Electronic Supplementary Information (ESI)

CR@BaSO$_4$: an acid rain - indicating material

Experimental

Apparatus and Materials

A photodiode array spectrometer (Model S4100, Sinco, Korea) was used to determine the colority and concentration of color compounds and the suspended substance liquids. A scanning electronic microscopy (SEM) (Model Quanta 200 FEG, FEI Co., USA) was used to measure the morphology of materials and a high resolution transmission electronic microscopy (HRTEM) (Model Tecnai G^2 F20 S-Twin, FEI Co., USA) (120 kV, 2.4 A resolution) to measure the inner structure of materials. A thermal analysis system (Model Q600 SDT Simultaneous DSC-TGA, TA instruments, USA) was used to determine thermal weight loss of the materials. A spreader (Model QTG-A, Tianjin, China) was used to paint the film in 250 μm of thickness. A colorimeter (Model WSC-Y, BOIF, China) was used to determine the color factors (*a, b* and *L*). A UV-VIS spectrophotometer (Model UV-2550, Shimadzu, Japan) with an integrating sphere was used to determine the absorption spectrum of a color plate. A digital camera (Model SBC-L5, Samsung, Korea) was used to photograph color change of the paint plates.

A series of the sulfuric-nitric solutions (pH 3.0, 3.5, 4.0, 4.5, 5.0 and 5.6) were prepared by mixing 0.5 M H_2SO_4 and 1 M HNO_3 (3:1) in distilled water and pH level maintained with a digital pH meter. A series of acetic acid - acetate sodium buffer solutions (pH 3.0, 3.5, 4.0, 4.5, 5.0 and 5.6) were prepared and then mixed with the sulfuric-nitric solutions according to 1:10 (v/v). They were used as the simulated acid rains.

Synthesis and characterization of the CR@BaSO$_4$ hybrid

The CR@BaSO$_4$ hybrid was prepared by the conventional organic-inorganic hybridization. After 100 ml of 2.0 mmol/L CR was mixed thoroughly into 400 ml of 0.02 mol/L sodium sulfate (AR, Aladdin Co.), 600 ml of 0.02 mol/L barium chloride (AR, Aladdin Co.) was added slowly under stirring. After 30 min, the suspending substance was precipitated and then washed twice with deionized water. The CR@$BaSO_4$ hybrid was collected and dispersed to 40% (w/v) with deionized water. The elemental analysis, ζ-potential, particle size distribution, TEM, SEM and TGA were applied to characterize the composition and morphology of the CR@$BaSO_4$ hybrid.

Preparation and measurement of acid rain - indicating (ARI) paint

20 ml of the hybrid liquid containing 40% CR@$BaSO_4$ was mixed into 100 g of the acrylic-based emulsion paint (Akzo Nobel Swire Paints, Shanghai) and the mixture used as the ARI paint. Simultaneously, the reference paint was prepared by adding inert pigments into the acrylic based emulsion paint without color difference from the ARI paint. The ARI paint was spread evenly on the plastic plates (60×60×2 mm^3) with a 250 μm - thickness spreader and then they placed on a simple raining device (Fig. S10). The simulated acid rains flowed across the ARI paint plates. The color change of the ARI plates was photographed after 5 min with a digital camera and their color factors (*a, b* and *L*) determined simultaneously with a colorimeter.

Testing of the ARI umbrella

The ARI paint was spread evenly on the interval sectors of an ordinary umbrella for 250 μm of thickness. The other sectors were coated using the reference paint without color difference from the ARI paint. A simulated acid rain rained over an ARI umbrella and the color factors of the ARI paint sector were determined. Simultaneously, the ARI umbrella was photographed with a digital camera.

