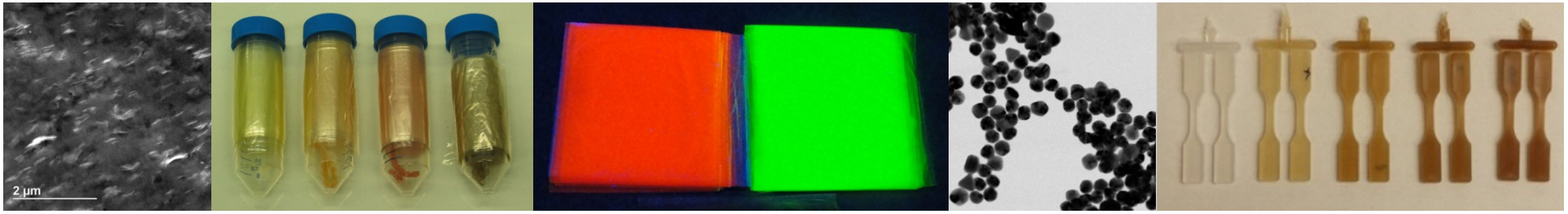
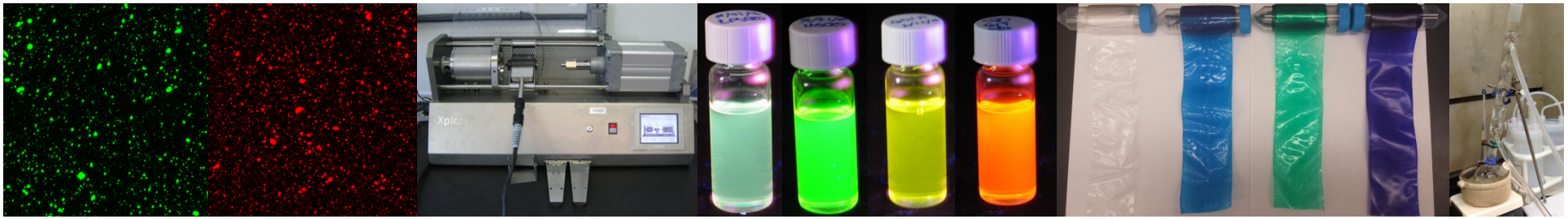


Demystifying dissolution of polymer-embedded nanoparticles: implications for polymer composites intended for use as food contact materials

Timothy V Duncan, PhD

U.S. FOOD & DRUG ADMINISTRATION

QEEN 2 Workshop, Washington DC, October 2018



Nanocomposites and food packaging

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UV-blockers
(ZnO, TiO_2)

Antimicrobials
(AgNPs, MONPs)

Sensing Applications
(QDs, AuNPs, etc.)

High Barrier Plastics
(Nanoclay, Graphite, etc.)

www.nanocor.com

Anti-Counterfeiting Inks
(Semiconducting NPs)

Processing Aids
(TiN)

Potential worldwide applications; not necessarily authorized in the U.S.

Nanoparticle release mechanisms

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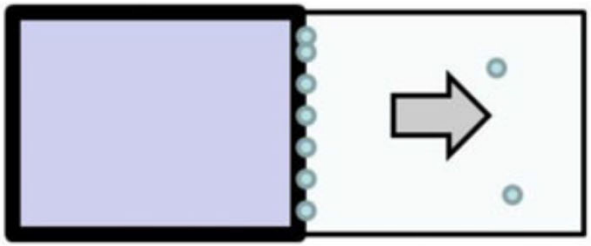
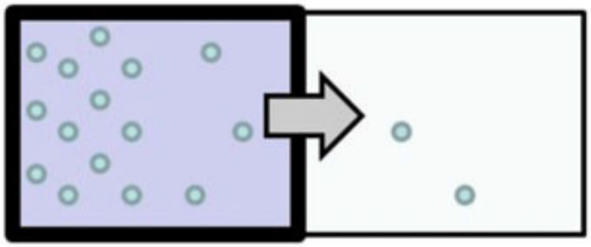
DESORPTION: Weak bonding to surface

