Polymer Particles Armored with Cobalt Oxide Nanosheets for the Catalytic Degradation of Bisphenol A

Maria Escamilla,[1§] Kevin Pachuta,[2‡] Kuan Huang,[3‡] Michael Klingseisen,[4] Huaixuan Cao,[5] Huichun Zhang,[3‡] Alp Sehirlioglu,[2‡] Emily Pentzer*[1,4§]

[1]Department of Chemistry, Texas A&M University, College Station, TX
[2]Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH
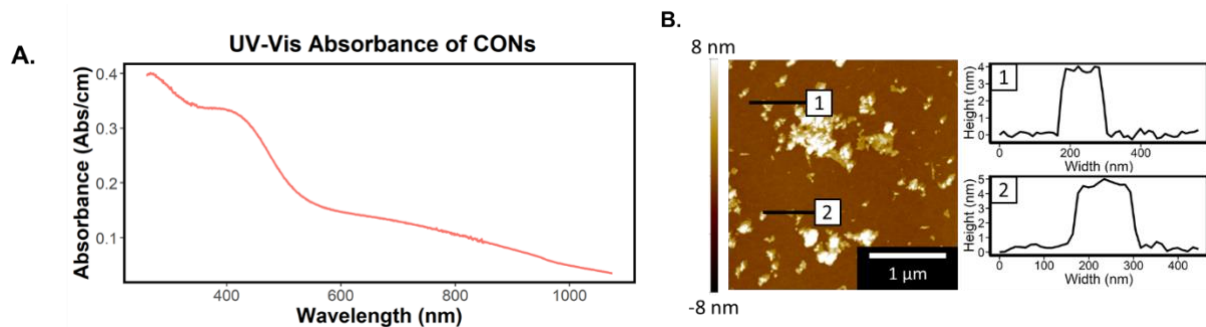[3]Department of Civil and Environmental Engineering, Case Western Reserve University, Cleveland, OH
[4]Department of Materials Science and Engineering, Texas A&M University College Station, TX
[5]Department of Chemical Engineering, Texas A&M University College Station, TX
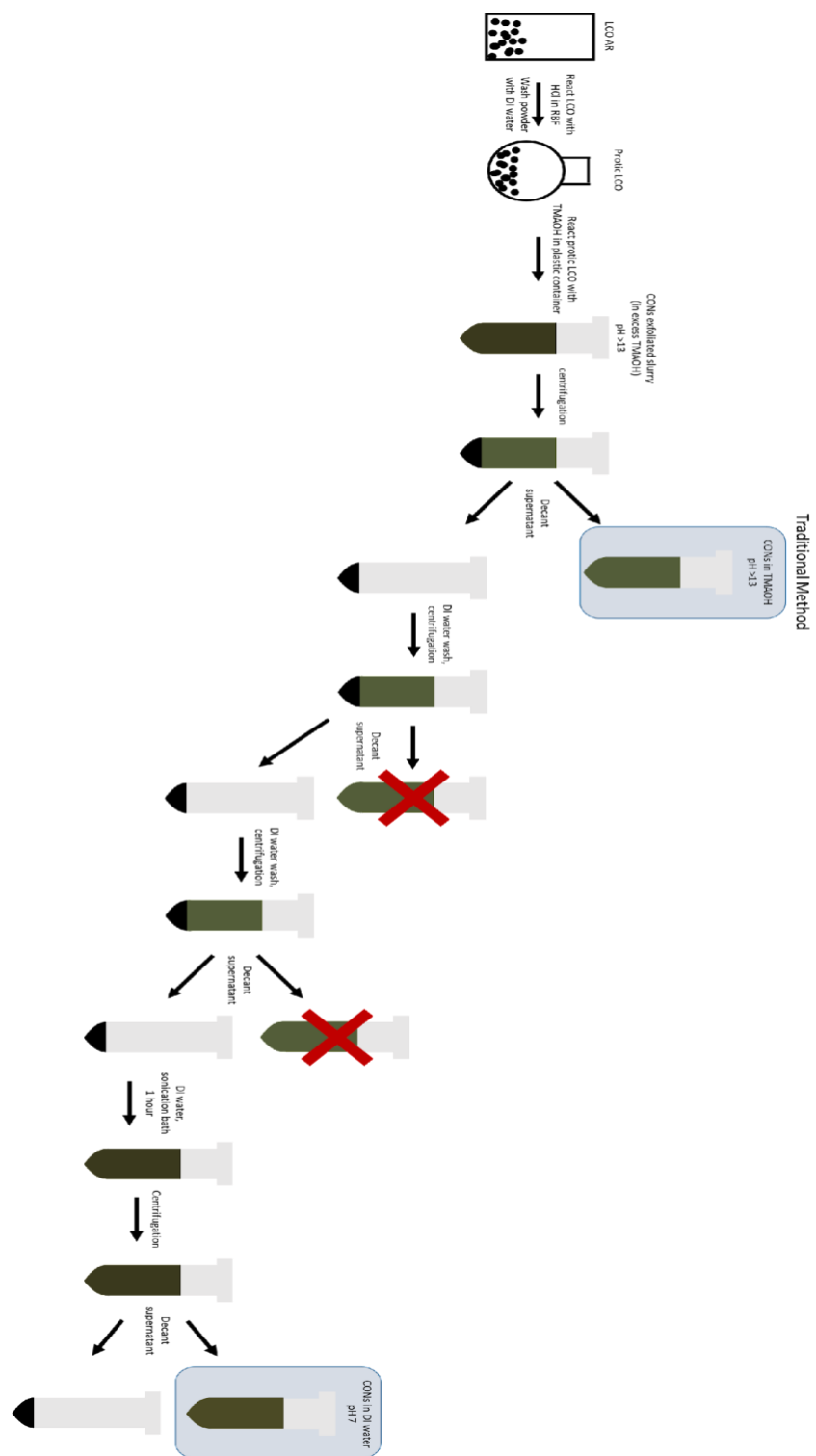
