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Interdisciplinary Collaborations to Address the Uncertainty Problem in Life Cycle Assessment of Nano-enabled Products: Case of the Quantum Dot-enabled Display

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Abstract

Life Cycle Assessment (LCA) is a powerful tool for assessing the environmental impacts of established processes and products. However, its use in decision-making for sustainable development of emerging technologies is challenging. High levels of uncertainty and lack of data over the complete value chain associated with nascent nano-enabled products (NEPs) makes it difficult to perform LCA studies early in the design process. This study addresses the uncertainty problem faced by LCA, and a demonstration is performed with a case study of quantum dot (QD)-enabled display. The study at hand proposes a dynamic life cycle assessment (*dLCA*) framework, which emphasizes iterative evaluation and collaborative efforts to tackle the data scarcity problem faced by retrospective (traditional) LCA. Experimental study of two commercially available QD-enabled displays (hand-held tablet with CdSe QD-enabled display and TV set with InP QD-enabled display) is performed for data collection of QD amount and release. After complete digestion, the experimental result shows that the concentration of CdSe (3.92 ± 0.32 μg/cm^2) in the QD enhancement film (QDEF) of Tablet is comparable with the concentration of InP (3.56 ± 0.24 μg/cm^2) in the QDEF of TV. After accounting for the experimental results, the second traversal of *dLCA* is performed, and it shows that cumulative energy demand (CED) per unit area for InP QD-enabled displays is 5.28 x 10^{-3} MJ/cm^2 (first traversal was 2.59 x 10^{1} MJ/cm^2) and CdSe QD-enabled displays is 3.92 x 10^{-4} MJ/cm^2 (first traversal was 4.32 x 10^{-2} MJ/cm^2). This study highlights the role of collaborative research between life cycle modelers and experimentalists to improve the credibility of LCA results for emerging NEPs. Even though this study is based on the case of QD-enabled displays, the proposed *dLCA* framework and interdisciplinary collaboration method can also be applied to other emerging technologies.

Environmental Significance

Uncertain and variable technology adoption trends for some nano-enabled electronic devices have the potential to release nanoparticles into the environment. Due to the lack of collaboration, LCA modelers and end-of-life experimentalists often require or collect data of limited suitability for the other disciplines. Herein, using quantum dot displays as a case, we show that by working together the team effectively conducted key experiments focused on filling critical LCA modeling data gaps and the results better inform environmental impact of nano-enabled devices. Moreover, the paper presents a generalizable model for collaborative and iterative environmental assessment called the dynamic LCA (*dLCA*) framework to guide the sustainable design of emerging nano-enabled products.

1. Introduction

Quantum Dots (QDs) are semiconductor nanocrystals (2-10 nm) with tunable bandgaps and near perfect luminescent properties that make them an ideal candidate for display application with the need for low electricity consumption and high color gamut—the emission of a wider array of more saturated colors.[1] QD-enabled display, embedded in different consumer devices, including TV, PC monitor, notebook, tablet and smartphone, is projected to have a growth rate of 64% annually during the period of 2016-2021.[2] QDs often utilized in displays contain cadmium (*CdSe core QDs*), which is restricted in consumer products (Cd < 100 ppm) by the European Union's Restriction of Hazardous Substances (RoHS) due to its toxic nature.[3] Cadmium is especially hazardous to the environment and is dangerous regarding occupational exposure during manufacturing and recycling. For this reason, there is an emphasis on developing and using Cd-free QDs,[4] and some manufacturers such as Samsung have already introduced InP-based displays. Though data directly related to the toxicity of indium-based QDs is limited, prior studies have highlighted the toxicity of indium compounds such as indium-tin oxide and indium (III) oxide at the nano-scale.[5, 6] Despite the lack of a clear understanding regarding the environmental costs and benefits of Cd and In QDs for display applications, manufacturers are moving away from cadmium--based QDs in consumer devices.[7, 8]