- Agitation
- Surfactants / detergents
- pH
- Temperature



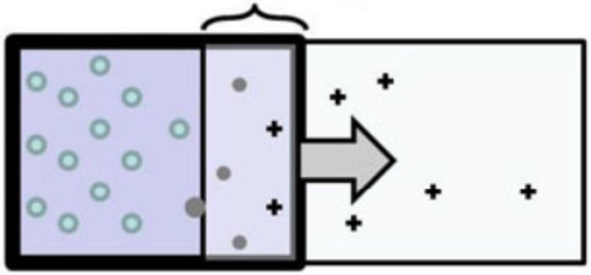
DIFFUSION: Migration to low concentration

- Concentration gradient
- Surface treatment
- Size and shape
- Polymer properties



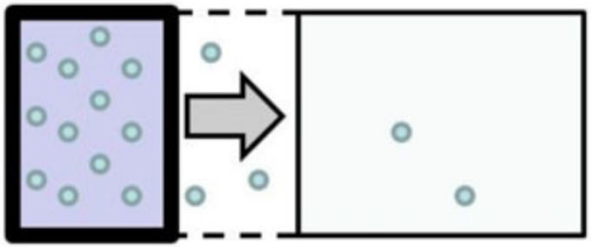
DISSOLUTION: Ions released into product

- pH
- Ionic strength
- Size and shape
- Concentration



DEGRADATION of MATRIX: Loss of polymer

- Mechanical abrasion
- UV exposure
- Material fatigue
- Hydrolysis / swelling



Noonan, Whelton, Carlander, Duncan. *Compr. Rev. Food Sci. Food Safety.* **2014**, 13, 679.

Dissolution as a release paradigm

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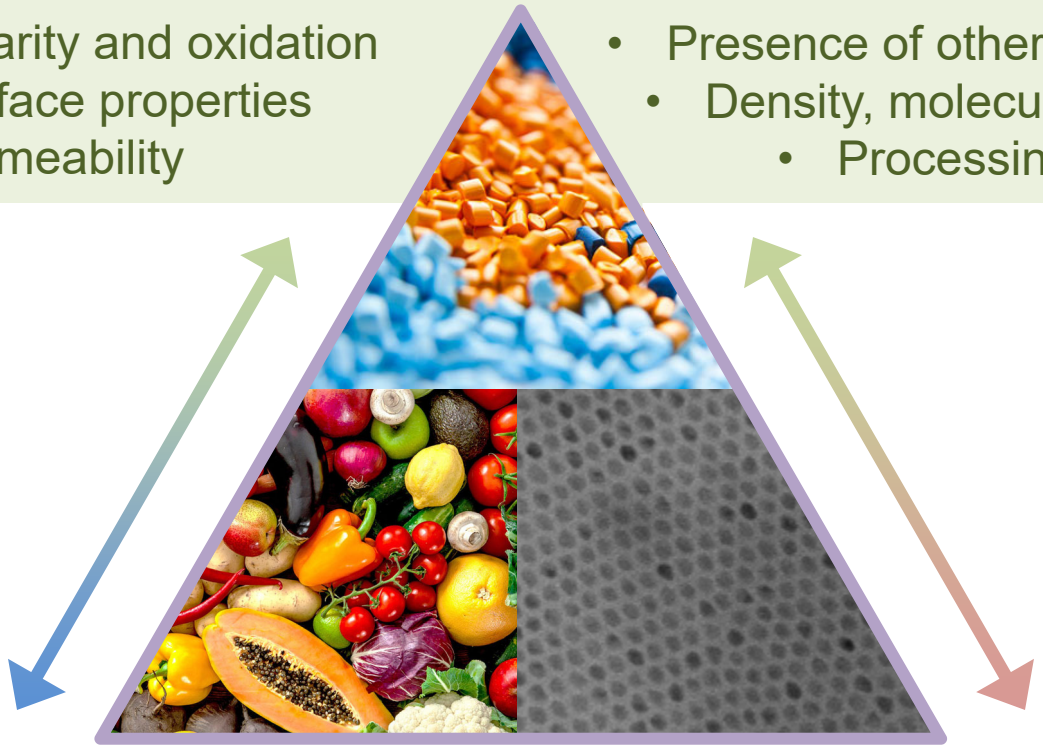
Host polymer characteristics

