

Supporting Information

TITLE Assessing the Environmental Effects Related to Quantum Dot Structure, Function, Synthesis and Exposure

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S1.1 Vapor phase synthesis

In vapor phase synthesis, the growth of the QD occurs through epitaxial self-assembly by deposition on the surface of a semiconductor layer that has a compatible lattice structure with that of the QD¹. Conditions necessary to ensure thermodynamic instability of the vapor-phase reactants compared to the QD to be synthesized are created. These conditions include chemical supersaturation of the reactants, in which, it is thermodynamically favorable for the vapor phase molecules to chemically react and form a condensed phase. This is often followed by nucleation and particle growth². Vapor phase synthesis of QD can be achieved by molecular beam epitaxy (MBE), sputtering, or aggregation of gaseous monomers³.

S1.2. Wet-chemical synthesis

Wet-chemical (liquid phase synthesis), also referred to as colloidal synthesis, involves dissolution of molecular or atomic precursors in organic solvents such as TOP, tributyl phosphine (TBP), or triisopropyl phosphine (i-TPP) and subsequent injection into a heated solvent¹. Nucleation and growth of QD in the solvent occurs by Ostwald ripening¹. Wet-chemical synthesis is scalable and has a high yield⁴⁻⁹. It also allows for fine-tuning of reaction conditions such as temperature, substrate concentration, and pH, to obtain desired QD shapes, sizes, and surface structures¹⁰. Wet-chemical synthesis of QDs can be performed via processes such as hydro/solvothermal, microemulsion, sol-gel, hot-solution decomposition, and microwave/ultrasonic synthesis^{10,11}.

Along with the intrinsic potential hazards associated with QDs, the actual synthesis of QDs often creates hazardous waste that can cause adverse effects to humans and the environment; therefore, there is a recent push towards “green” manufacturing processes for QDs. This includes reducing the use of tri-n-octylphosphine oxide (TOPO) in the preparation of CdTe by substituting with di-n-octylphosphine oxide (DOPO)¹². Aqueous synthesis of QDs is typically more environmentally friendly because it does not include an additional post-treatment step with toxic capping agents or hydrophobic ligands.

S2 Amount of QDs used in products

Displays are the most developed market for QDs¹³, and the amount of QDs in selected display units is available in the literature¹⁴. Compared to display applications, very little is known

about the amount of QDs in products such as solar cells, thermoelectrics, and LED lights. Although 0.65 wt% of steric acid/TOPO- capped ZnSe was used in a white-light-emitting diode (WLED)¹⁵, which is higher compared to the amount of QD obtainable in display technology (Table S2).

CdSe and InP are two of the most used QDs in display technology. Chopra et al.,¹⁴ and Brown et al.,¹⁶ found comparable concentrations of CdSe and InP in quantum-dot enhancement film (QDEF) of Kindle Fire tablet and Samsung SUHD TV, respectively. Leached Zinc (Zn) concentrations were three orders of magnitude higher in both devices compared to Cd and In. Chopra et al.,¹⁴ estimated the amount of QDs in other products based on their display sizes and the unit amount of CdSe and InP QDs obtained experimentally, assuming the products are enabled with QDEF technology. The result obtained is shown in Table S2 below. Similarly, we estimated the amount of QD in commercially available thin film displays using data collected from Brown et al.,¹⁶. Broadly speaking, TV displays have higher amounts of QDs than computer monitors, notebooks, tablets, and smartphones. Overall, the amount of QDs in displays largely depend on the product size.

S3 Release of QDs from product matrix

S3.1 Mechanisms of QD release from products

QDs may be released from the matrix of products via active or passive mechanisms (Figure S2). Active release mechanism involves the degradation of the matrix in which QDs are embedded. Matrix degradation occurs via mechanical abrasion, thermal decomposition, hydrolysis and photodegradation. Active release of QDs is relevant to matrices that experience weathering and/or landfill conditions¹⁷. Studies on active release of QDs from products are rare. In a recent study investigating active weathering of CdSe- and CdSe/ZnS-embedded poly (methyl methacrylate), the authors reported release of polymer fragments with QDs and metal ions, but free-standing QDs was not detected (possibly due to the limitation of the method used)¹⁸.

Passive release of QDs occur without matrix degradation and via passive diffusion, desorption or dissolution into external liquid media¹⁷. Release of QDs by passive mechanism often involve short-term or prolonged exposure of matrix to a liquid environment during which QD moves from an area of high concentration (matrix) to that of low concentration (external environment)¹⁷. Desorption occurs when QDs are located on the surface of the matrix and adhered to the substrate by electrostatic interaction while diffusion is common in matrices with QDs

dispersed within the host material rather than deposited on the surface¹⁹. Although the release of QD particles from the core of matrices cannot be ruled out, diffusion of nanoparticles through polymers occur at timescales that are too slow to be relevant²⁰. Dissolution involves transformation of QDs from particulate form into ionic constituents¹⁹.

