Supporting Information

for

Degradation products from consumer nanocomposites – a case study on quantum dot lighting

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Supporting information: 7 Pages, 7 Figures

Additional Details on Methods

Fluorescence Intensity Analysis of Aged QD-Embedded Polymers.

The QD degradation within the polymer host was monitored by fluorescence intensity change using an Olympus IX71 Inverted Microscope equipped with an X-Cite® exacte light source and a 581 nm fluorescence filter (ET-mCherry Texas Red® ET560/40x, Chroma technology Corp. VT). The QD-embedded polymer films were exposed to simulant fluids at a ratio of 1 mg/mL followed by rotation at 60 rpm in the dark for 7 days, during which time polymer samples were taken out for fluorescence imaging every 24 hours and were then re-exposed to fresh simulant fluids. The fluorescence images were acquired with a UPlanApo 10× objective and an XM10 monochrome camera using a fluorescence lamp intensity at 4% of maximum, exposure time of 1.5 s (HNO_3 and gastric acid) or 2.5 ms (TCLP, MHRW, SHA, SFA, PBS and H_2O_2) and resolution of 1376×1038. Image analysis was performed using CellSens® Dimension Imaging software to obtain the mean fluorescence intensity of the acquired area. 20 fluorescence intensities of each sample were recorded for statistic purpose.

Additional Details on Results and Discussion

Analysis of equilibrium Cd^{2+} adsorption on NOM using Langmuir-Freundlich (LF) model.

The Langmuir-Freundlich (LF) model is giving by[1,2]:

$$Q_e = \frac{Q_{max} K_{SM} C_e^n}{1 + K_{SM} C_e^n} \qquad \text{(eq.1)}$$

where, C_e is the equilibrium concentration of the metal cations (mg/L), Q_e is the amount of adsorbed metal per unit mass of adsorbent at equilibrium (mg/mg), Q_{max} is the maximum adsorption capacity of metal per unit mass of adsorbent (mg/mg), K_{SM} is the equilibrium binding constant, and n is a heterogeneity index that varies from 0 to 1. Figure S5B presents Cd^{2+} adsorption isotherms fit to a this model. The least squares LF parameters (Q_{max}, K_{SM}, and n) are given in Fig. S5 caption.

Estimation of Typical Diffusion Time in Prototype Acrylate Polymer Films

Diffusion times in porous media can be estimated as follows:

$$t \sim L^2/D_{eff} \qquad \text{(eq. 2)}$$

where L is the diffusion length (thickness of polymer film ~100 µm), D_{eff} is the effective diffusion coefficient that describes diffusion through the pore space of porous media, which is given by:

$$D_{eff} = D\theta/\tau \qquad \text{(eq. 3)}$$

where D is the diffusion coefficient in liquid phase (typically 10^{-5} cm^2/s), θ is the porosity available for transportation, and τ is the tortuosity (typically varies between 2 and 6[3], here we use 4).

The porosity is calculated by:

$$\theta = V_V/V_T \qquad \text{(eq. 4)}$$

where V_V is the volume of void-space and V_T is the bulk volume of polymer. We use water infiltration (0.11 g/g polymer) and a typical acrylate polymer density of 1.2 g/cm^3 to estimate θ:

$$\theta = \frac{0.11\text{g}/(1\text{g/cm}^3)}{1\text{g}/(1.2\text{g/cm}^3)} = 0.132$$

Together, the estimated diffusion time in prototype acrylate polymer films is ~ 303 s.

