

Supporting Information

Water-Sensitive Phase-transition of Carbon Dots-Calcium Carbonate Composite for Moisture Detection in Organic Solvents

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1. Experimental Section

Chemicals and Materials. Ammonium citrate tribasic and ammonium bicarbonate were from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Calcium chloride was from Shanghai Lingfeng Chemical Co., Ltd. Ethanol and 3A molecular sieves were from Shanghai Titan Scientific Co., Ltd. Acetonitrile was from Amethyst Chemicals (J&K Scientific, China). Ultrapure water (18.2 M Ω) used throughout in this study was obtained from the Millipore Simplicity system (Millipore, USA).

Synthesis of carbon dots. The synthesis of CDs was based on a reference with certain modifications.¹ Briefly, 0.1 g ammonium citrate tribasic was grinded using a mortar and pestle, and then transferred to a 50-mL beaker. The beaker was placed in a hot air oven and heated at 180°C for 2 h. A black bubble-like product was obtained. After being crushed into pieces, the product was dissolved in 100 mL absolute ethanol and sonicated for 30 min, before centrifuged down with 12,000 rpm for 20 min to remove large particles.

Synthesis of amorphous calcium carbonate (ACC) nanoparticles. The synthesis of ACC nanoparticles was based on a reference with certain modifications.² Briefly, 0.4 g calcium chloride was dissolved in 100 mL absolute ethanol. A glass bottle containing this solution was covered by plastic wrap with three pinholes and placed in a sealed transparent plastic jar with certain amount of ammonium bicarbonate powder in another open bottle. After about one day of incubation at ambient temperature, slightly opalescent ACC nanoparticles formed. The nanoparticles were centrifuged down at 12,000 rpm for 20 min and redispersed in absolute ethanol dried with 3A molecular sieves under the assistance of water-bath sonication. The obtained ACC nanoparticle dispersion was stored at -20°C when not in use.

Synthesis of CD-ACC nanocomposite. The synthesis of CD-ACC nanocomposite was the same as above synthesis of ACC except that before incubation, 3 mL of as-synthesized CDs was added into the solution and the incubation time was longer up to about two days until the dispersion became opalescent. The nanocomposite powder was obtained by vacuum drying.

Characterization. Scanning electron microscopy (SEM) images were obtained on a HITACHI-S3400N scanning electron microscope. Transmission electron microscopy (TEM) image of CDs was collected in a JEOL JEM-2100 transmission electron microscope. Other TEM images were taken by a JEOL JEM-1400 transmission electron microscope. X-ray powder diffraction analyses were conducted on a D/max 2550 VB/PC rotating anode X-ray powder diffractometer (Rigaku Corporation, Japan). Element analyses (C, H, O and N) were carried out on a Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Germany). Zeta potentials were measured using a Zetasizer nano ZS (Malvern Instruments). Fluorescence spectra were recorded in a fluorescence microplate reader (Bio-Tek Instrument, Winooski, USA) using a black 96 well microplate (WHB, Shanghai, China). Photographs were taken with a digital camera under white light or a 365 nm UV lamp excitation.

General Method. In a specific measurement, 50 μ L of CD-ACC nanocomposite dispersion was

added into 0.5 mL organic solvent to be tested. After 30 min of incubation, aggregate was centrifuged down at 10,000 rpm for 2 min, and the supernatant was transferred in to a 96 well microplate (200 μ L per well). The fluorescence intensity of the supernatant was measured in a microplate fluorescence reader (BioTek FLx800, USA), excitation at 360 nm (bandwidth 40 nm) and emission at 460 nm (bandwidth 40 nm).

2. Reference

- (1) Lai, I. P.; Harroun, S. G.; Chen, S.; Unnikrishnan, B.; Li, Y.; Huang, C. *Sensors Actuators B. Chem.* **2016**, 228, 465–470.
- (2) Chen, S.F.; Cölfen, H.; Antonietti, M.; Yu, S.H. *Chem. Commun.* **2013**, 49 (83), 9564-9566.