S3.2 Factors influencing release of QDs from products

The release of QDs from products is mainly controlled by the environmental conditions the product is exposed to, the nature of the product matrix, QD diameter, and time^{21, 22}. Brown and coworkers reported low release of metals (including cadmium, indium, and zinc) from seven commercial QD-enabled photovoltaic and display technologies due to the protective effect of the products matrices from harsh experimental conditions (that is, simulated landfill environments and extreme case leaching scenarios)¹⁶. Less than 0.2 µg/L of In and Cd were released from the display films tested (Kindle and TV), due to the strong polyethylene terephthalate (PET) matrix¹⁶. However, matrix infiltration by acidic media promoted the release of metal ions from CdSe/ZnS core/shell QD-enabled acrylate and low-density polyethylene (LDPE) polymer matrices^{21, 22}. Overall, the permeability of the product matrix is possibly the most important factor in release of dissolved metals from metallic QDs embedded in consumer products.

Ambient light had no significant effect on the release of cadmium from a CdSe/ZnS QD-enabled acrylate polymer²¹. However, low pH conditions, obtained with 1 M nitric acid and gastric acid, promoted Cd release from the polymer nanocomposite (1.10 – 1.20 mg/g polymer after 30 days) due to solution infiltration into the polymer. Release of Cd from the polymer was lower (<0.10 mg/g polymer) in the presence of hydrogen peroxide (an oxidant), moderately hard reconstituted water (MHRW), humic acid, fulvic acid, phosphate buffered saline, and toxicity characteristic leaching procedure (TCLP) extraction fluid. Pillai et al.,²² also confirmed the enhancement of metals (Cd, Se, and Zn) released from QD-polymer nanocomposites by low pH and observed that the total mass of metals released increases over time (although the release rate slows over time) when CdSe/ZnS QD polymer nanocomposite was immersed in solutions simulating food contact scenarios.

In addition, the size of QD embedded in polymer nanocomposites has a significant impact on metal release, with a higher total metal mass released from a LDPE composite embedded with 4.3 nm CdSe/ZnS QD compared to the same polymer containing a similar weight fraction of 5.5

nm CdSe/ZnS QDs ²². The trend was also confirmed when metals release from polymer nanocomposites embedded with either 5.6 nm or 8.5 nm CdSe/ZnS QDs were compared ²². The role of size in metal release was attributed to the greater specific surface area of smaller nanoparticles, which enhance dissolution rates. The effect of QD particle size was more pronounced in acidic medium compared to pure water, due to the promotion of dissolution by low pH. All existing studies performed with metallic QDs show that QD metal release was mainly from the dissolution of surface and embedded QDs, and/or desorption of nanoparticles at the surface of QD-enabled polymers ²².

The release mechanism of metal ions from polymer nanocomposites was attributed to solution infiltration of matrix, partial dissolution of CdSe/ZnS QD, and diffusion of the dissolution product from the matrix in which the QD is contained while the polymer matrix remained intact ²³.

S4 Estimation of QDs released into the environment

QDs released into different environmental phases were estimated according to the method described by Keller and Lazareva ²⁴. While other models, such as probabilistic model using Monte Carlo ²⁵, and material flow analysis ²⁶, have been used to estimate the environmental release of nanoparticles, the model by ²⁴ was selected because it relies on market studies with data collected from manufacturers instead of unspecified sources. Global QDs production data was obtained from Future Markets Technology report ²⁷, which provided a production estimate based on the production volume of three different companies. The quantity of QDs likely to be released into natural and engineered systems was estimated from the global production estimate. QDs release was categorized as low and high estimates. Low estimate considers lower production estimate in a specific year and low release tendencies during each stage of products' lifecycle.

S4.1 Release during manufacture

Release of QD during manufacture was estimated as 0.1 - 2% (low – high estimate) of the total production (Table S3). It was assumed that release during manufacturing of QDs and production of QD-containing products are covered within the low and high estimates. For low estimate, 10%, 10%, and 80% of the QDs released during manufacture were released into air, water prior to wastewater treatment, and landfill, respectively. For high estimate, 40% was allocated to

release into both air and water prior to wastewater treatment, while 20% was attributed to release to landfill.

S4.2 Release during use

Release during use was estimated based on the different application of QDs as reported in the market report (Future_Markets, 2019), and the literature ^{26,28}. The applications considered are electronics and optics (which include displays and lighting), medical, packaging, sensors, and paper and board. Similar to release during manufacture, low and high estimates were considered in release during use of QD-based devices. The amount of QDs released during use in different applications vary and the low and high estimate is showed in Table S4. The amount released into air, wastewater treatment plants (WWTP) and soil are represented in Table S4.

S4.3 Release during disposal

Release during disposal is categorized into five (5) groups based on result from previous studies ²⁹⁻³¹, depending on whether the devices end up in waste incineration plants or wastewater treatment plants. Estimated release from waste incineration plants is 0.05 – 1% into air, 1 – 50 % into slag and 50 – 98% trapped in filters (Table S5). Release into WWTP is either by sludge removal estimated as 75 – 97% or release into effluent (3 – 25%). For both low and high estimate, the release from WWTP sums up to a 100% with 3% released into effluent and 97% released into sludge for low estimate and 25% released into effluent and 75% released into sludge. This explains why the high estimated release from WWTP into sludge is lower than that released into sludge for low estimate.