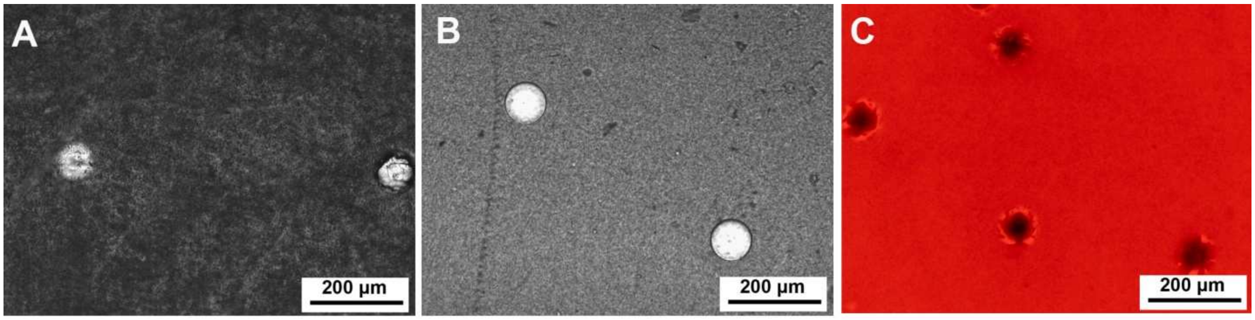

Figure S1. Optical images of QD-embedded polymer nanocomposites. (A) Bright field image of as-received sample; (B) bright field image of DI water rinsed sample; and (C) fluorescence image of as-received sample. Images were acquired using Olympus IX71 Inverted Microscope at 10× magnification.

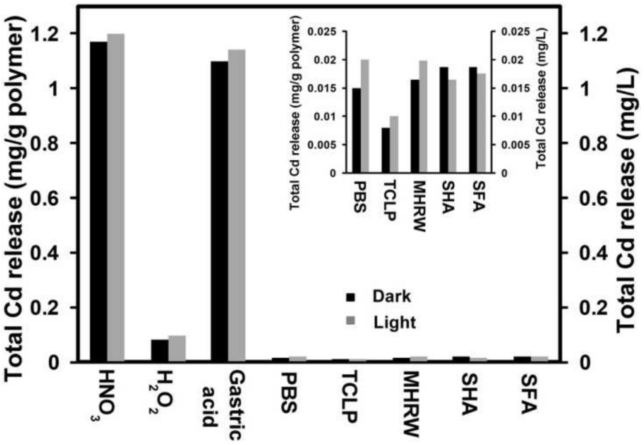

Figure S2. Total Cd release after 30 day dark or light exposure to simulant fluids. QD-embedded polymers were exposed at 1 mg polymer/mL solution, and were rotated under dark or ambient light at 60 rpm.

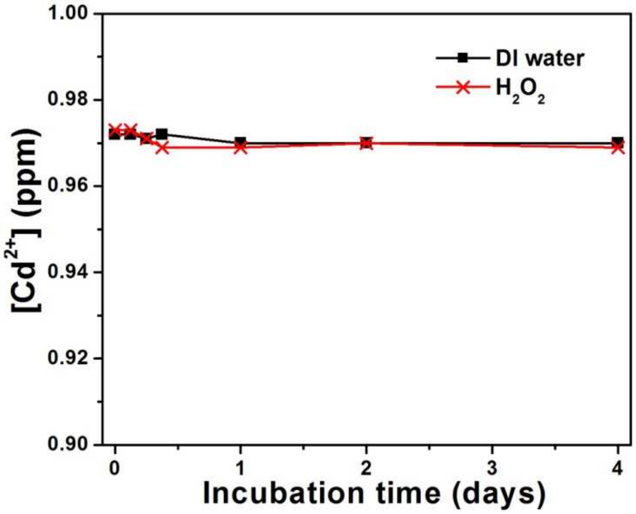

Figure S3 Time dependent measurements of Cd^{2+} concentration during incubation of QD-free polymer with $CdCl_2$ in DI water and 1 mM H_2O_2. The experiment was conducted at 25 °C in the dark, and QD-free polymer was used at 1 mg polymer/mL.