- Polarity and oxidation
- Surface properties
- Permeability
- Presence of other additives
- Density, molecular weight
- Processing method



Environmental characteristics

- pH
- Ionic strength
- Composition
- Temperature
- Light/dark
- Humidity

Dispersed particle characteristics

- Aggregation state
- Capping agent
- Size / morphology
- Composition
- Purity
- Age

Research strategy

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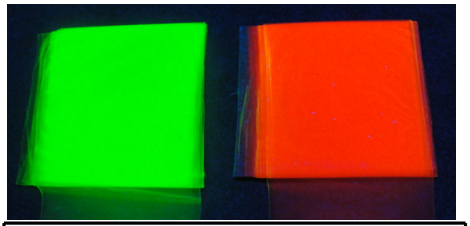
1. System design

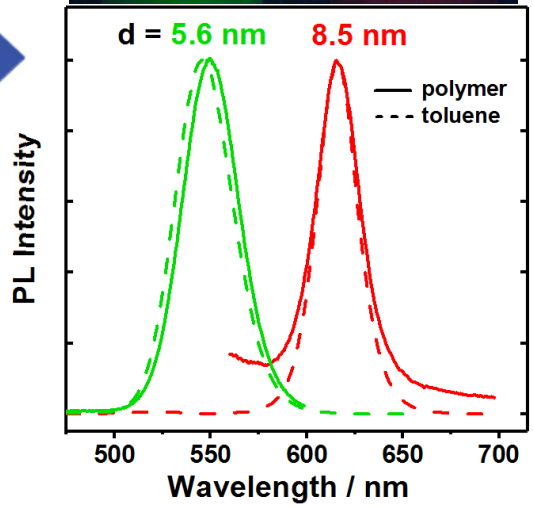