As evident from the substitution of Cd-based QDs with Cd-free variants, the material substitution approach to enhance the environmental sustainability of nano-enabled products (NEP) tends to focus on replacing toxic elements, chemicals precursors and engineered nanomaterials (ENMs). However, the toxic elements/ENMs only become hazardous during their release and exposure to the environment, and in turn to humans. This means that the toxicity can be limited/avoided by control of release and exposure. Simplistic material substitutions that do not consider indirect environmental implications on other stages of the life cycle often fail to uncover the tradeoffs between a product's environmental performance and risk.[9] For this reason, the design of environmentally sustainable NEPs, such as QD-enabled displays, require systematic assessment of a) upstream environmental impacts quantified through life cycle assessment (LCA) and b) downstream environmental and human health risks associated with the release of QD from the latest *Cd-* and *Cd-free* QD-enabled displays estimated through risk assessment (RA). Linkov and colleagues recognize that the development of environmentally relevant datasets cannot keep up with the rapidly innovating nanotechnologies.[10] They suggest a shift towards a decision-driven approach that integrates the results of LCA and RA in a multi-criteria decision analysis (MCDA). Similarly, other studies have recommended the coupling of decision-oriented evaluation of LCA results to understand which sources of uncertainty are more critical.[11-13] While such approaches are capable of identifying the variables that contribute uncertainty in LCA, there is still a need to design research aimed at narrowing uncertainty of such variables. There is a need to develop collaborative interdisciplinary teams to drive research dynamically to bridge data gaps, uncertainty and variability issues for emerging ENMs and NEPs.[14, 15] Gilbertson and colleagues emphasize the need to coordinate research between experimental environmental scientists and modelers to develop new datasets to addresses the problem of lack of data that is up to date with the evolution of the technology.[15]

Researchers have invested considerable efforts to investigate the upstream life cycle impacts corresponding to the design decisions on NEP production,[16-20] as well as the downstream transportation and transformation of ENM released from NEPs.[21-24] While independently, these areas have made significant advances in our understanding of the environmental implications of NEPs, there are challenges faced by both life cycle modelers and experimentalists concerned with ENM release from NEPs. On the one hand, LCA is plagued with the issue of high parameter uncertainty due to data gaps given the proprietary nature of most NEPs.[25-27] On the other hand, experimental studies simulating ENM release tend to employ synthetic or well-characterized pristine ENM under controlled conditions for estimating its environmental risk and implications, which may not be relevant for real-world applications.[14, 28] Data collection from unrealistic scenarios results in datasets insufficient for modeling ENM fate processes and exposure routes for estimating ENM-specific human health and environmental toxicity characterization factors. Improved coordination between LCA modelers and experimentalists investigating ENM release can mitigate these challenges.[15] Through collaborations, modelers and experimentalists can frame mutually beneficial research objectives that will result in realistic release scenarios predicated on the product's life cycle, which in turn fill specific data gaps that reduce the uncertainty from the LCA results.

This study takes QD-enabled displays as a case study to demonstrate the importance of collaborations between LCA modelers and experimentalists to better inform the environmental impact of NEPs. Additionally, we present an LCA framework with such collaborations at the core specifically for emerging NEPs, referred henceforth as the dynamic LCA (*dLCA*) framework.

1.1 Challenges for Life Cycle Assessment of QD-enabled Displays

Experimental work aimed at assessing the loading and release of QDs from such consumer products is still limited. Despite the data shortage, preliminary studies on the life cycle environmental impacts associated with QD enabled displays as well as other QD enabled products have been conducted.[29-31] Most previous LCA studies on QDs limited the assessment to the production stage,[32-34] not including the use and disposal stages. Insights based on such stand-alone, snapshot "cradle-to-gate" studies can be quite misleading, and regulatory decisions based on them may result in unintended consequences.[19, 35] The main reason LCA has not realized its potential for assessing environmental impacts across the entire life cycle of QD-enabled displays is that there are two main data gaps: 1) the amount of QDs incorporated in QD-enabled display, and 2) the release of these QDs from QD-enabled display. These data gaps inadvertantly lead to high uncertainties associated with the estimates for life cycle impacts for ENMs.