3. Zeta Potential Measurement

Table S1. Zeta potentials of bare CD, ACC (red) and CD-ACC nanocomposites prepared from different amount of calcium ions and CD. **means not measured

Carbon dots (mL) \ Calcium chloride (mg)	Zeta potential of as-synthesized ACC-CD nanocomplex (mV)					
	0	50	100	150	200	250
0	**	**	**	**	+6.09	**
0.5	-7.57	**	**	+4.49	+5.26	+6.84
1		**	+7.92	+5.8	**	**
1.5		**	**	+5.2	**	**
2		**	**	+6.79	**	**
2.5		+6.27	**	+5.38	+5.19	+5.67

4. Characterization of ACC and CD

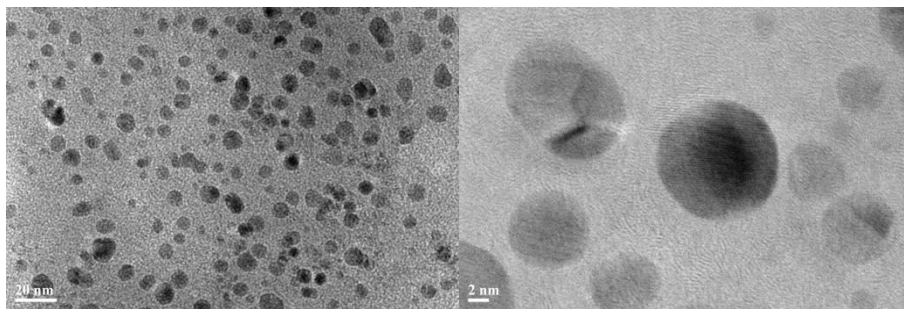


Figure S1. HRTEM images of ACC.

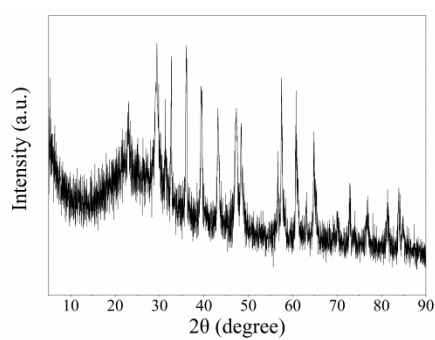


Figure S2. XRD pattern of ACC.

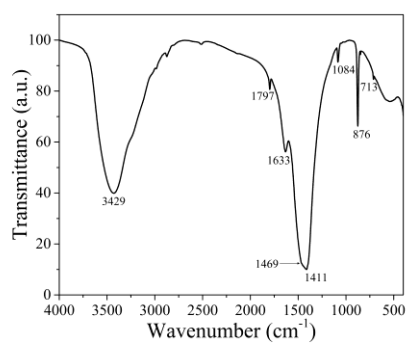


Figure S3. FTIR spectrum of ACC.

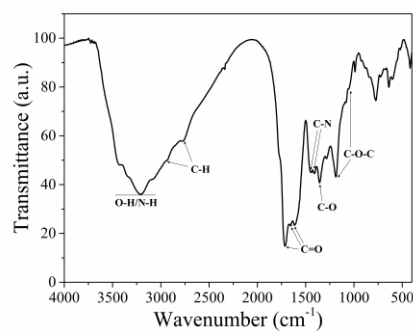


Figure S4. FTIR spectrum of CDs.