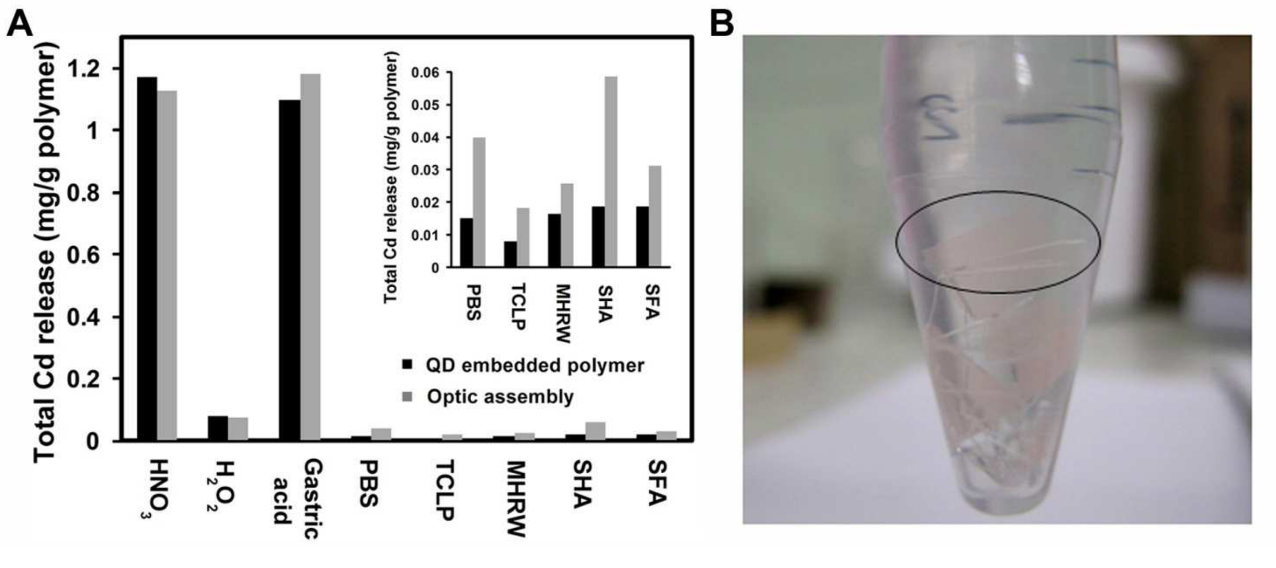

Figure S4. Comparison of Cd release from the full prototype optic and bare polymer. (A) 30-day total Cd release. Samples were exposed to simulant fluids for 30 days at 27.4 mg optic/mL solution (equivalent to 0.6 mg polymer/mL) or 1 mg polymer/mL solution respectively, and were rotated in the dark at 25 °C. The concentration of Cd in leachate (mg/L) = Cd release (mg-Cd/g polymer) × polymer dosage (g/L) (B) Photograph of prototype optic after 4 day exposure in TCLP showing detachment of QD-embedded polymer from glass plate housing (indicated by circle). The optic assembly was cut into small pieces (~ 7 mm×7 mm) and exposed to TCLP by rotating at 60 rpm in dark.