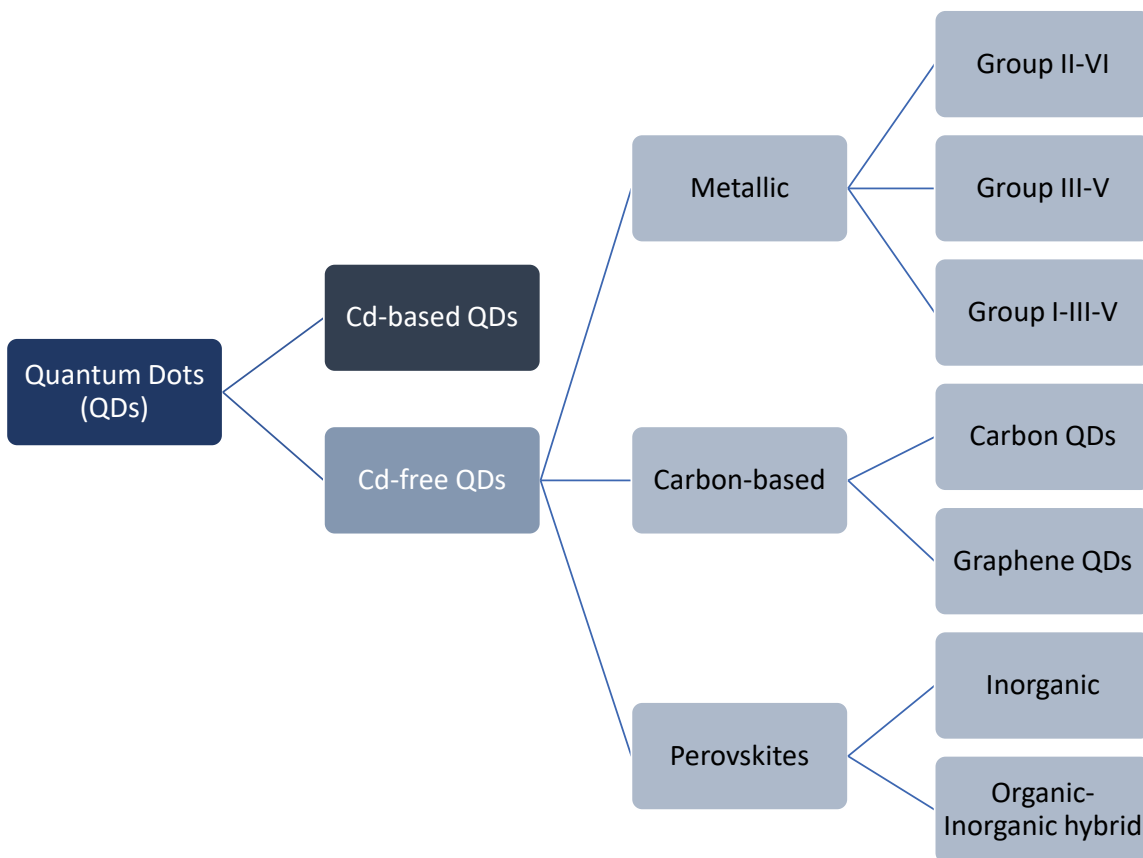


Figure S1. Classification of QDs based on composition.

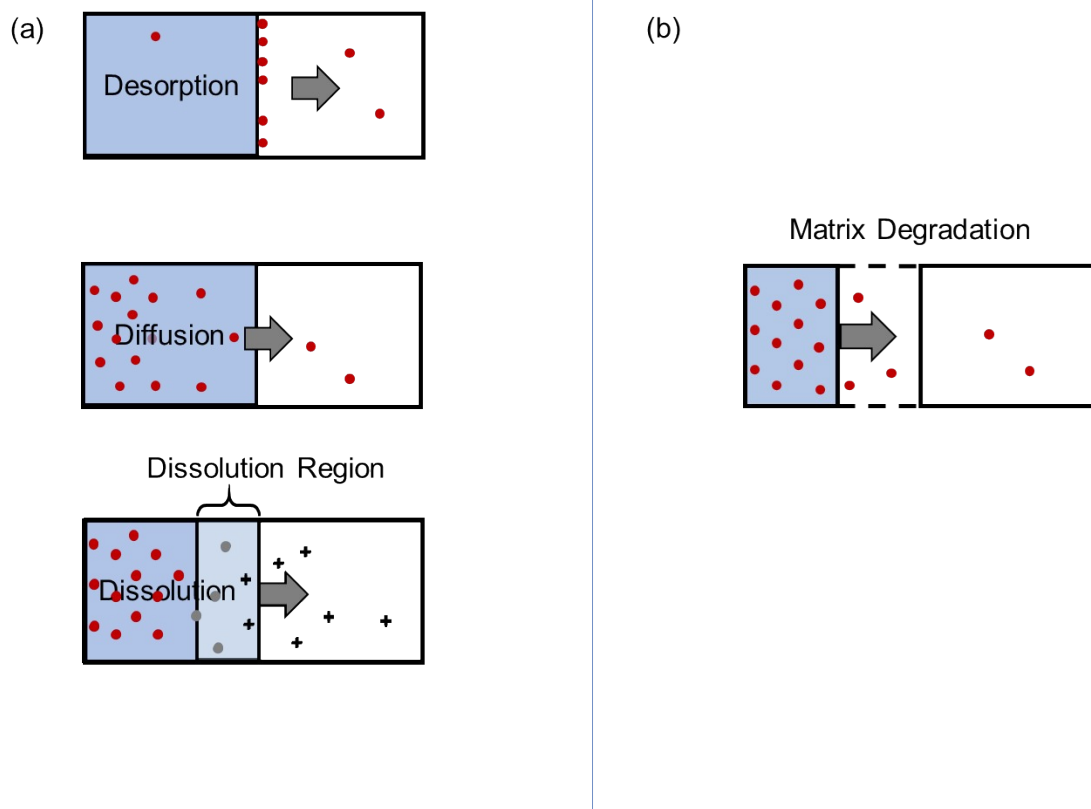


Figure S2. Release of QDs from matrices via (a) passive and (b) active release mechanisms. Specific release processes under active release include mechanical abrasion, thermal decomposition, hydrolysis, and photodegradation. Figure was adapted from Duncan and Pillai,³².