Fig. S1 – Fig. S10

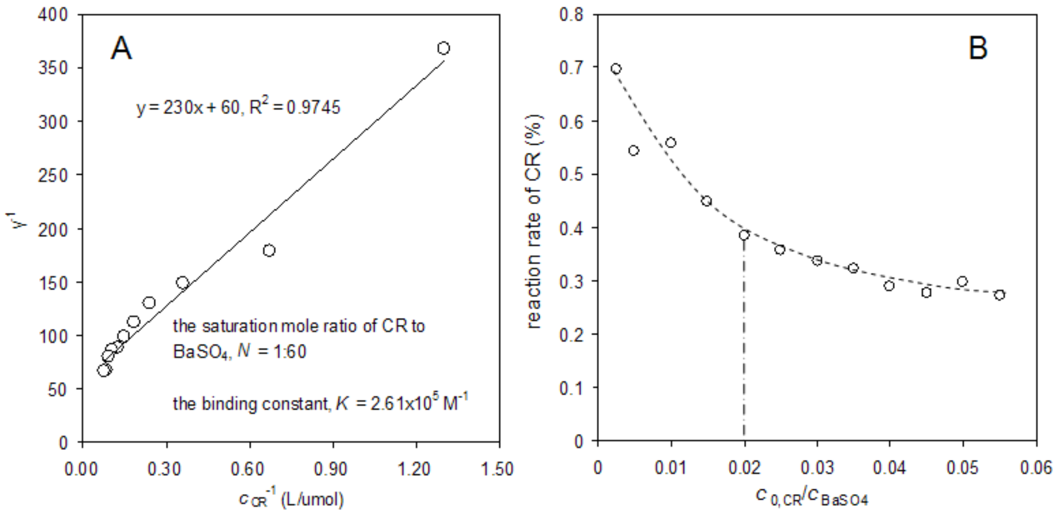

Fig. S1 Effects of CR on its binding mole number (A) and reaction rate (B). $c_{0,CR}$ and c_{CR} are the initial and equilibrium molarity, c_{BaSO4} is the initial molarity of SO_4^{2-} and γ the mole ratio of CR to $BaSO_4$ in the CR@$BaSO_4$ hybrid

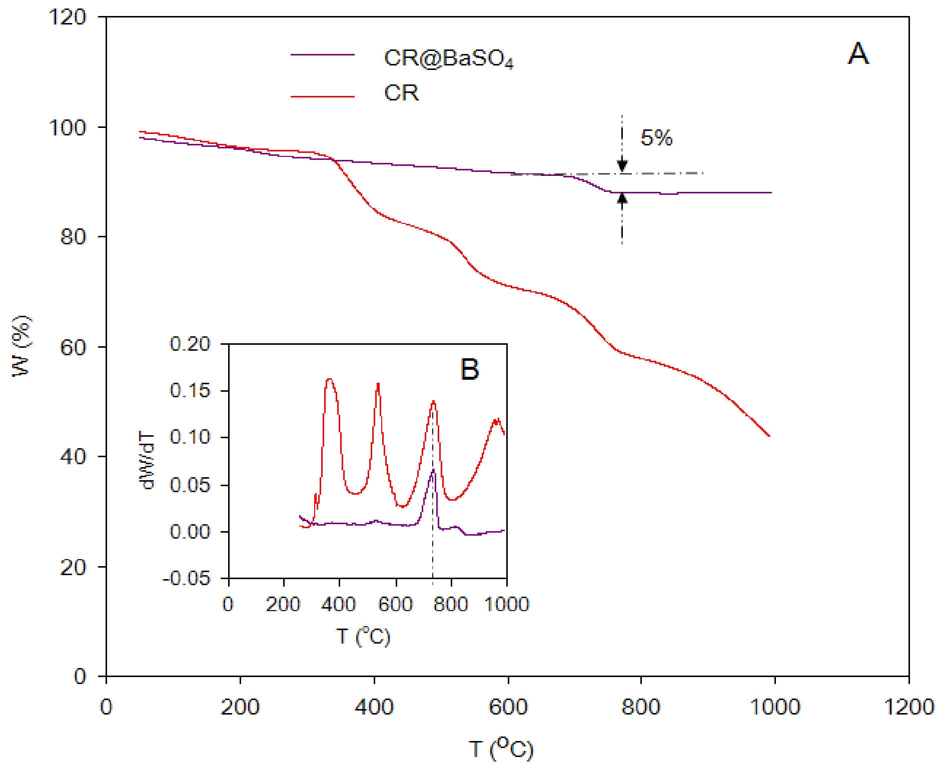

Fig. S2 Thermal curves of CR (red line) and the CR@$BaSO_4$ hybrid (violet line)