Polymer resin

CdSe@ZnS QDs

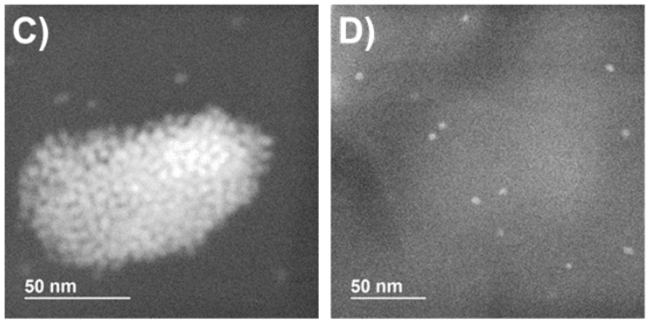
2. Materials manufacture

3. Film characterization

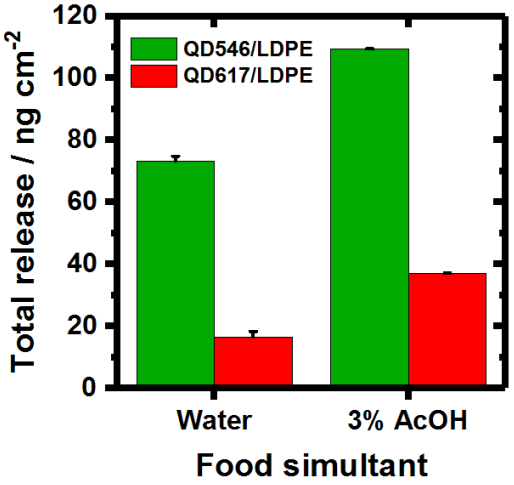




4. Embedded particle characterization



5. Release experiments



Pillai et al. *Environ Sci: Nano* **2016**, 3, 657-669

A deeper exploration of solution pH

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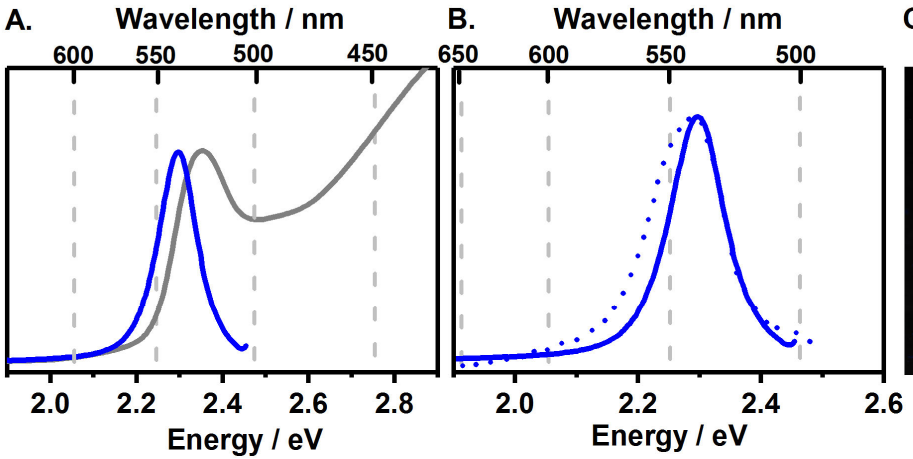
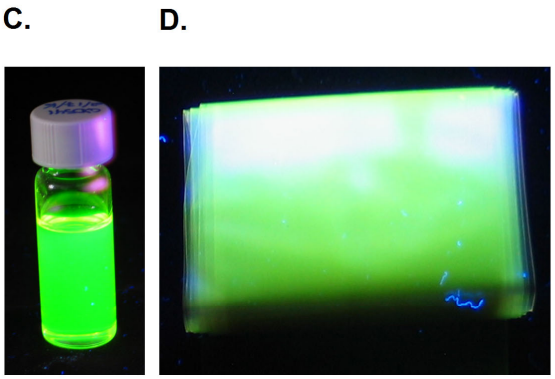
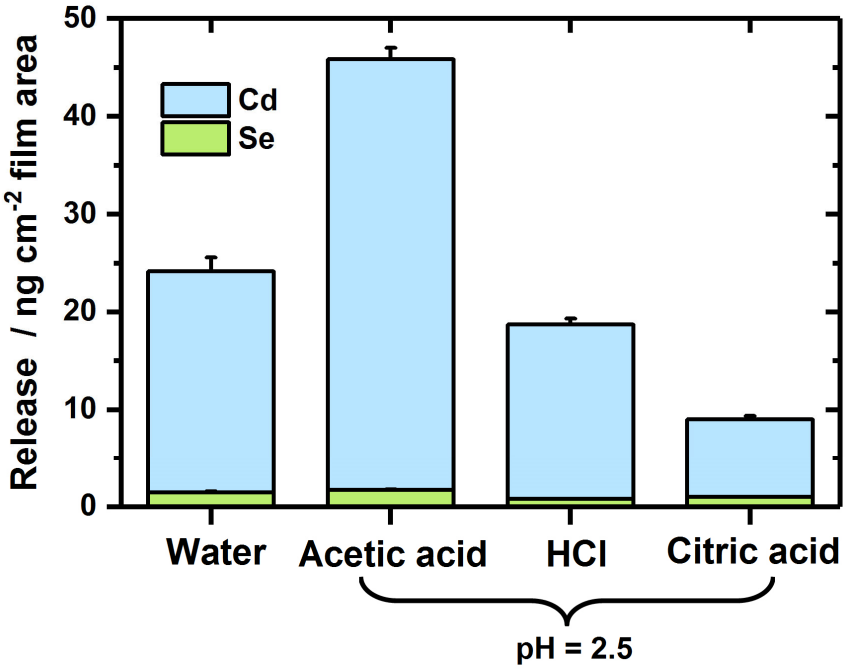
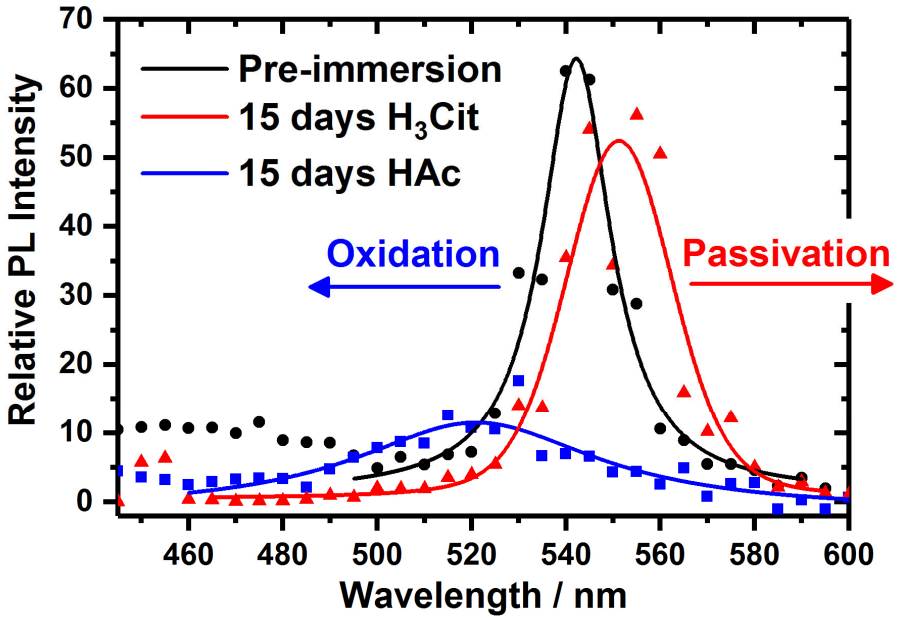