Table S1. Major quantum dots (QDs) synthesis techniques

Approach	Synthesis method	Properties	Merits	Demerits	References
Top-down	Arc discharge	Requires very high temperature and can be used to synthesize carbon based QDs	QDs synthesized by arc-discharge have good water solubility	Energy intensive. QDs synthesized have large particle size distribution and particle size decreases specific surface area	33
	Electrochemical synthesis	Involves selective oxidation and reduction of electrolyte. Electrochemical synthesis offers flexibility in the choice of solvent and supporting electrolyte by varying the applied potential.	QDs synthesized are highly stable and the uniform size distribution	Requires pretreatment of raw materials used in the synthesis and purification of synthesized QDs which is often time consuming	34-36
	Laser ablation	Requires the use of high-energy laser pulse to generate high temperature and pressure	Surface of synthesized QDs can be modified by selecting suitable organic solvent during laser ablation. It is also effective in the preparation of narrow size distribution of	Cost intensive and complicated	37-39

			QDs		
	Acidic oxidation	Requires the use of acid to decompose bulk material.	Suitable for the synthesis of hydrophilic QDs and improved fluorescent properties. QDs synthesized by acidic oxidation possess excellent electrocatalytic properties.	Level of oxidation and hence efficiency of the method is controlled by oxidant concentration, as such, can be cost intensive.	40-42
Bottom-up	Sol-gel	Involves the hydrolysis of a suitable metal precursor in an acidic or basic medium. The synthesis occurs in steps; hydrolysis, condensation, and growth	Simple, cost effective and suitable for large scale applications	QDs synthesized have broad size distribution and high concentration of defects	43
	Microemulsion	Involves chemical conversion of soluble precursors into insoluble nanosized materials using a surfactant.	The size of QDs synthesized can be optimized and controlled easily. It also results in narrow size distribution of synthesized QDs	Low yield. QDs synthesized could contain impurities and defects	44, 45

	Hydrothermal/Solvothermal synthesis	Involves growth of QDs from aqueous solution under controlled pressure and temperature.	Simple and easy operation. QDs synthesized have uniform size distribution. Size of QDs can also be controlled by changing pressure, temperature and reactants in the synthesis process	Synthesis can be energy intensive and costly. The reaction process cannot be monitored.	46-48
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Table S2. QDs amount embedded in several kinds of display devices assuming QDEF technology. Data sources Chopra et al.,¹⁴ and Brown et al.,¹⁶.

Devices (size range)	Amount of QDs (mg) ^a		^b CdSe (wt%×10 ³)	^b InP (wt%×10 ³)	ZnS (wt%)
	CdSe	InP			
TV displays (32-60")	19.1 – 38.9	10 – 35.3	0.17 - 0.21	0.11 - 0.15	-
PC monitors (15-25")	2.4 – 6.2	5.7 – 2.2	0.12 - 0.18	0.29 - 0.64	-
Notebooks (10-17")	1.1 – 3.1	1 – 2.8	0.14 - 0.12	0.13 - 0.11	-
Tablets (7-10")	0.5 – 1.1	0.5 – 1	0.13 - 0.24	0.13 - 0.22	-
Smartphones (3.5-6.9")	0.1 – 0.5	0.1 – 0.5	0.13 - 0.39	0.13 - 0.39	-
TV film	-	-	-	0.2123	2.3
TV display	-	-	-	-	-
Kindle film	-	-	4.92	-	1.0
Kindle Display	0.87	-	0.29	-	3.5

^aThe amount of QDs is expressed in lower and upper bound. The lower bound corresponds with the amount of QDs in the small size device and the upper bound with the large size device. Each device is assumed to contain either CdSe/ZnS or InP/ZnS core/shell QD.

^bWt% calculated by expressing the ratio of mass of QDs to total mass of device in percent.