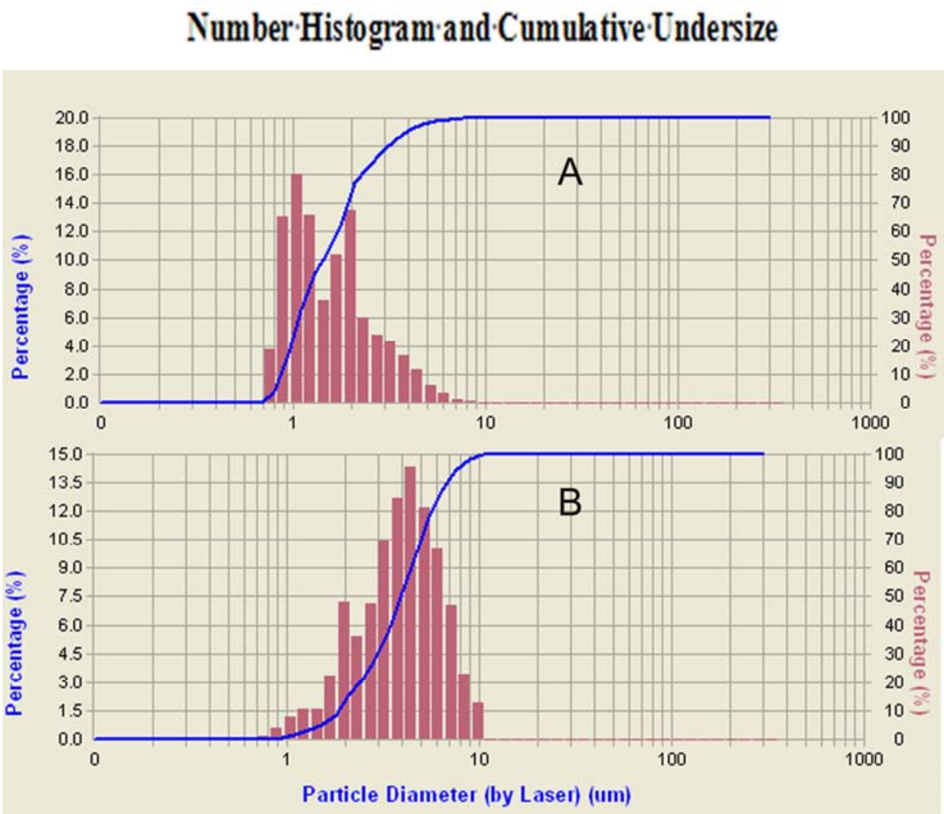

Fig. S3 Particles distribution of $BaSO_4$ (A) and the CR@$BaSO_4$ hybrid (B)