Figure S1. Synthetic scheme for the synthesis of cobalt oxide nanosheets CONs.

Figure S2. (A) UV-vis absorbance spectrum of an aqueous dispersion of cobalt oxide nanosheets (CONs) in deionized (DI) water. A highly concentrated CONs solution was produced through the exfoliation method shown in Figure S1. (B) Atomic force microscopy (AFM) image of the aqueous dispersion of CONs drop cast onto freshly cleaved mica. Two-line scans show the height of the CONs and their 2D nature.
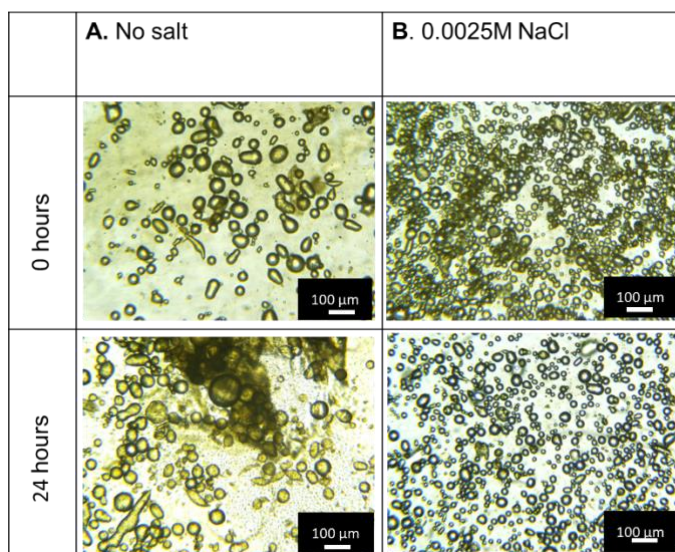

Figure S3. Optical microscopy images of CONs stabilized styrene-in-water emulsions at 0 hrs and 24 hrs. A) no salt addition and B) with the addition of 0.0025M NaCl. Aqueous dispersion of CONs (1.2 mg/mL) and 1:5 oil:water ratio was used.