Core-only QDs are more sensitive to environmental changes





Gray et al. *Environ. Sci Technol.* **2018**, *52*, 9468−9477

AgNP composition and release

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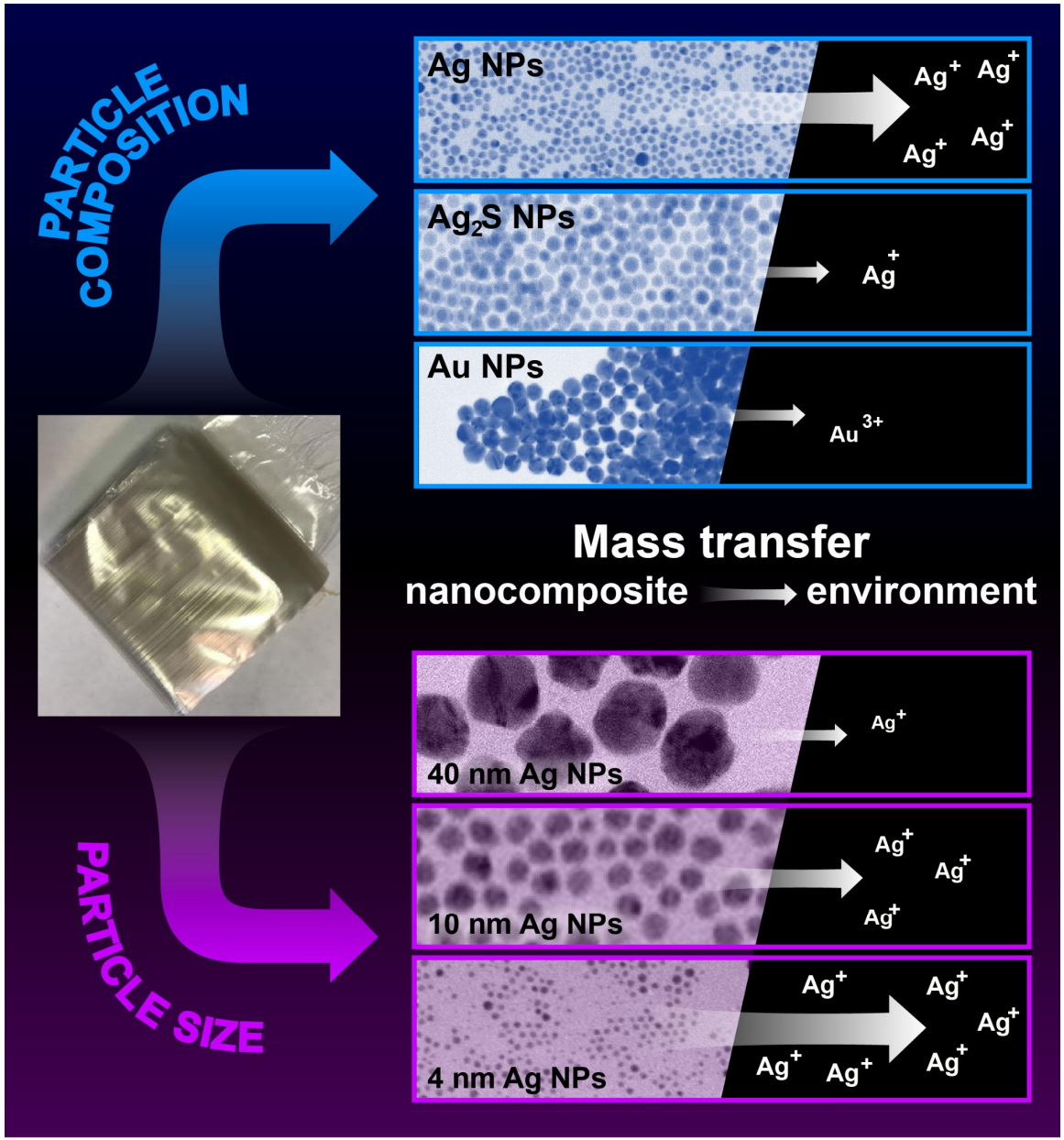