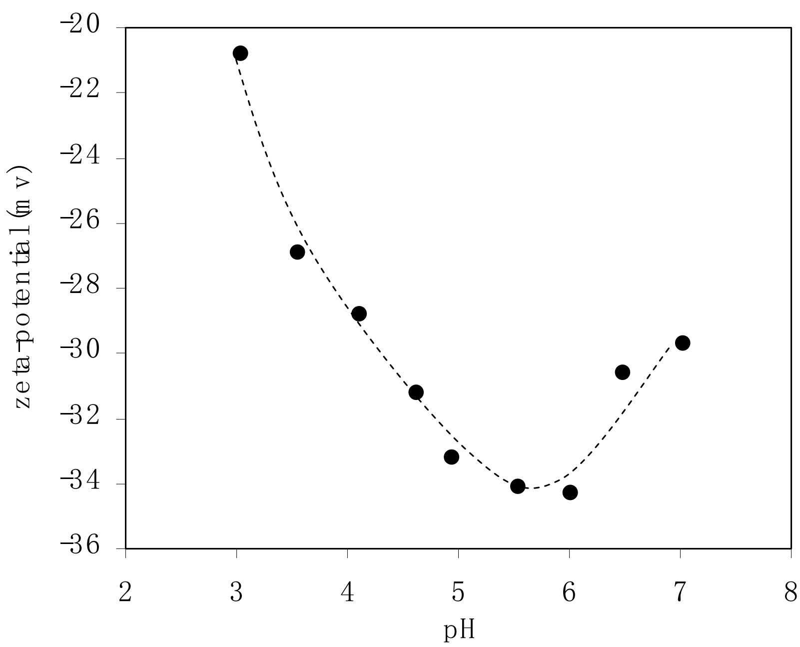

Fig. S4 Change of ζ-potential of the CR@$BaSO_4$ hybrid in various pH media

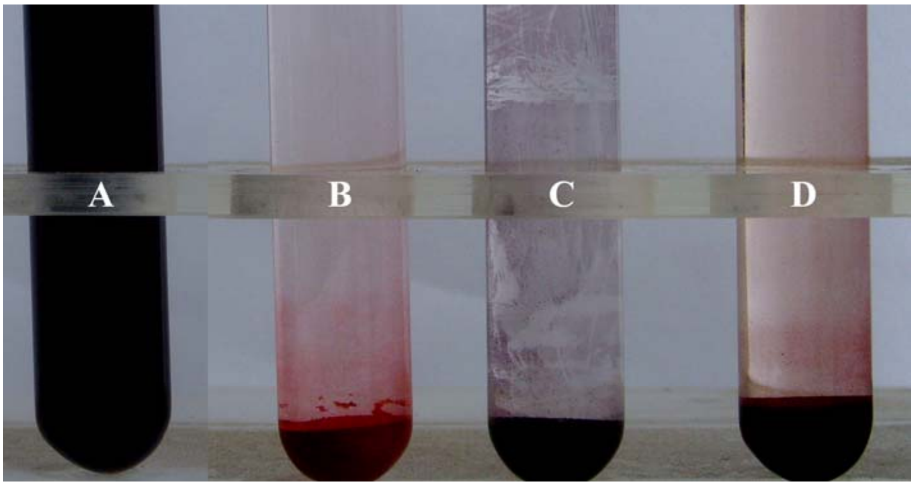

Fig. S5 Photographs of the CR@$BaSO_4$ hybrid (2%) immersing into aqueous media (B) and the simulated acid rains (C and D). A: CR-only solution containing the same CR amounts, i.e. approximately 35 mM as that embedding in the hybrid; B: for 330 days; C: pH 3 for 24 h and D: pH 4.5 for 24 h.