Table S3. Release pathways of quantum dots (QDs) during synthesis

QD Synthesis Phase				
Synthesis Methods	Type of QDs and (Yield)	Loss of QDs during synthesis	Release pathways	References
Thermal pyrolysis	CQD (9 – 53%)	<ul style="list-style-type: none"> • Removal of large particles after dilution with water, and at purification step using a cellulose ester membrane bag for removing excessive glycerol • Loss can occur during purification step using petroleum ether • Loss can also occur during multistep precipitation/redispersion process of purification and finally dried as solid powders 	Wastewater, and solid waste (from membrane disposal) Emissions/fumes	49 50 51, 52
Microwave-assisted carbonization	CQD (11.2%)	<ul style="list-style-type: none"> • Loss during washing of CQD dots with methanol or ethanol and in the form of fumes during decomposition at high temperature 	Wastewater, Emissions/fumes	53, 54
Solvothermal	CQD (10.8 - 65.9%)	<ul style="list-style-type: none"> • Removal of large particles from the reaction mixture after centrifugation, and loss of ions or nanoparticles during solvents removal • Loss of nanoparticles (NPs) or large particles when the suspensions containing CQDs 	Wastewater, and solid waste (from disposal of membranes)	55, 56 57

		<ul style="list-style-type: none"> are filtered via membrane Loss of NPs during purification of suspension via silica column chromatography 		
Solution processed method	CdSe/CdS QDs (90%)	<ul style="list-style-type: none"> Loss of QDs during purification step and during replacement of original ligands by 1-dodecanethiol which were dispersed and in solvent and filtered before use 	Wastewater, and solid waste (from filters disposal)	58
Hot injection method	Cd _x Zn _{1-x} S _y Se _{1-y} QDs (89%)	<ul style="list-style-type: none"> Loss of large particles, ions or QDs during purification step repeated several times by precipitation/ redispersion processes using solvents 	Wastewater	59
Low temperature synthesis method	CdSe/ZnS (~90%)	<ul style="list-style-type: none"> Loss of QDs, ions or large particles when precipitated in acetone and rinsing with ethanol 	Wastewater	60

CQD = carbon quantum dots; CdSe/CdS QDs = cadmium selenide/cadmium sulfide quantum dots; Cd_xZn_{1-x}S_ySe_{1-y} QDs = alloyed quantum dot based on cadmium, zinc, sulfur, and selenide; CdSe/ZnS QDs = cadmium selenide/zinc sulfide quantum dots.

Table S4. Estimates of quantum dots (QDs) released into the environment during manufacturing. Global production estimate was based on the production of three large QDs producers.

Total release during manufacturing								
Global production volume	Total release during manufacturing (tons/year)		To air (tons/year)		To water prior to WWTP (tons/year)		To landfill (tons/year)	
	Low estimate	High estimate	Low estimate	High estimate	Low estimate	High estimate	Low estimate	High estimate
57	0.057	1.14	0.0057	0.456	0.0057	0.456	0.0456	0.228

Table S5. Estimates of quantum dots (QDs) released into the environment during use.

Use of QDs	Release into air (tons/year)	Release into air (tons/year)	Release into WWTP (tons/year)	Released into WWTP (tons/year)	Release into soil (tons/year)	Release into soil) (tons/year)	Total release during use (tons/year)	
	Low estimate	High estimate	Low estimate	High estimate	Low estimate	High estimate	Low estimate	High estimate
Electronics and optics	0.0285	0.1425	0.0285	0.1425	0.513	2.565	0.57	2.85
Medical	0.1425	0.7125	2.565	12.825	0.1425	0.7125	2.85	14.25
Packaging	0	0	0.1425	0.7125	2.7075	13.5375	2.85	14.25
Paper and board	0	0	0.1425	0.7125	2.7075	13.5375	2.85	14.25
Sensors	0	0	0.01425	0.0285	0.27075	0.5415	0.285	0.57

Table S6. Estimates of quantum dots (QDs) released into the environment from disposal systems

	Release from disposal system				
	Release from WIP into air (tons/year)	Release from WIP into slag (tons/year)	Release from WIP into filters (tons/year)	Release from WWTP into effluent (tons/year)	Release from WWTP into sludge (tons/year)
Low estimate	0.0285	28.5	28.4715	1.71	55.29
High estimate	0.57	0.57	55.86	14.25	42.75

Table S7. Summary of current studies on release of quantum dots (QDs) at end-of-life phase

End-of-Life				
Types of QDs	Product	Release scenario	Pathway to the environment	References
CdSe and CdSe/ZnS QD	Polymer nanocomposites	Released into aqueous media due to matrix degradation or weathering	Wastewater	18
CdSe QD	TV, tablet, or mobile phone's screen	Screen breakage and become trash. Cd ²⁺ , could be released into the environment	Emissions via furnace (in case of incineration), wastewater effluents, solid waste	61
CdSe QD	Kindle Fire Tablet 2011	About 1.34 µg L ⁻¹ Cd could be released from landfill disposal	Solid waste	14
InP QD	Samsung TV 2016	Approximately 0.077 µg L ⁻¹ In was reported to release from the QD enabled displays from landfill disposal	Solid waste	14
CdSe/ZnS & InP/ZnS QDs	Photovoltaic panels	Released into the atmosphere as particulates	Solid waste and recycling	16
CdSe QD	Paper and plastics	Released as particulates matter during incineration with some of the QD retained in bottom ash or flue dust after incineration	Solid waste and recycling	62
CdSe/ZnS QDs	LED	Waste recycling	Solid waste and recycling	63

CdSe QDs = cadmium selenide quantum dots; InP QD = indium phosphide quantum dots; CdSe/ZnS QDs = cadmium selenide/zinc sulfide quantum dots; LED = light-emitting diode