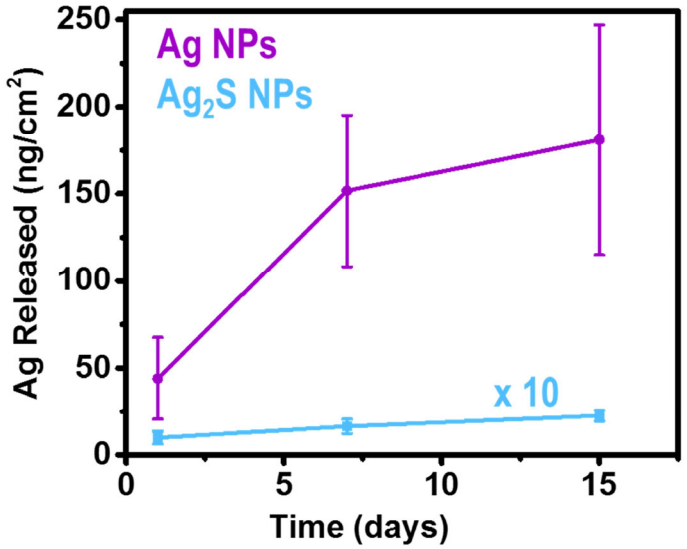

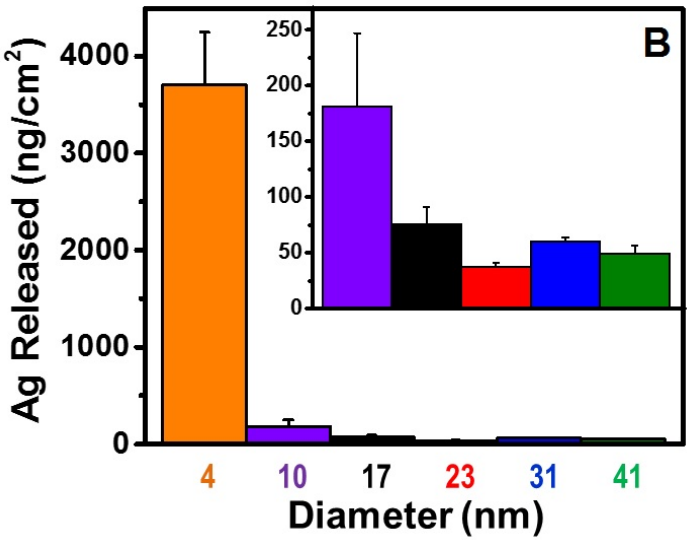

Weiner et al. *ACS Appl. Nano Mater.* **2018**
DOI: 10.1021/acsanm.8b0124

What have we learned?