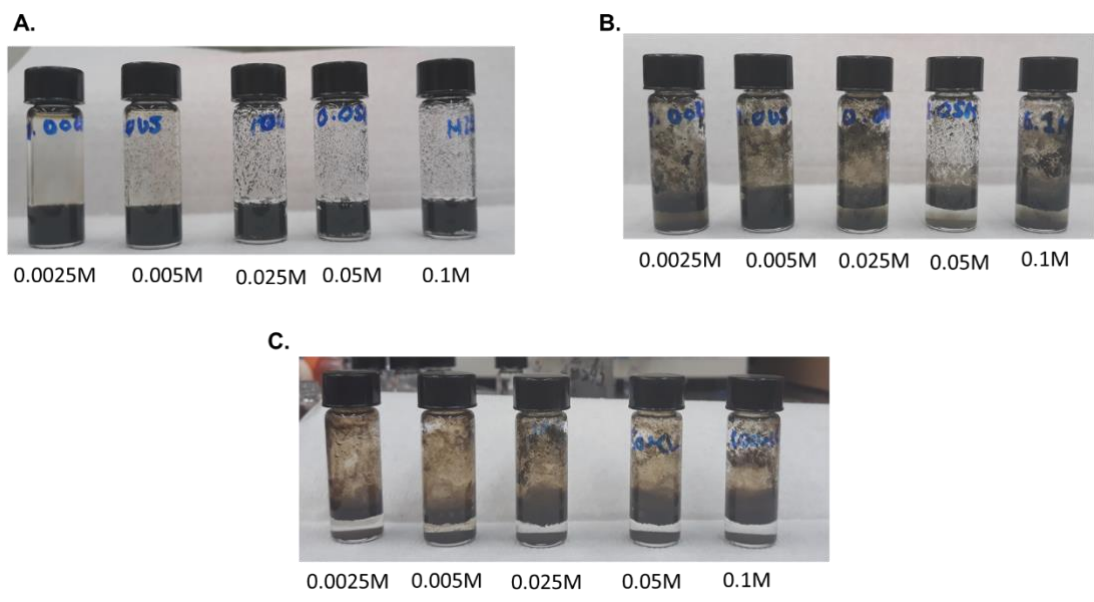
Figure S4. Photographs of A) NaCl flocculated CONs in water, B) Styrene-in-water emulsions stabilized by NaCl-flocculated CONs immediately after preparation. C) Emulsions shown in B after 24 h left unagitated. An initial aqueous CONs dispersion of 1.2 mg/mL was used, the oil:water ratio is 1:5, and salt concentrations are as shown. In B and C, the lower clear phase is water and the emulsion droplets can be identified as the dark opaque upper portion.
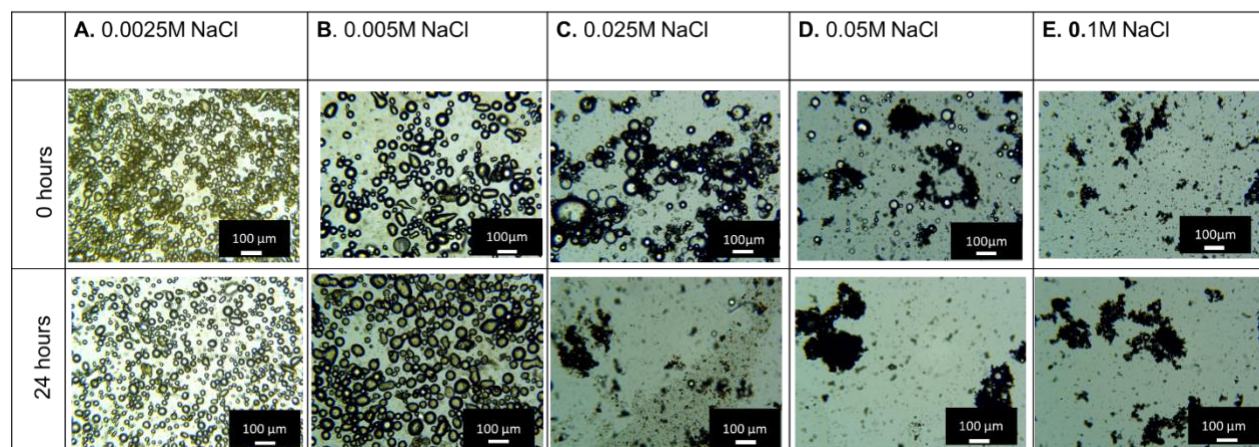

Figure S5. Stability Study. Styrene-in-water Pickering type emulsions stabilized by NaCl flocculated CONs with A) 0.0025 M, B) 0.005 M, C) 0.025 M, D) 0.05 M, E) 0.1 M NaCl. Aqueous dispersion of CONs (1.2 mg/mL) and a 1:5 oil:water ratio was used.