References

1. H. Sengül and T. L. Theis, in *Nanotechnology Applications for Clean Water*, eds. N. Savage, M. Diallo, J. Duncan, A. Street and R. Sustich, William Andrew Publishing, Boston, 2009, pp. 561-582.
2. M. T. Swihart, Vapor-phase synthesis of nanoparticles, 2003, **8**, 127-133.
3. D. Bera, L. Qian, T.-K. Tseng and P. H. Holloway, Quantum Dots and Their Multimodal Applications: A Review, 2010, **3**, 2260-2345.
4. W. Bi, M. Zhou, Z. Ma, H. Zhang, J. Yu and Y. Xie, CuInSe₂ ultrathin nanoplatelets: novel self-sacrificial template-directed synthesis and application for flexible photodetectors, 2012, **48**, 9162-9164.
5. B. Mahler, V. Hoepfner, K. Liao and G. A. Ozin, Colloidal Synthesis of 1T-WS₂ and 2H-WS₂ Nanosheets: Applications for Photocatalytic Hydrogen Evolution, 2014, **136**, 14121-14127.
6. J. S. Son, J. H. Yu, S. G. Kwon, J. Lee, J. Joo and T. Hyeon, Colloidal Synthesis of Ultrathin Two-Dimensional Semiconductor Nanocrystals, 2011, **23**, 3214-3219.
7. C. Tan and H. Zhang, Wet-chemical synthesis and applications of non-layer structured two-dimensional nanomaterials, 2015, **6**, 7873.
8. D. D. Vaughn, S.-I. In and R. E. Schaak, A Precursor-Limited Nanoparticle Coalescence Pathway for Tuning the Thickness of Laterally-Uniform Colloidal Nanosheets: The Case of SnSe, 2011, **5**, 8852-8860.
9. D. Yoo, M. Kim, S. Jeong, J. Han and J. Cheon, Chemical Synthetic Strategy for Single-Layer Transition-Metal Chalcogenides, 2014, **136**, 14670-14673.
10. A. Nikam, B. Prasad and A. J. C. Kulkarni, Wet chemical synthesis of metal oxide nanoparticles: a review, 2018, **20**, 5091-5107.
11. D. Chen and X. Chen, Luminescent perovskite quantum dots: synthesis, microstructures, optical properties and applications, *Journal of Materials Chemistry C*, 2019, **7**, 1413-1446.
12. H. B. Shen, X. D. Jiang, S. J. Wang, Y. T. Fu, C. H. Zhou and L. S. Li, Facile preparation of metal telluride nanocrystals using di-n-octylphosphine oxide (DOPO) as an air-stable and less toxic alternative to the common tri-alkylphosphines, *Journal of Materials Chemistry*, 2012, **22**, 25050-25056.
13. S. Coe-Sullivan, W. Liu, P. Allen and J. S. Steckel, Quantum dots for LED downconversion in display applications, *ECS Journal of Solid State Science and Technology*, 2012, **2**, R3026.
14. S. S. Chopra, Y. Bi, F. C. Brown, T. L. Theis, K. D. Hristovski and P. Westerhoff, Interdisciplinary collaborations to address the uncertainty problem in life cycle assessment of nano-enabled products: case of the quantum dot-enabled display, *Environmental Science: Nano*, 2019, **6**, 3256-3267.
15. H. S. Chen, S. J. J. Wang, C. J. Lo and J. Y. J. A. P. L. Chi, White-light emission from organics-capped ZnSe quantum dots and application in white-light-emitting diodes, 2005, **86**, 131905.
16. F. C. Brown, Y. Bi, S. S. Chopra, K. D. Hristovski, P. Westerhoff and T. L. Theis, End-of-Life Heavy Metal Releases from Photovoltaic Panels and Quantum Dot Films: Hazardous Waste Concerns or Not?, 2018, **6**, 9369-9374.
17. T. V. Duncan, Release of engineered nanomaterials from polymer nanocomposites: the effect of matrix degradation, *ACS applied materials & interfaces*, 2015, **7**, 20-39.
18. M. J. Gallagher, J. T. Buchman, T. A. Qiu, B. Zhi, T. Y. Lyons, K. M. Landy, Z. Rosenzweig, C. L. Haynes and D. H. Fairbrother, Release, detection and toxicity of fragments generated during artificial accelerated weathering of CdSe/ZnS and CdSe quantum dot polymer composites, *Environmental Science: Nano*, 2018, **5**, 1694-1710.