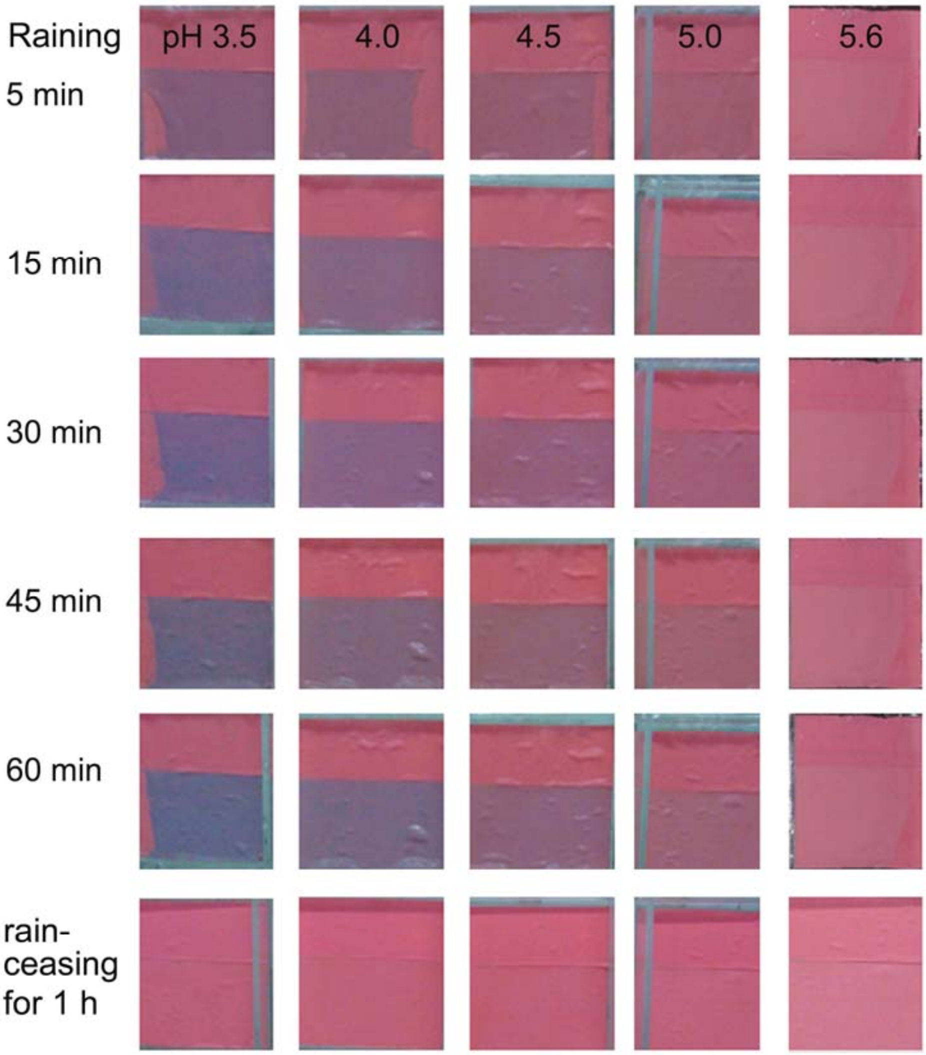

Fig. S6 Effect of time on the ARI plates' color raining with the simulated acid rains (pH 3.5 – 5.6)

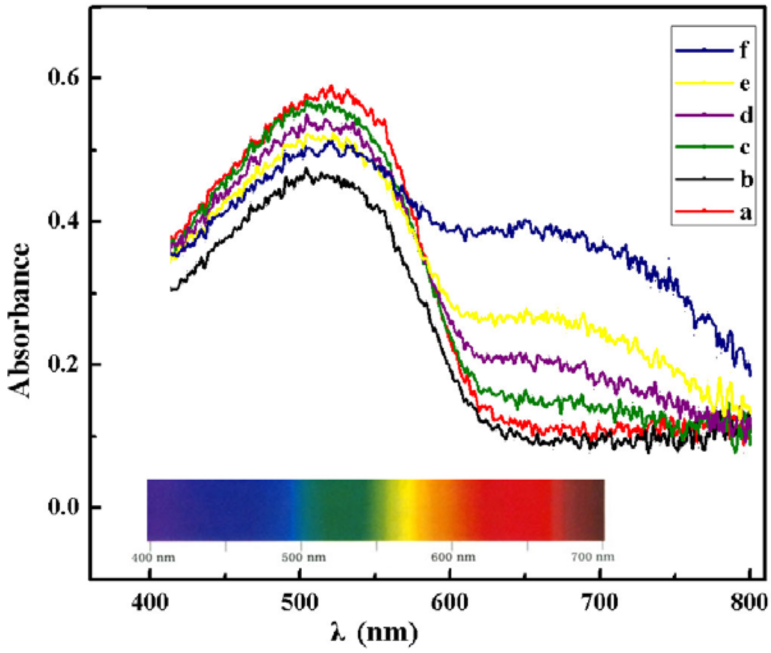

Fig. S7 Adsorption spectra of the ARI plates raining for 15 min with the simulated acid rains. a: distilled water, b – f: pH 5.6, 5.0, 4.5, 4.0 and 3.5