4
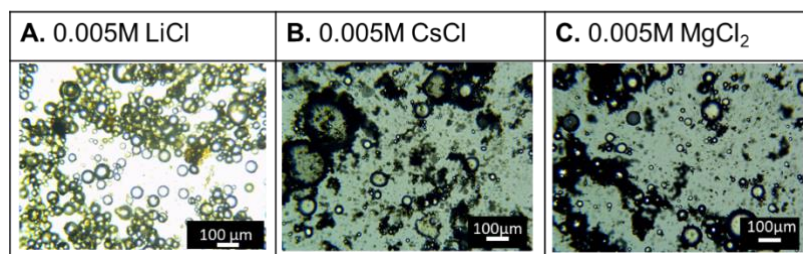
Figure S6. Styrene-in-water emulsions stabilized by 0.005 M salt (ionic strength in paretheses): A) LiCl (0.005 M), B) CsCl (0.005 M), and C) $MgCl_2$ (0.015 M). Aqueous dispersion of CONs (1.2 mg/mL) and a 1:5 oil:water ratio was used.
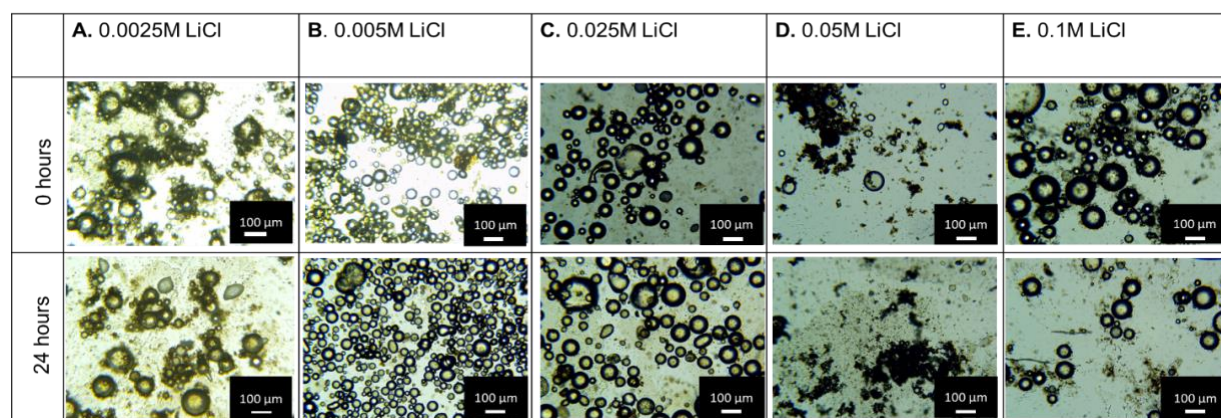

Figure S7. Stability study. Styrene-in-water Pickering type emulsions stabilized by LiCl flocculated CONs A) 0.0025 M, B) 0.005 M, C) 0.025 M, D) 0.05 M, E) 0.1 M LiCl. Aqueous dispersion of CONs (1.2 mg/mL) and a 1:5 oil:water ratio was used.
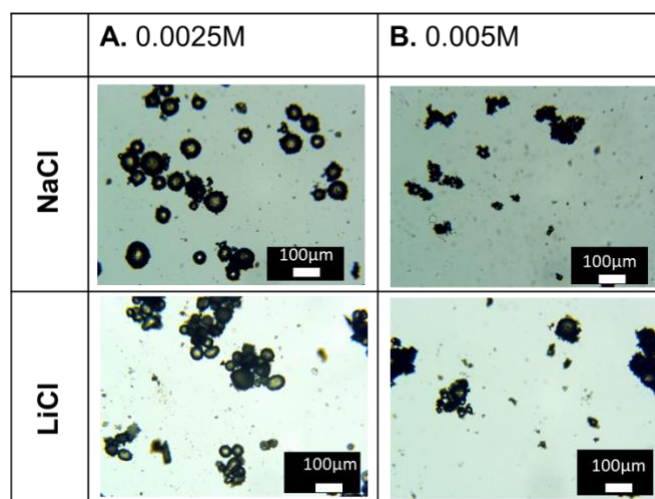
Figure S8. Optical microscopy images of CONs armored polystyrene particles prepared by flocculating the nanosheets with NaCl and LiCl at A) 0.0025M and B) 0.005M. Aqueous dispersions of CONs (1.2 mg/mL) and a 1:5 oil:water ratio were used.