19. G. O. Noonan, A. J. Whelton, D. Carlander and T. V. Duncan, Measurement Methods to Evaluate Engineered Nanomaterial Release from Food Contact Materials, 2014, **13**, 679-692.
20. P. ŠIMON, Q. Chaudhry, D. J. J. o. F. BAKOŠ and N. Research, Migration of engineered nanoparticles from polymer packaging to food--a physicochemical view, 2008, **47**.
21. J. Liu, J. Katahara, G. Li, S. Coe-Sullivan and R. H. Hurt, Degradation Products from Consumer Nanocomposites: A Case Study on Quantum Dot Lighting, 2012, **46**, 3220-3227.
22. K. V. Pillai, P. J. Gray, C.-C. Tien, R. Bleher, L.-P. Sung and T. V. Duncan, Environmental release of core-shell semiconductor nanocrystals from free-standing polymer nanocomposite films, 2016, **3**, 657-669.
23. J. Liu, J. Katahara, G. Li, S. Coe-Sullivan and R. H. Hurt, Degradation products from consumer nanocomposites: a case study on quantum dot lighting, *Environmental science & technology*, 2012, **46**, 3220-3227.
24. A. A. Keller and A. Lazareva, Predicted releases of engineered nanomaterials: from global to regional to local, *Environmental Science & Technology Letters*, 2013, **1**, 65-70.
25. F. Gottschalk, T. Sonderer, R. W. Scholz, B. J. E. s. Nowack and technology, Modeled environmental concentrations of engineered nanomaterials (TiO₂, ZnO, Ag, CNT, fullerenes) for different regions, 2009, **43**, 9216-9222.
26. Y. Wang and B. J. E. p. Nowack, Dynamic probabilistic material flow analysis of nano-SiO₂, nano iron oxides, nano-CeO₂, nano-Al₂O₃, and quantum dots in seven European regions, 2018, **235**, 589-601.
27. Future-Markets, *Future Markets Technology Reports: The Global Market for Quantum Dots*, 2019.
28. F. Gottschalk, C. Lassen, J. Kjoelholm, F. Christensen, B. J. I. j. o. e. r. Nowack and p. health, Modeling flows and concentrations of nine engineered nanomaterials in the Danish environment, 2015, **12**, 5581-5602.
29. A. A. Keller, S. McFerran, A. Lazareva and S. Suh, Global life cycle releases of engineered nanomaterials, 2013, **15**, 1692.
30. M. M. Shafer, J. T. Overdier, D. E. J. E. T. Armstong and C. A. I. Journal, Removal, partitioning, and fate of silver and other metals in wastewater treatment plants and effluent-receiving streams, 1998, **17**, 630-641.
31. N. C. Mueller, B. J. E. s. Nowack and technology, Exposure modeling of engineered nanoparticles in the environment, 2008, **42**, 4447-4453.
32. T. V. Duncan and K. Pillai, Release of Engineered Nanomaterials from Polymer Nanocomposites: Diffusion, Dissolution, and Desorption, 2015, **7**, 2-19.
33. X. Xu, R. Ray, Y. Gu, H. J. Ploehn, L. Gearheart, K. Raker and W. A. Scrivens, Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments, 2004, **126**, 12736-12737.
34. J. Zhou, C. Booker, R. Li, X. Zhou, T.-K. Sham, X. Sun and Z. Ding, An Electrochemical Avenue to Blue Luminescent Nanocrystals from Multiwalled Carbon Nanotubes (MWCNTs), 2007, **129**, 744-745.
35. J. Deng, Q. Lu, N. Mi, H. Li, M. Liu, M. Xu, L. Tan, Q. Xie, Y. Zhang and S. Yao, Electrochemical Synthesis of Carbon Nanodots Directly from Alcohols, 2014, **20**, 4993-4999.
36. Y. Hou, Q. Lu, J. Deng, H. Li and Y. Zhang, One-pot electrochemical synthesis of functionalized fluorescent carbon dots and their selective sensing for mercury ion, 2015, **866**, 69-74.
37. S. R. M. Santiago, T. N. Lin, C. H. Chang, Y. A. Wong, C. A. J. Lin, C. T. Yuan and J. L. Shen, Synthesis of N-doped graphene quantum dots by pulsed laser ablation with diethylenetriamine (DETA) and their photoluminescence, *Physical Chemistry Chemical Physics*, 2017, **19**, 22395-22400.