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1. **Most mass transfer from PNCs to liquid media is driven by oxidative dissolution of embedded particles**
   - Possible some release may be due to whole particle diffusion when particle size < a few nm.
2. **Parameters that impact the sensitivity of embedded nanoparticles to oxidation will impact exposure:**
   - Polymer characteristics (barrier properties, processing method)
   - Particle characteristics (size/shape, composition)
   - Environmental characteristics (composition, oxygen content)
3. **Need for more studies that explore the complicated landscape of nanoparticle dissolution chemistry in polymers.**
   - The dissolution triangle: 2D and 3D studies needed
4. **Need for analytical methods that can measure the properties of polymer-embedded nanoparticles**
   - Especially surface properties and composition

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Article

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pubs.acs.org/est

Influence of Different Acids on the Transport of CdSe Quantum Dots from Polymer Nanocomposites to Food Simulants

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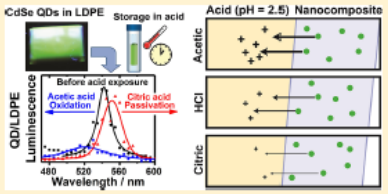
Supporting Information

ABSTRACT: We fabricated polymer nanocomposites (PNCs) from low-density polyethylene and CdSe quantum dots (QDs) and used these materials to explore potential exposure after long-term storage in different acidic media that could be encountered in food contact applications. While the low-level release of QD-associated mass into all the food simulants was observed, exposure to dilute acetic acid resulted in more than double the mass transfer compared to that which occurred during exposure to dilute hydrochloric acid at the same pH. Conversely, exposure to citric acid resulted in a suppression of QD release. Permeation experiments and confocal microscopy were used to reveal mechanistic details underlying these mass-transfer phenomena. From this work, we conclude that the permeation of undissociated acid molecules into the polymer, limited by partitioning of the acids into the hydrophobic polymer, plays a larger role than pH in determining exposure to nanoparticles embedded in plastics. Although caution must be exercised when extrapolating these results to PNCs incorporating other nanofillers, these findings are significant because they undermine current thinking about the influence of pH on nanofiller release phenomena. From a regulatory standpoint, these results also support current guidance that 3% acetic acid is an acceptable acidic food simulant for PNCs fabricated from hydrophobic polymers because the other acids investigated resulted in significantly less exposure.



INTRODUCTION

Polymer nanocomposites (PNCs), polymeric materials incorporating nanoscale fillers, have received attention for their potential use in infrastructure and construction,[1,2] packaging,[3−6] biomedicine,[7−9] textiles,[10−12] and high-performance automotive and aerospace components.[4,13−15] Commercial interest in PNCs has motivated calls for data on the diverse interactions between these materials and environmental systems. In particular, there is a need to determine the likelihood that humans or the environment may be exposed to embedded nanoparticles or their components, the form and quantity of released mass, and the environmental or other extrinsic factors that influence these processes.

For PNCs intended for food-packaging applications, additional information is needed on the effects of long-term exposure of PNCs to liquid media under a wide variety of conditions relevant to food processing and storage. Previous experimental efforts have established that low concentrations of mass deriving from nanoparticles embedded in polymers are passively leached to liquid environments under many test conditions.[16] Although PNCs intended to function as food contact surfaces have received significant attention,[17−36] the diversity of host materials, nanofiller structure and composition, dispersion type (e.g., internally embedded versus surface immobilized nanofillers), and experimental conditions makes it challenging to construct broad predictive frameworks. Some studies on passive release phenomena have reported observing whole nanoparticles in food simulants during experimental time scales. However, recent theoretical[37] and experimental[38,39] efforts indicate that release of whole nanofillers originating from polymeric interiors is unlikely to occur over time scales relevant to intended product use cycles, owing to the slow diffusion rates of nanoparticles through comparatively small polymeric void volumes. As a result, in most cases, the released material is likely composed of dissolved metal ions originating from the surfaces of embedded particles. The incidental release of whole nanoparticles weakly bound at the interface between the PNC and the food simulant or along cut edges of PNC test samples or the reconstitution of

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Gray, et al. *Environ. Sci Technol.* **2018** *52*, 9468−9477