It is important to note that the data gaps mentioned above are not unique to QD-enabled displays. This is the case for most emerging NEPs. To address this, LCA modelers need to go beyond the paradigm of conducting LCAs as snapshots of an emerging NEP in its course of development and focus on continuously updating the LCA models by gathering relevant data through collaborations with experimentalists. After all, as the technology evolves, so would the environmental impacts associated with the respective NEP.

To address the data scarcity problem faced by retrospective (traditional) LCA of emerging NEPs, we propose the *dLCA* framework, a holistic, interdisciplinary methodology specifically designed to assess future trajectories of QD-enabled displays while reducing the inherent uncertainties in the LCA with each traversal (Fig. 1). The framework directs research activities to proceed in close interaction with experimentalists and life cycle modelers, in order to identify the most influential parameters that are responsible for propagating uncertainty in the LCA model and integrating these data needs into the experimental design early in the project. To exemplify the strength of this framework, experimental studies on QD-enabled displays will be performed to fill in the data gap regarding QD types and amounts incorporated and released. The empirical data retrieved from experimental research will, in turn, be fed into updated LCA models in order to reduce uncertainties. Lastly, the framework presented in this study responds to calls for greater coordination between experimental and modeling efforts to characterize environmental and human health impacts associated with NEPs.[15]