38. I. Ka, V. Le Borgne, D. Ma and M. A. El Khakani, Pulsed laser ablation based direct synthesis of single-wall carbon nanotube/PbS quantum dot nanohybrids exhibiting strong, spectrally wide and fast photoresponse, *Advanced Materials*, 2012, **24**, 6289-6294.
39. R. L. Calabro, D.-S. Yang and D. Y. Kim, Liquid-phase laser ablation synthesis of graphene quantum dots from carbon nano-onions: comparison with chemical oxidation, *J. Colloid Interface Sci.*, 2018, **527**, 132-140.
40. D. Iannazzo, A. Pistone, M. Salamò, S. Galvagno, R. Romeo, S. V. Giofrè, C. Branca, G. Visalli and A. Di Pietro, Graphene quantum dots for cancer targeted drug delivery, *International journal of pharmaceutics*, 2017, **518**, 185-192.
41. N. Kushwaha, J. Mittal, S. Pandey and R. Kumar, High temperature acidic oxidation of multiwalled Carbon nanotubes and synthesis of Graphene quantum dots, *International Journal of Nano Dimension*, 2018, **9**, 191-197.
42. Z. Shen, C. Zhang, X. Yu, J. Li, Z. Wang, Z. Zhang and B. Liu, Microwave-assisted synthesis of cyclen functional carbon dots to construct a ratiometric fluorescent probe for tetracycline detection, *Journal of Materials Chemistry C*, 2018, **6**, 9636-9641.
43. A. Sashchiuk, E. Lifshitz, R. Reisfeld, T. Saraidarov, M. Zelner and A. Willenz, Optical and conductivity properties of PbS nanocrystals in amorphous zirconia sol-gel films, *Journal of sol-gel science and technology*, 2002, **24**, 31-38.
44. M. Darbandi, R. Thomann and T. Nann, Single quantum dots in silica spheres by microemulsion synthesis, *Chemistry of materials*, 2005, **17**, 5720-5725.
45. M. H. Entezari and N. Ghows, Micro-emulsion under ultrasound facilitates the fast synthesis of quantum dots of CdS at low temperature, *Ultrasonics sonochemistry*, 2011, **18**, 127-134.
46. A. Aboulaich, D. Billaud, M. Abyan, L. Balan, J.-J. Gaumet, G. Medjadhi, J. Ghanbaja and R. I. Schneider, One-pot noninjection route to CdS quantum dots via hydrothermal synthesis, *ACS applied materials & interfaces*, 2012, **4**, 2561-2569.
47. L. Xue, C. Shen, M. Zheng, H. Lu, N. Li, G. Ji, L. Pan and J. Cao, Hydrothermal synthesis of graphene-ZnS quantum dot nanocomposites, *Materials Letters*, 2011, **65**, 198-200.
48. B. Xue, Y. Yang, R. Tang, Y. Sun, S. Sun, X. Cao, P. Li, Z. Zhang and X. Li, One-step hydrothermal synthesis of a flexible nanopaper-based Fe³⁺ sensor using carbon quantum dot grafted cellulose nanofibrils, *Cellulose*, 2020, **27**, 729-742.
49. L.-H. Mao, W.-Q. Tang, Z.-Y. Deng, S.-S. Liu, C.-F. Wang and S. Chen, Facile access to white fluorescent carbon dots toward light-emitting devices, *Industrial & Engineering Chemistry Research*, 2014, **53**, 6417-6425.
50. F. Wang, Z. Xie, H. Zhang, C. y. Liu and Y. g. Zhang, Highly luminescent organosilane-functionalized carbon dots, *Advanced Functional Materials*, 2011, **21**, 1027-1031.
51. X. Zhang, Y. Zhang, Y. Wang, S. Kalytchuk, S. V. Kershaw, Y. Wang, P. Wang, T. Zhang, Y. Zhao and H. Zhang, Color-switchable electroluminescence of carbon dot light-emitting diodes, *ACS nano*, 2013, **7**, 11234-11241.
52. F. Wang, S. Pang, L. Wang, Q. Li, M. Kreiter and C.-y. Liu, One-step synthesis of highly luminescent carbon dots in noncoordinating solvents, *Chemistry of Materials*, 2010, **22**, 4528-4530.
53. L. Fang, M. Wu, C. Huang, Z. Liu, J. Liang and H. Zhang, Industrializable synthesis of narrow-dispersed carbon dots achieved by microwave-assisted selective carbonization of surfactants and their applications as fluorescent nano-additives, *Journal of Materials Chemistry A*, 2020, **8**, 21317-21326.
54. D. Li, C. Liang, E. V. Ushakova, M. Sun, X. Huang, X. Zhang, P. Jing, S. J. Yoo, J. G. Kim and E. Liu, Thermally Activated Upconversion Near-Infrared Photoluminescence from Carbon Dots Synthesized via Microwave Assisted Exfoliation, *Small*, 2019, **15**, 1905050.

55. K. Jiang, S. Sun, L. Zhang, Y. Wang, C. Cai and H. Lin, Bright-yellow-emissive N-doped carbon dots: preparation, cellular imaging, and bifunctional sensing, *ACS applied materials & interfaces*, 2015, **7**, 23231-23238.
56. M. Wu, J. Zhan, B. Geng, P. He, K. Wu, L. Wang, G. Xu, Z. Li, L. Yin and D. Pan, Scalable synthesis of organic-soluble carbon quantum dots: superior optical properties in solvents, solids, and LEDs, *Nanoscale*, 2017, **9**, 13195-13202.
57. Z. Wang, F. Yuan, X. Li, Y. Li, H. Zhong, L. Fan and S. Yang, 53% Efficient Red Emissive Carbon Quantum Dots for High Color Rendering and Stable Warm White-Light-Emitting Diodes, *Advanced Materials*, 2017, **29**, 1702910.
58. X. Dai, Z. Zhang, Y. Jin, Y. Niu, H. Cao, X. Liang, L. Chen, J. Wang and X. Peng, Solution-processed, high-performance light-emitting diodes based on quantum dots, *Nature*, 2014, **515**, 96-99.
59. H. Osman, W. Li, X. Zhang, F. Chun, W. Deng, M. Moatasim, X. Zheng, W. Deng, H. Zhang and W. Yang, One-step hot injection synthesis of gradient alloy $\text{Cd}_x\text{Zn}_{1-x}\text{Se}_y\text{Se}_{1-y}$ quantum dots with large-span self-regulating ability, *Journal of Luminescence*, 2019, **206**, 565-570.
60. H. Zhu, A. Prakash, D. N. Benoit, C. J. Jones and V. L. Colvin, Low temperature synthesis of ZnS and CdZnS shells on CdSe quantum dots, *Nanotechnology*, 2010, **21**, 255604.
61. A. D. Maynard, Are new quantum dot TVs bad for the environment? *Journal*, 2015.
62. E. P. Vejerano, E. C. Leon, A. L. Holder and L. C. Marr, Characterization of particle emissions and fate of nanomaterials during incineration, *Environmental Science: Nano*, 2014, **1**, 133-143.
63. A. Gzásó, D. Fuchs, S. Grefsler, F. Part and M. Huber-Humer, Environmentally Relevant Aspects of Nanomaterials in Products at the End-of-life Phase, *Eur. J. Risk Reg.*, 2015, **6**, 638.