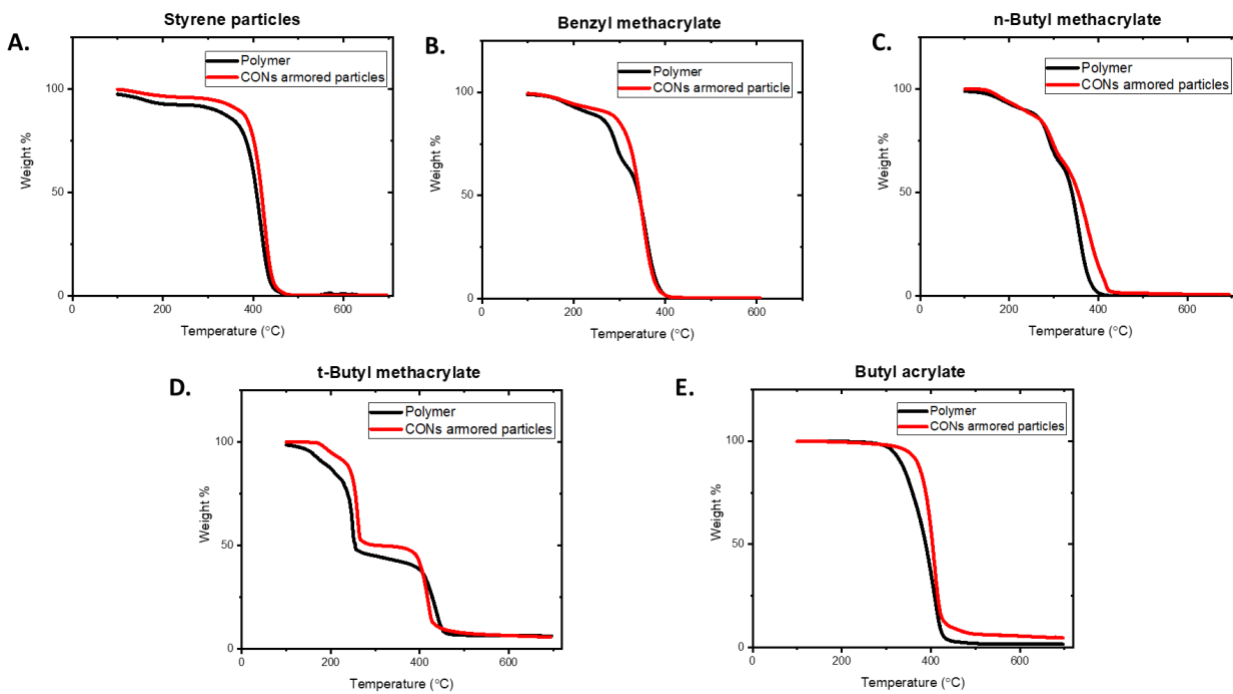
Figure S9. Thermal gravimetric analysis of polymer (black traces) and CONs-armored polymer particles (red traces) for: A) Polystyrene, B) Poly(benzyl methacrylate), C) Poly(n-butyl methacrylate), D) Poly(t-butyl methacrylate), and E) Poly(n-butyl acrylate).