5. Moisture Detection Results

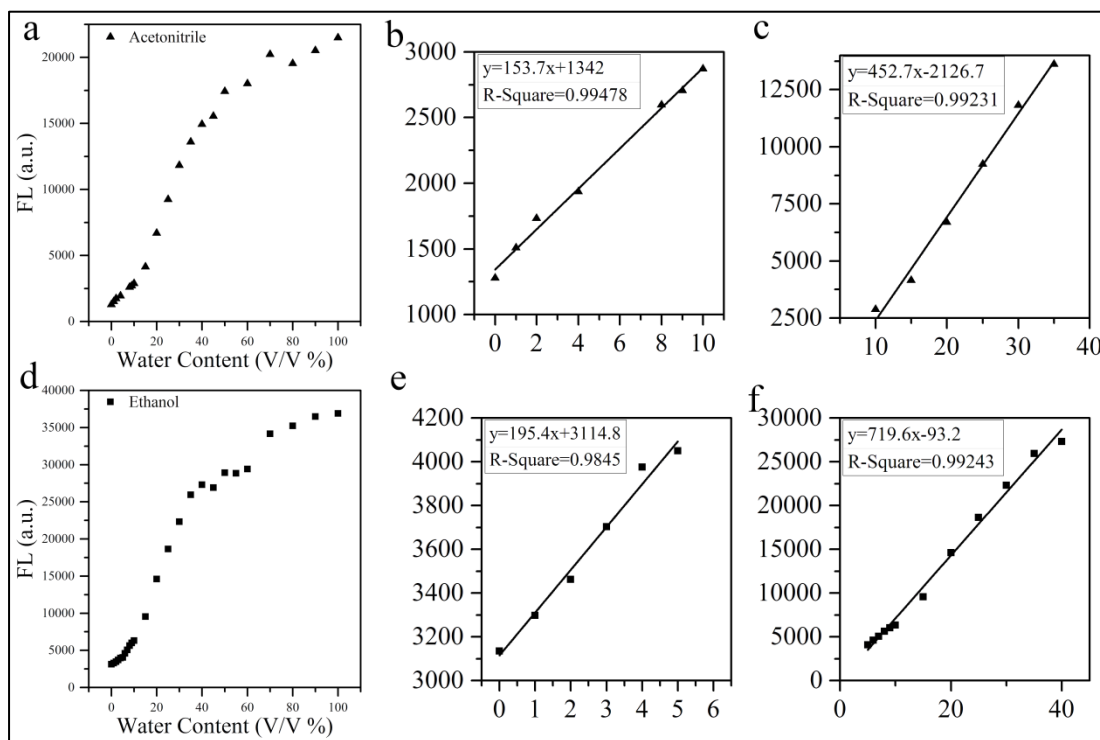


Figure S5. Fluorescence intensity as a function of wide range water content for (a) acetonitrile and (d) ethanol dispersion of CD-ACC nanocomposite. The fitting curves between fluorescence intensity and water content in acetonitrile (b, c) and ethanol (e, f).

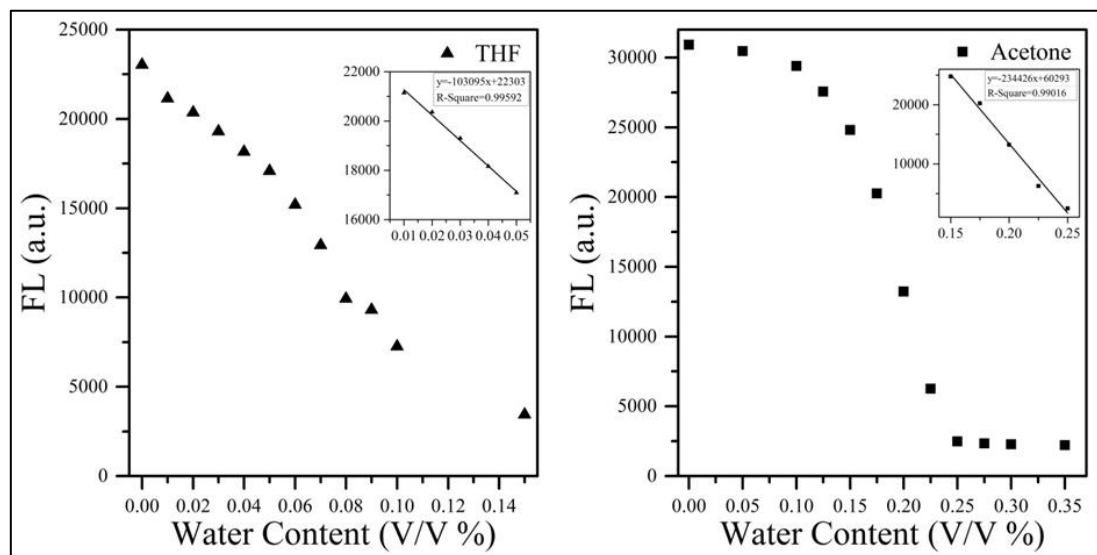


Figure S6. Plots of fluorescence intensity as a function of trace water content for THF and acetone dispersion of CD-ACC nanocomposite. Inset: the fitting curve of fluorescence intensity versus water content.