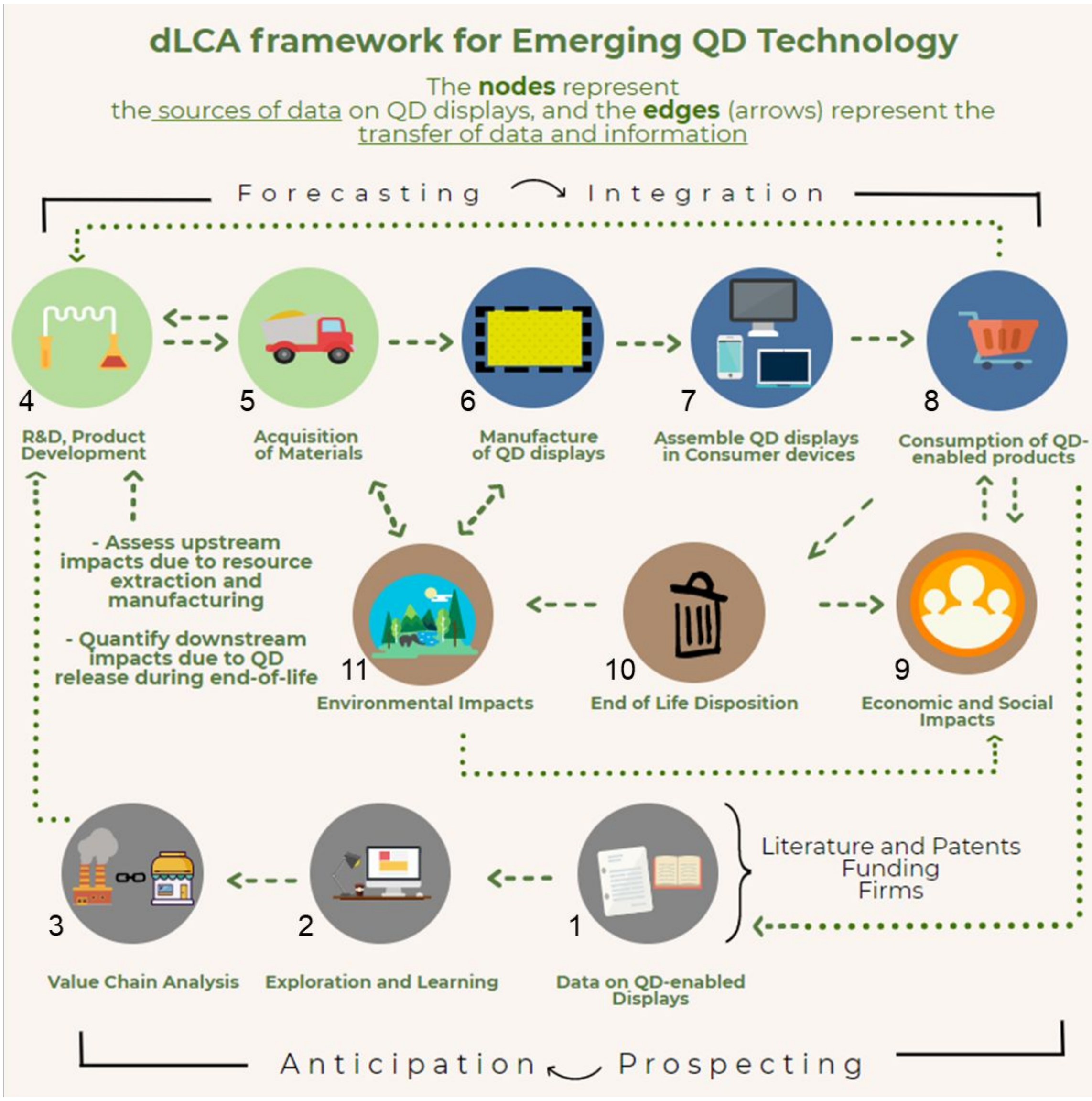

Fig. 1 Dynamic life cycle assessment (*dLCA*) framework identifies nodes 1-11 where interdisciplinary collaborations can assist the generation of new empirical data sets. Its application to the case study on QD-enabled displays focuses on two aspects, a) experimentalists generate empirical data regarding node 6 and transfer to LCA modelers to improve estimates of upstream life cycle impacts, and b) experimentalists generate release data at node 10 to quantify downstream impacts in subsequent traversals of the *dLCA* framework.

2. Dynamic life cycle assessment (*dLCA*) framework

A *dLCA* framework is proposed to evaluate the environmental and human health impact of emerging QD-enabled displays, as shown in Fig. 1. The *dLCA* takes a reasonable time frame as the temporal system boundary (i.e., the time frame is determined based on the evolution of the technology being considered) and tracks the flows over appropriate time scales. Unlike the traditional LCA that assesses environmental impacts at a technological snapshot, the *dLCA* framework emphasizes iterative assessment of the QD-enabled display as the technology evolves and focuses on directing experimental design to gather high-quality empirical data to reduce uncertainty in the model. This is consistent with the anticipatory LCA approach that assesses scenarios to determine the future environmental burdens of such emerging technologies.[16, 36] The dynamic approach differs from the retrospective in that levels of uncertainty in data quantity, quality, and impact assessment, and variations in stakeholder behavior and valuation are explicitly incorporated into the analysis. The framework is compatible with latest integrative assessment tools (such as LICARA nanoSCAN) that combine LCA and RA with structured decision analysis techniques,[37] as well as populate Ashby-like plots for ENM selection and design of sustainable NEPs.[38] As shown in Fig. 1, the *dLCA* framework is defined as clockwise traversal and includes two parts, e.g., *prospecting* → *anticipation*, and *forecasting* → *integration*, that are described in detail here.