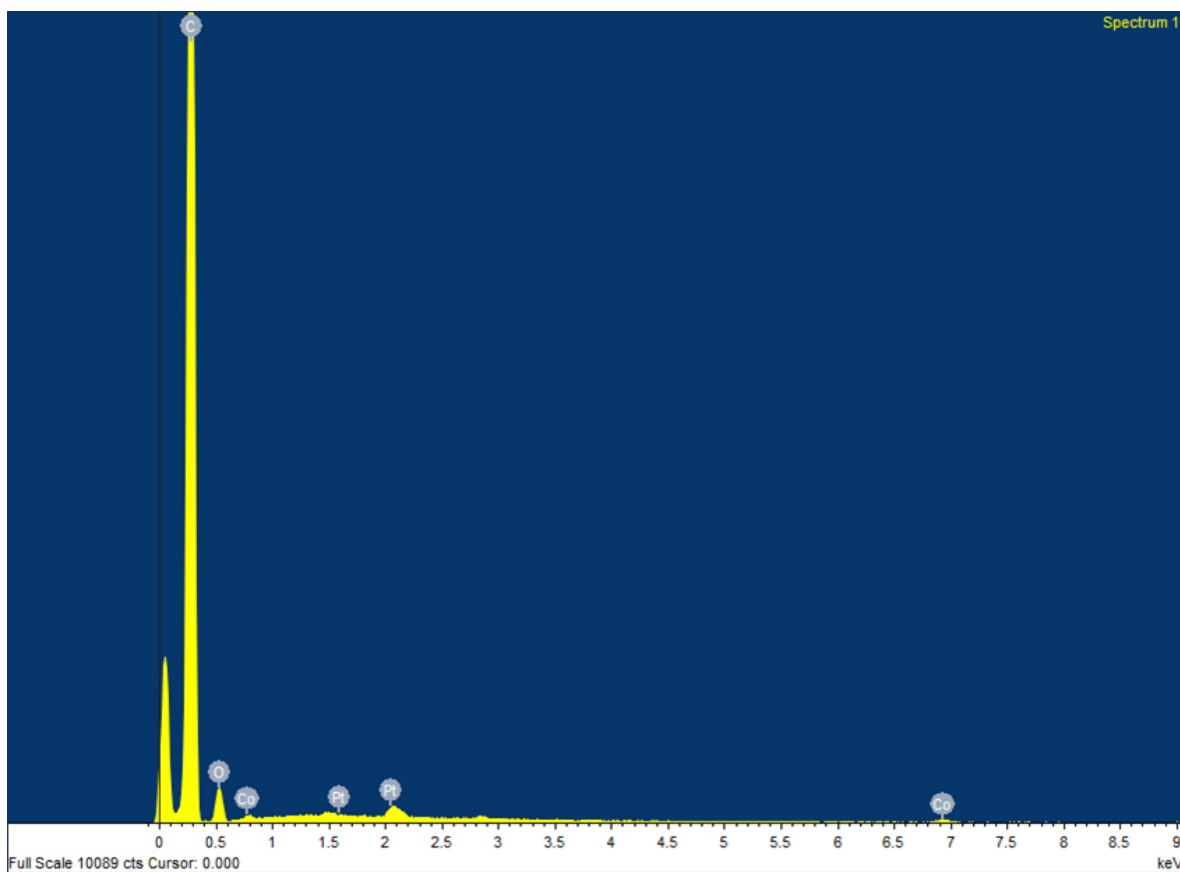
| Element	Weight%	Atomic%
C K	88.48	92.12
O K	9.82	7.68
Co K	0.63	0.13
Pt M	1.06	0.07
Totals	100.00	

Figure S10. Energy dispersive X-ray spectroscopy (EDS) analysis of CONs armored polystyrene particles.
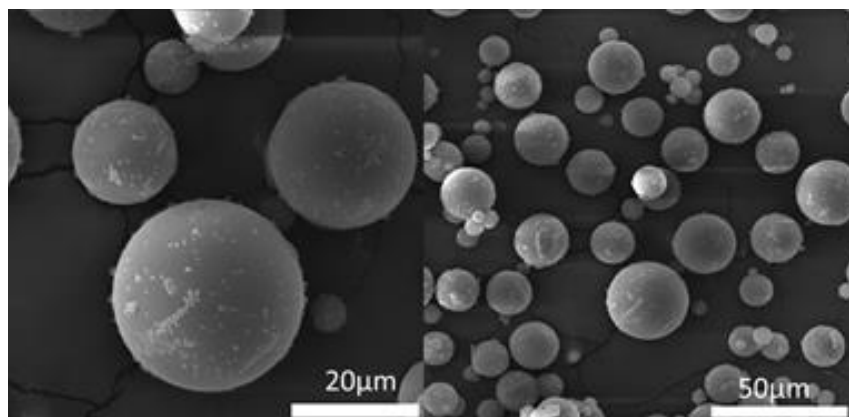
Figure S11. SEM images of polystyrene particles prepared by suspension polymerization using sodium lauryl sulfate as surfactant. An aqueous concentration of 8.5 mM surfactant was used and a 1:5 oil:water ratio.