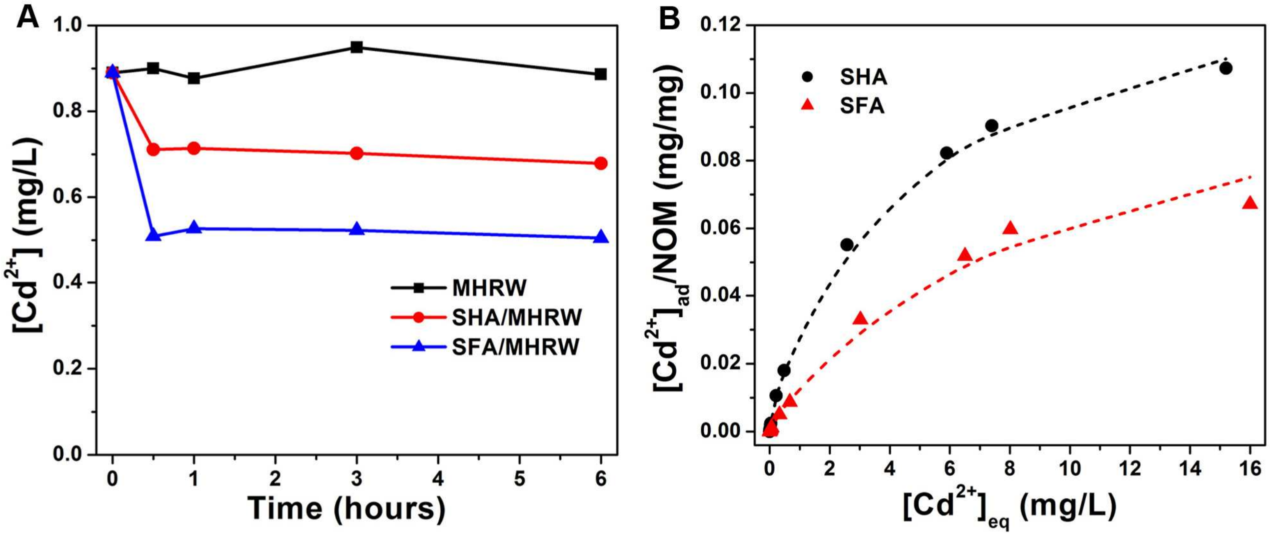

Figure S5. Cd^{2+} adsorption on NOM. (A) Time dependent measurements of Cd^{2+} concentration in MHRW and NOM, showing rapid Cd^{2+} adsorption on NOM. The experiment was conducted at 25 °C and NOM was added at 20 mg/L. (B) Equilibrium adsorption isotherms for Cd^{2+} binding to SHA, SFA at 25 °C. NOM was used at 20 mg/L in MHRW, and the NOM/bound-Cd^{2+} phase was removed by centrifugal ultrafiltration prior to analysis. The dotted lines give the calculated adsorption isotherms derived from Langmuir-Freundlich isotherm model, where Q_{max} (SHA) = 0.156 mg/mg, K_{SM} (SHA) = 0.249 L/mg, n (SHA) = 0.830, and Q_{max} (SFA) = 0.131 mg/mg, K_{SM} (SFA) = 0.114 L/mg, n (SFA) = 0.890.

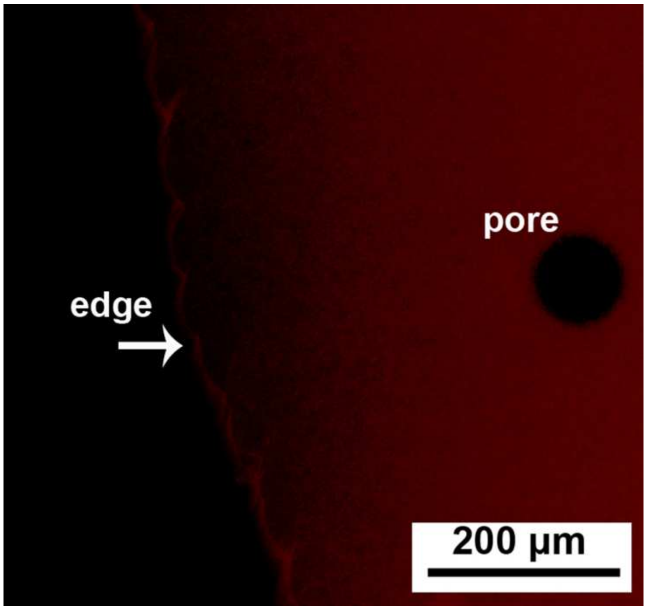

Figure S6. Fluorescence microscope image of QD-embedded polymer after 1-day exposure to 1 mM H_2O_2, showing the bleaching of fluorescence is more pronounced at the edge.