Prospecting → *anticipation*: Prospecting identifies candidate QD-enabled displays worthy of further investigation, and anticipation explores a range of potential scenarios that may result from those QD-enabled displays. Value chain analyses (VCA) is included in the prospecting and anticipation part to account for future trajectories of QD-enabled displays In the prospecting and anticipation part, QD research funding and peer-reviewed literature, patents and subsequent formation of firms associated with QD production are traced, which allowed the systematic narrowing of the scope of inquiry to those QD types that are being commercially applied. Besides, the scope of the analysis is not restricted to the current QD material types and technologies that used to incorporate QD material into displays; with each traversal of the prospecting and anticipation node of the *dLCA* framework, this list will be updated based on the improvements and innovations in the technology scope. For instance, in addition to CdSe and InP QDs, subsequent traversals may include newer configurations like InPSe QDs, etc.

Forecasting → *integration*: Forecasting and integration applies to those life cycle stages that suffer from a scarcity of data, and require a greater level of research and analysis. The forecasting and integration part of *dLCA* framework includes the basic elements of the LCA, i.e., R&D, product development, acquisition of materials, manufacture of QD displays, assembly of QD displays in consumer devices, consumption of QD-enabled products, end of life disposition, environmental impacts, and economic and social impacts. For implementing *dLCA* for QD-enabled displays, detailed information is required on 1) QD incorporation in consumer devices, 2) market potential of displays, 3) fate, transport and transformation of QD on release for environmental characterization, and 4) disposal of devices with QD-enabled displays for end-of-life (EOL) scenario development. While all this information needs to be collected for conducting a complete cradle-to-cradle *dLCA* for QD displays, the current paper focuses on the first point (QD incorporation in a consumer device) for a cradle-to-gate assessment.

In general, a single traversal of the framework based on the flowchart in Fig. 1 is unlikely to be conclusive for quantifying life cycle of QD-enabled displays, but it can direct future research necessary to continually narrow uncertainty. Moreover, although the general direction around the research flowchart is clockwise, the specific pathway for a given QD-enabled display is not smooth; the pathway is defined by a series of iterative feedback loops (arrows) that become activated as information is constantly being transferred and analyzed by collaborators.

The reduction of uncertainty plays a central role in dLCA. Commonly, three types of uncertainties are discussed in the context of LCA: parameter, scenario, and model uncertainty.[39-41] Parameter uncertainty is contributed by scarce or low-quality input data for the development of life cycle inventory (LCI).[40, 41] Scenario uncertainty emanates from the normative choices made (such as the choice of the functional unit or impact category) by the LCA modeler.[40, 41] Model uncertainty is introduced by assumptions and simplifications underlying the model.[40, 41] It is important to note that the dLCA framework is concerned with each of the three uncertainty types. It aims to coordinate and leverage new information to minimize one or all three uncertainty types with each traversal. In addition, the dLCA framework seamlessly integrates with the three main methods for uncertainty analysis in LCA: 1) Monte-Carlo (MC) simulation models, 2) sensitivity analysis, and 3) MCDA and other decision-oriented approaches. MC simulation models are widely integrated with LCAs to understand realistic levels of uncertainty in material flow analysis, chance events, and probabilistic outcomes.[30, 42, 43] Sensitivity analysis identifies those uncertainties that are most significant, which the dLCA framework to identify new investigations that sharpen the confidence in overall assessment.[41, 43] Likewise, decision-oriented tools such as MCDA and lately Value of Information (VOI) coupled with LCA can detect sources of uncertainties most relevant to decision-makers.[44, 45] The dLCA framework specifically prioritizes research collaborations in accordance with decision-maker and/or stakeholder knowledge needs.[46] Multiple decisions regarding the sustainable development of emerging NEPs have to be made based on models with uncertain data. In the case of QD enabled display technology, these include the selection of competing products, processes, materials, or technology pathways, prioritization among research questions or pathways, and evaluation of policy prescriptions. The information obtained from repeated traversal of the dLCA framework to inform decisions of early-stage manufacturers with respect to ENM technology selection and support regulatory benchmarking for Cd and Cd-free QD materials for manufacturing different display devices.