ACS APPLIED NANO MATERIALS

Article

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Assessment of Mass Transfer from Poly(ethylene) Nanocomposites Containing Noble-Metal Nanoparticles: A Systematic Study of Embedded Particle Stability

Rebecca G. Weiner,[†] Ashutosh Sharma,[‡] Haiqi Xu,[‡] Patrick J. Gray,[†] and Timothy V. Duncan*[,†]

[†]Center for Food Safety and Applied Nutrition, US Food and Drug Administration, Bedford Park, Illinois 60501, United States
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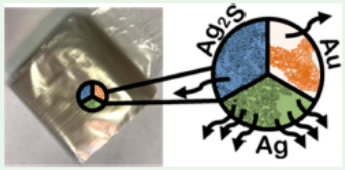
Supporting Information

ABSTRACT: Polymer nanocomposites (PNCs), which consist of a polymer host and a nanomaterial filler, may become useful as food packaging materials due to their enhanced properties compared to neat polymers. Many studies have explored release of embedded nanomaterials or their components from PNCs into foods and food simulants. However, more studies are needed that systematically study the mechanistic role that nanopartide (NP) and polymer characteristics play in determining mass transport from these materials. Here, noble-metal-containing nanoparticle (NP)/low density poly(ethylene) (LDPE) PNCs were used as model food contact materials to decouple the impact of nanofiller size, composition, and stability on release into two food simulants (water and 3% acetic acid). PNCs containing Ag NPs ranging in diameter from 4 to 41 nm were first evaluated. We found that ∼1% of Ag mass was released from PNCs incorporating Ag NPs > 10 nm, but the percent of released Ag increased dramatically when the Ag NP diameter was <10 nm (52% release was measured when the NP diameter was 4 nm). By comparison, mass transfer from PNCs incorporating similarly sized, more stable Ag_2S NPs and Au NPs was very low (<0.1%). We also found that the simulant chemistry and experiment time impact total mass transfer from these PNC films. These experiments are the first to show a direct link between NP size/composition and potential mass transfer to food simulants, and they support a model in which NP stability against oxidative dissolution plays a dominant role in determining consumer exposure in a food contact application. The results will help inform design strategies for PNCs that have reduced likelihood of mass transfer to aqueous environments.

KEYWORDS: *nanocomposite, silver, gold, silver sulfide, food packaging, exposure*



INTRODUCTION

Polymer nanocomposites (PNCs) consist of a polymer and a nanomaterial filler, which are generally reported to have at least one dimension between 1 and 100 nm, although materials have shown size-dependent properties at larger sizes.[1] PNCs have properties that may make them desirable for a variety of applications including food packaging,[2] electronics,[3] biomedical devices,[4] sports equipment,[5] textiles,[6] and construction materials.[7,8] Some of these enhanced properties include: self-healing,[9] antimicrobial,[6,10] mechanical toughness,[7,11] and barrier strength.[12]

In the event that PNCs are utilized as food contact materials, embedded nanomaterials may release from the polymer into foods under intended conditions of use.[13−15] It is important to quantify this release due to the potential for consumer exposure,[16−21] and several studies have done so with commercial materials.[16−18] Many previous studies[14−16,18,22−25] have focused on Ag release from both commercial and homemade PNCs incorporating Ag nanoparticles (NPs), because Ag NP/polymer composites have been explored for antimicrobial food packaging use outside of the United States. Studies on commercial Ag-containing materials have revealed that some Ag mass is invariably released to food simulants under a variety of test conditions, and they have also loosely established that factors like pH, particle composition, and polymer composition may affect the release process. However, embedded Ag NP size, shape, and composition (e.g., pure Ag vs Ag contaminated with AgCl, Ag_2O, Ag_2S, etc.) in commercial and even many homemade test materials is frequently unknown or poorly characterized, which makes it difficult to decouple the role such NP-specific parameters play in the release process. The lack of systematic studies on NP release thus constitutes a fundamental knowledge gap toward creation of a systematic predictive model for NP-associated mass transfer from PNCs to food simulants.

To address the need for more information on NP release from PNCs during storage in aqueous media, we recently studied the impact of polymer-embedded NP size on mass-

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708-924-0607

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