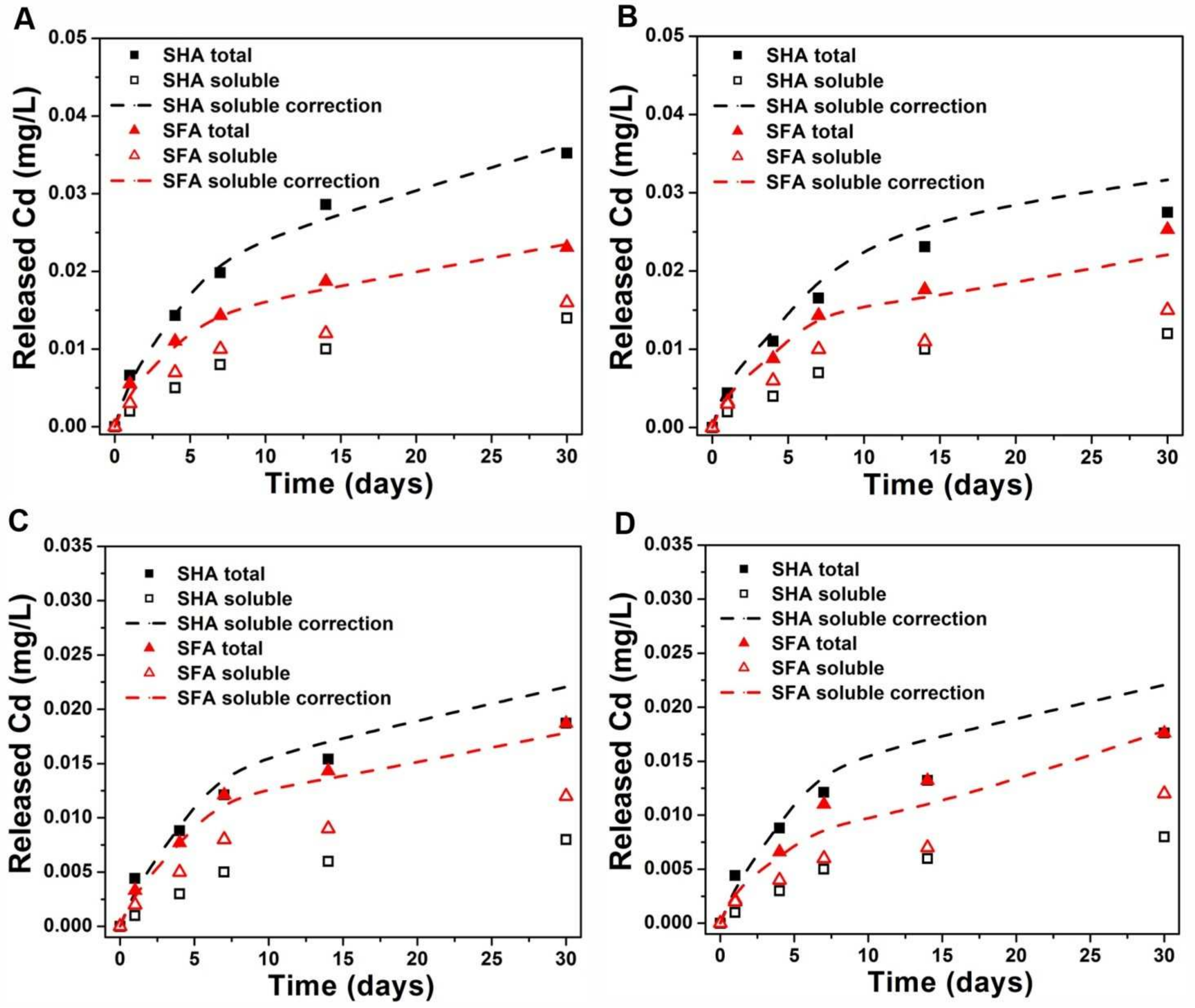

Figure S7. Total and soluble Cd release from QD optic samples in the presence of SHA and SFA (points) and correction of the soluble release for Cd^{2+} bound NOM (dashed lines). (A) Glass protected optic assembly under dark exposure; (B) Glass protected optic assembly under light exposure; (C) QD-embedded polymer under dark exposure; and (D) QD-embedded polymer under light exposure. The dashed lines give the calculated total Cd release based on Langmuir-Freundlich fitting of soluble Cd, suggesting the difference between total and soluble Cd is primarily due to ion adsorption on NOM.

References

1. Janoš, P.; Sypecká, J.; Mlčkovská, P.; Kuráň, P.; Pilařová, V.; Removal of metal ions from aqueous solutions by sorption onto untreated low-rank coal (oxihumolite). *Separ. Purif. Technol.* **2007**, *53* (3), 322-329.

2. Umpleby, R. J.; Baxter, S. C.; Chen, Y.; Shah, R. N.; Shimizu, K. D. Characterization of molecularly imprinted polymers with the Langmuir-Freundlich isotherm. *Anal. Chem.* **2001**, *73* (19), 4584-4591.

3. Evans, J. R.; Davids, W. G.; MacRae, J. D.; Amirbahman, A. Kientics of cadmium uptake by chitosan-based crab shells. *Water Res.* **2002**, *36* (13), 3219-3226.