Prior references to the term dynamics in LCA focused on accounting for future trajectories of development for inputs in LCI,[47] and modeling time-sensitive LCIA.[48, 49] Instead of considering time as a variable in a static LCA, *dLCA* accumulates data over time and/or as data quality improves to make dynamic forecasts about emerging technologies as they mature. As shown by Gavankar and colleagues in regards to carbon nanotubes, the environmental impacts associated with an emerging technology are influenced by the readiness of the technology.[50] For this reason, it is imperative to evaluate the environmental impacts over time, tracing the evolution of the emerging technology in order to inform decision making towards sustainable design. *dLCA* can be viewed as a quantitative and qualitative scenario development tool used to inform research, investment, and policy decisions. Such an approach is especially valuable when limited data from the laboratory stage or conflicting data from the literature and patents, or preliminary data from other LCA phases are all that are available.

The structure and data flow in this study are shown in Fig. 2. Section 3 will discuss the results of the initial LCA of QD-enabled displays, which we refer to as the first traversal in this paper. This section will identify the assumptions that contributed to the uncertainty in the model. Section 4 will describe the experimental research to be undertaken to avoid the assumptions from the first traversal, and section 5 will result in the new dataset that will used as an input in the new model. Lastly, section 6 will share the findings from the second traversal of the *dLCA* framework for QD-enabled displays.