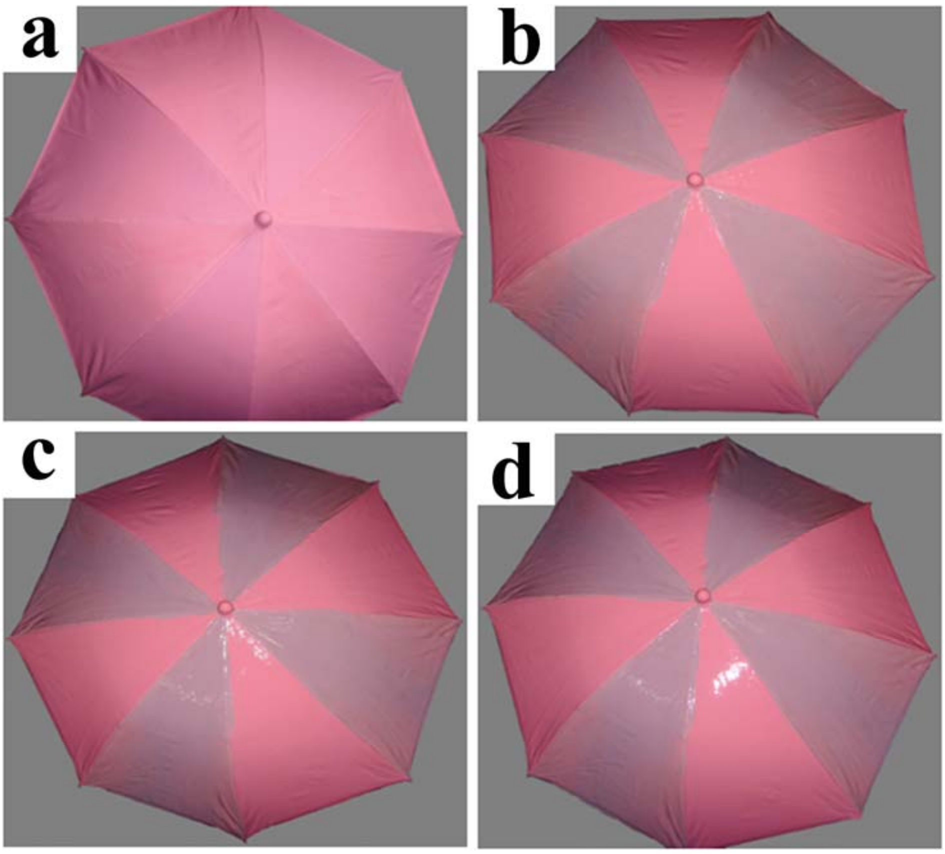

Fig. S8 Change of the ARI umbrella raining with the simulated acid rain of pH 4.5. a: before raining, b – d: 5, 10 and 15 min

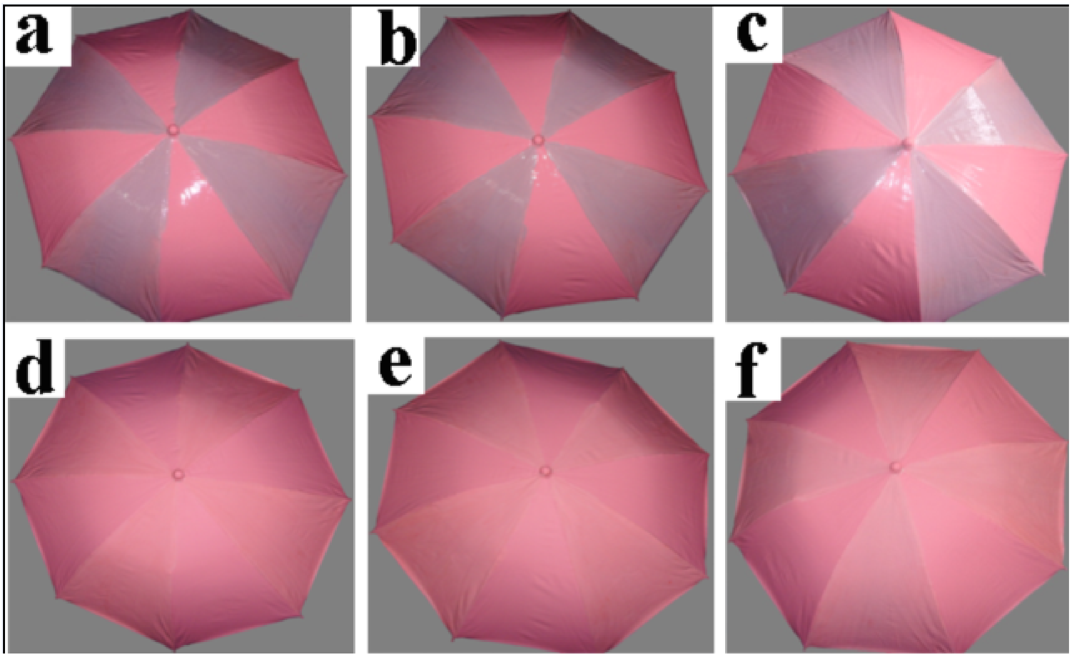

Fig. S9 Change of the ARI umbrella raining repeatedly with the simulated acid rain of pH 4.5. The first raining for 15min (a) and then indoor airing for 2 h (d) were carried out and followed the second cycle (b and e) and the third cycle (c and f).

Fig. S10 A simple raining device was designed, which consists of four independent units. Each unit involves a tank, an oblique baffle plate with a 60×80×3 mm^3 groove, a water distributor and a submerged pump (water flow rate, 230 L/h). Each ARI plate (60×60×2 mm^3) was placed on the oblique baffle plate's groove.