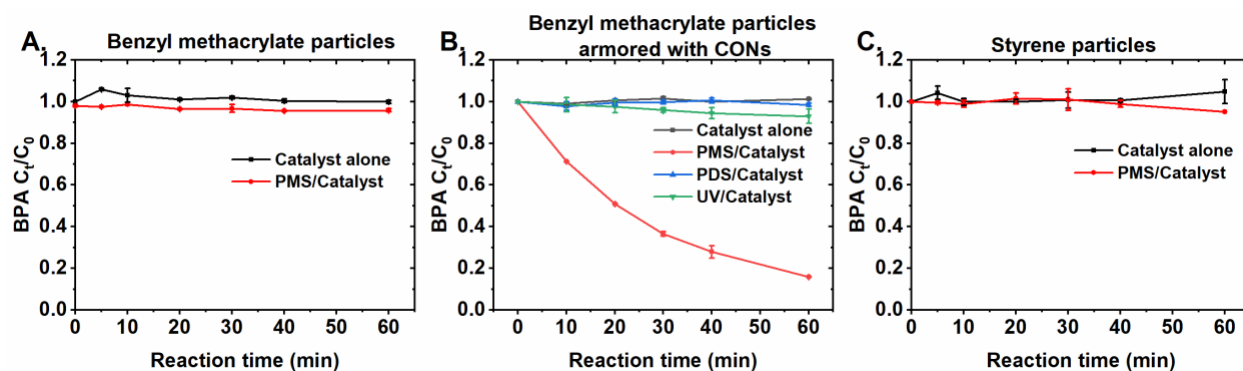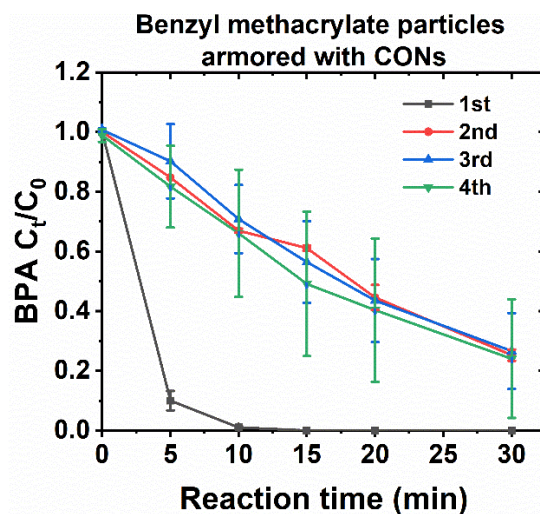

Figure S12. Catalytic oxidation of BPA by PMS by activation with A) Poly(benzyl methacrylate) particles, B) Poly(benzyl methacrylate) particles armored with CONs, and C) Polystyrene particles. Experimental conditions: $[PMS]_0 = 500$ µM; $[BPA]_0 = 5$ µM; [catalyst] = 0.04 g/L; pH = 5 with 0.02 M acetate buffer. Error bars stand for data ranges of experimental replicates (n $\geq$ 2).
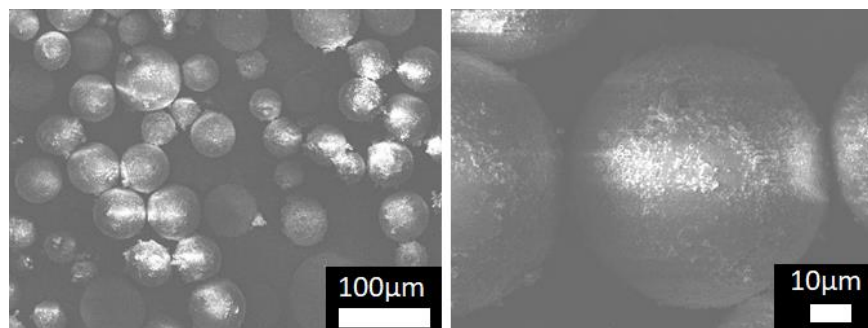
S13. SEM images of CONs-armored poly(benzyl methacrylate) particles.

Figure S14. Reusability of poly(benzyl methacrylate) particles armored with CONs. Experimental conditions: $[PMS]_0 = 500$ μM; $[BPA]_0 = 5$ μM; pH = 5 with 0.02 M acetate buffer. 4.8 mg of the catalyst was coated onto a graphite sheet, which was dipped into the solution for the catalytic oxidation of BPA. Error bars stand for data ranges of experimental replicates ($n \geq 2$).