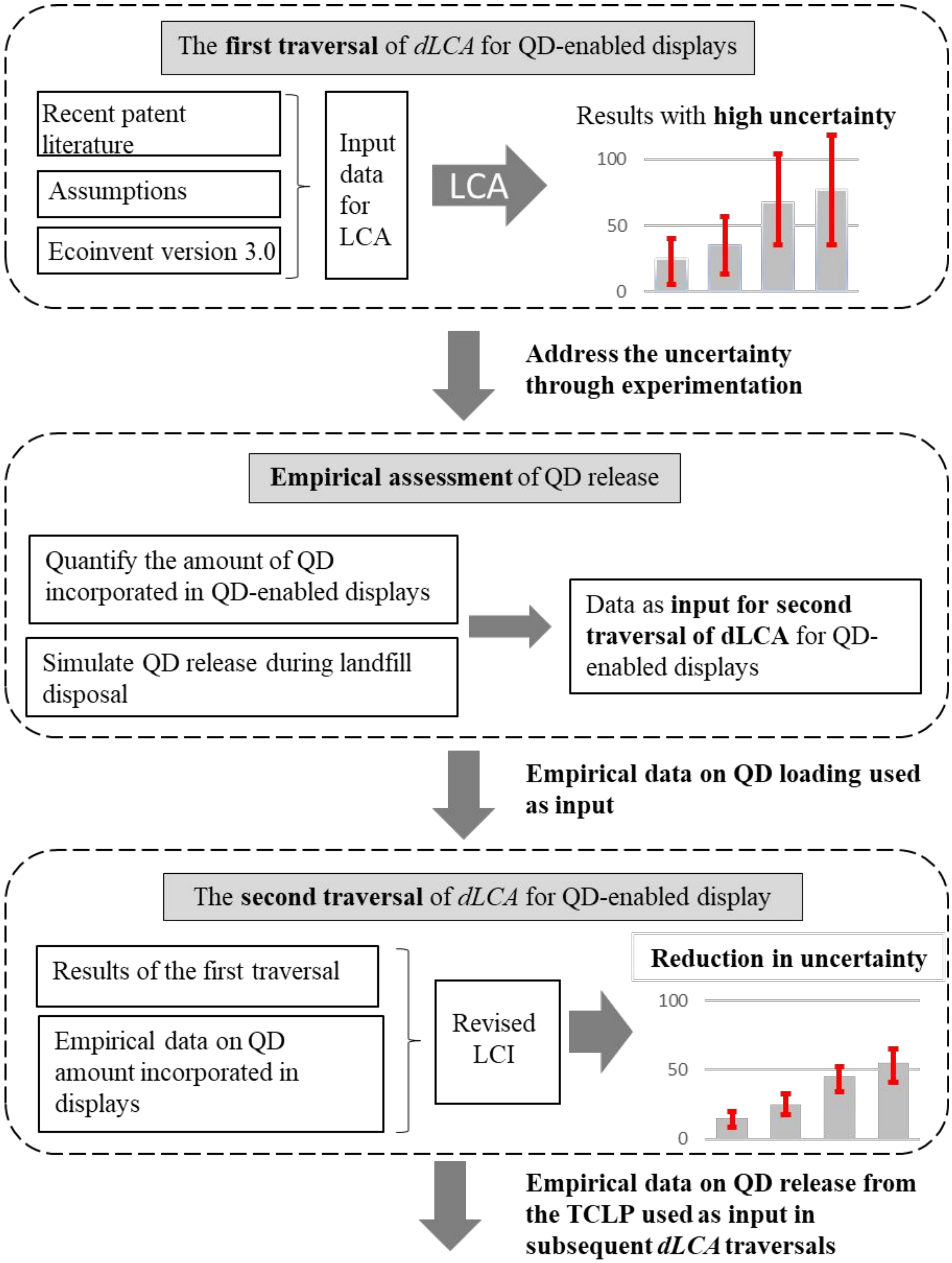

Fig. 2 Structure and data flow of this study.

3. The first traversal of *dLCA* for QD-enabled displays

The first traversal of *dLCA* for QD-enabled displays was performed and has been published in our previous paper.[29] The scope of the first traversal of *dLCA* is cradle-to-gate, and some critical input data (e.g. incorporated QD amount in displays) wasassumed. More details about the first traversal of *dLCA* for QD-enabled displays are briefed as follows.

Process data of the state-of-the-art colloidal synthesis of CdSe and InP multishell QDs was obtained from the most recent patent literature. Patent literature is the most detailed source of data available on large-scale production of QDs for display application since these documents contain production processes that are believed to be technically feasible and considered to have economic value.[51] Patents held by QD Vision Inc. (recently acquired by Samsung) were used as the main sources for the CdSe QD synthesis system, and patents held by Nanosys Inc. were the data source for InP QD synthesis system. While patent literature is often used for modeling production of emerging technologies, it is considered premature data and may even include misleading information that can result in unreliable analysis.[50] For this reason, life cycle inventory (LCI) data from the first traversal of *dLCA* has uncertainty due to lack of data (e.g., the amount of CdSe/InP incorporated in the QD-enabled display and the release of Cd/In from the disposal of the QD-enabled display). One assumption made in the paper was regarding the amount of QD incorporated in the displays. Since there was no empirical information available about this in the literature, it was assumed that 40 times more InP QD than CdSe QD is needed for comparable picture quality in LCD, which was obtained from detailed reports submitted by QD display manufacturers to EU to receive a RoHS exemption.[52]

Information from patent literature was used to quantify the rate of generation of products, byproducts, and wastes; minimum energy requirements; raw material requirements; efficiency of raw material usage; and an upper limit on efficiency of raw materials usage (i.e. how much waste is being produced compared to what is the least amount of waste that can be produced) for QD production. Ecoinvent version 3.0, a comprehensive LCA database, was used as the source for life cycle inventory data for established precursors and solvents in the synthesis process.[53] For organic compounds whose synthesis process and reaction stoichiometry is unknown, a molecular structure-based tool, FineChem, was used to estimate their environmental impacts.[54, 55]

The first traversal of *dLCA* revealed that the production of multishell InP QDs is more energy intensive in comparison to CdSe QDs.[29] Also, lower performance of InP QDs was found in comparison with CdSe QDs as measured by color accuracy and quantum yield. While the results presented in this paper provided the first estimates of the environmental impacts, the results were based on some assumptions that have contributed to the model uncertainty. For this reason, we coordinated an experimental study (as described above) to generate data to further improve the confidence in the LCA results from the second traversal.

