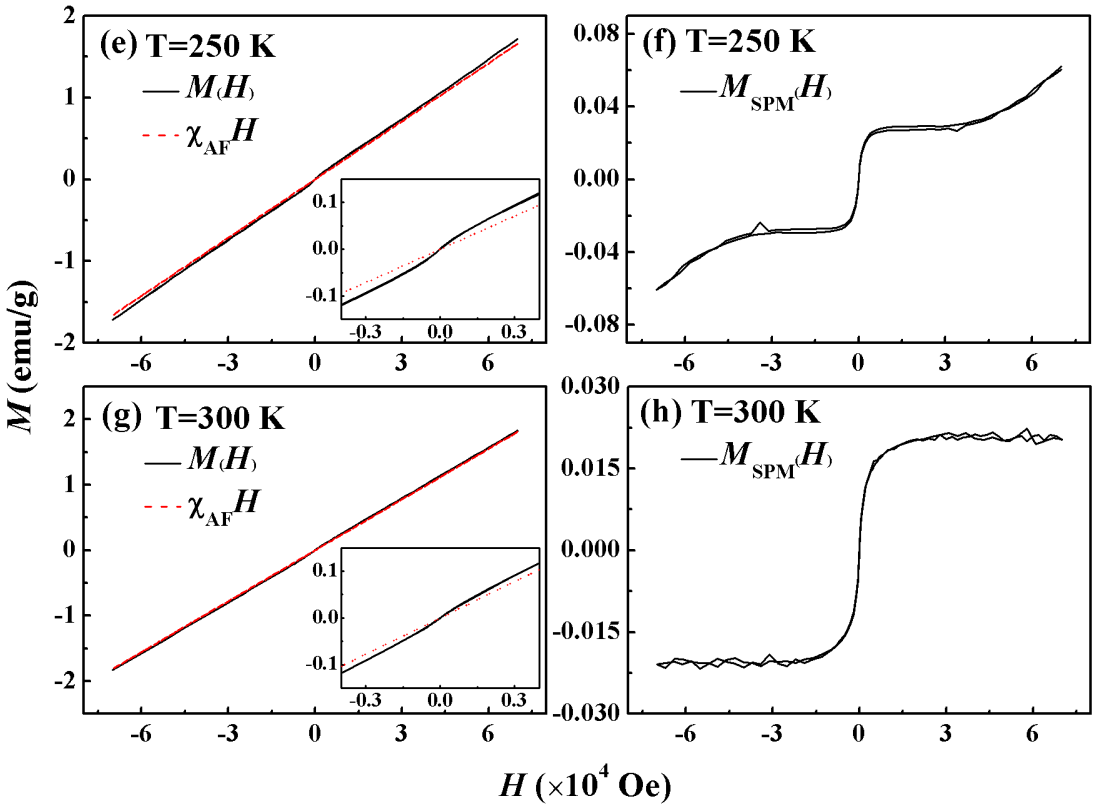


Fig. S3 *M-H* curves of Cr_2O_3 nanoparticles and the fitted AF signals (χ_{AF}**H*) at (a) 20 K, (c) 170 K, (e) 250 K, and (g) 300 K. The insets show the *M-H* curves in lower field. The SPM and SF signals after subtracting AF contributions from the *M-H* curves are shown in (b) 20 K, (d) 170 K, (f) 250 K, and (h) 300 K.

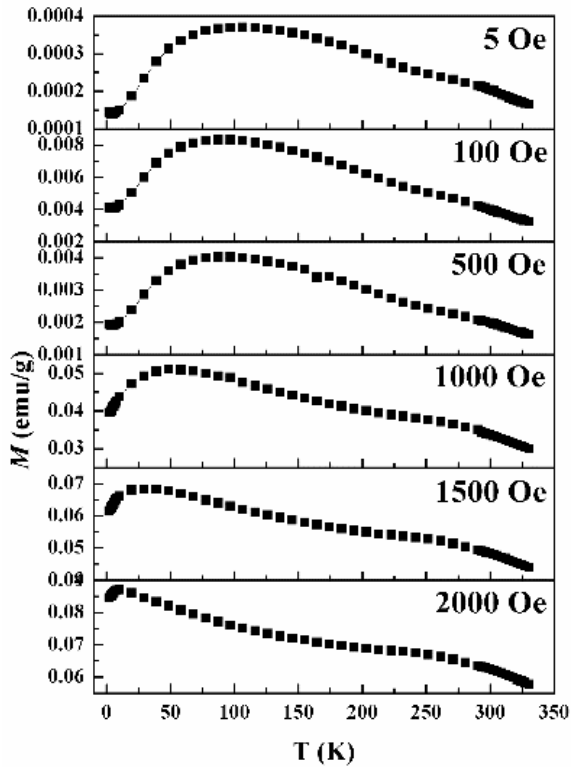


Fig. S4 Field dependence of ZFC curves measured from 2 to 330 K at 5, 100, 500, 1000, 1500, and 2000 Oe.

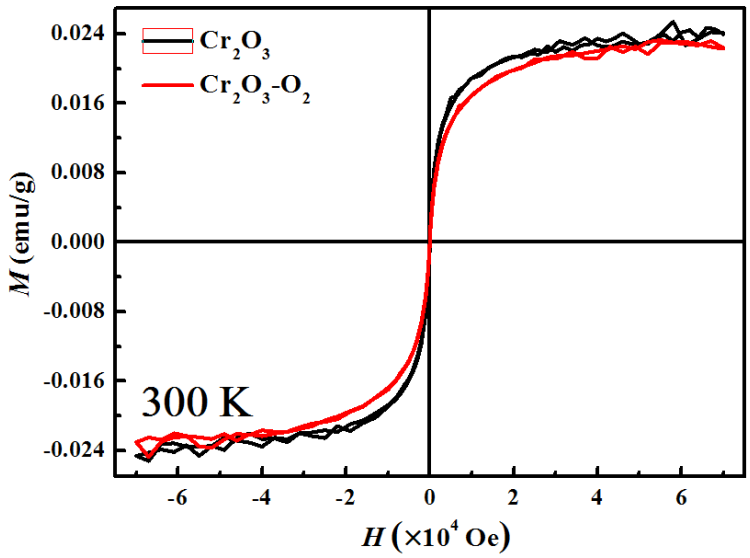


Fig. S5 *M-H* curves of Cr_2O_3 (black line) and Cr_2O_3-O_2 (red line) nanoparticles measured at 300 K (after subtracting AF signals)

1. S. A. Makhlouf, H. Al-Attar and R. H. Kodama, *Solid State Commun.*, 2008, **145**, 1-4.
2. S. Mandal, S. Banerjee and K. S. R. Menon, *Phys. Rev. B*, 2009, **80**, 214420.