4. Experiments on QD-enabled displays

As mentioned earlier, the *dLCA* framework emphasizes iterative data collection through coordination with experimentalists. Hence, two commercial electronic products using QD-enabled displays were purchased and analyzed (summarized in Table 1) for the quantity of QD. Even though the sample size is limited, the analysis provides valuable information on the loading of Cd- and Cd-free QDs in commercial displays. The products are Kindle Fire Tablet (2011 model) and Samsung KS8000 SUHD TV (2016 model) (Table1), both of which were marketed to use quantum dot technology in the display unit. QDs were incorporated in the LCD assembly in a polymeric quantum dot enhancement film (QDEF) for both devices (on-surface technology*)*.[56] While it is valuable to use actual products for realistic analysis, given the early-stage of commercialization, only two products were found that use the same QDEF technology but utilize different QD materials. The small sample size is definitely a limitation of the study. Even though QDs can also be incorporated in the LCD assembly in a glass capillary at the display edge (on-edge technology) technically, no commercial products are currently available for experimentation.

Table 1 List of commercially available QD-enabled displays to be tested

Display make and model	Device type and size	QD material type	Technology for QD incorporation
2011 Amazon Kindle Fire HDX	Tablet; 7 inch	CdSe (core) QD[1]	On-surface technology
2016 Samsung SUHD Quantum Dot	TV; 49 inch	InP (core) QD[1]	On-surface technology

Note: [1]QD material producer: QD Vision Inc.

4.1 Quantification of the amount of QD incorporated in QD-enabled displays

As the QD-enabled LCD architecture contains several films to control LED light, a 365 nm UV light source (Spectroline™ benchtop UV transilluminator) was first used to identify the quantum dot enhancement film (QDEF) based on fluorescence emission response. Each QDEF has a three-layer structure to prevent water vapor and oxygen diffusion: an upper barrier film, a middle QD layer containing a small amount of quantum dots dispersed in polymer matrix, and a lower barrier film. To determine QD contents in the QDEF, a destructive dry ashing procedure was performed on ~1 g films (20 – 40 cm^2) at 800 °C for 30 min using a muffle furnace following the ASTM standard D5630 – 13. The ashed materials were then digested in concentrated nitric acid on a hot plate for one hour until the volume was reduced to ~ 5 mL. The digested samples were diluted in 2% nitric acid and analyzed by a Thermo XSeries II ICP-MS. Because the QD materials were either CdSe/ZnS or InP/ZnS core-shell nanomaterials, the concentrations of Cd, In, and Zn were analyzed in all digested samples. The quantity of the QD was used as the basis for the maximum amount of potential release through the life cycle of the products. All laboratory glassware and plasticware was washed with 10% nitric acid and rinsed with ultrapure water (18.2 MΩ/cm) at least three times before use. At least triplicate samples were digested for the QDEF in each device. In addition, it is assumed that ENMs present in the QD-enabled displays are not released in their pristine nano-form but instead, they are liberated as metal ions. The experimental procedure to quantify the incorporated QD in the two sample QD-enabled displays is depicted in Figure S1 in the Supporting Information.

4.2 Simulation of QD release during landfill disposal

The potential release of QDs and their constituent metals in a landfill disposal scenario is evaluated by US EPA Toxicity Characteristic Leaching Procedure (TCLP) SW-846 Method 1311.[57, 58] The procedure is designed to determine whether heavy metal concentrations in the leachate exceed toxicity characteristic hazardous waste limits during simulated sanitary landfill disposal. The leaching of heavy metal contaminants from QD film onlyas well asthe rest of LCD components were evaluated in order to obtain the upper boundary and background for QD release.

The TCLP for QD leaching is as shown in Fig. 3. Briefly, the QD films separated from the display assembly (Kindle and TV) were cut into ~1 by 2 inches pieces. For the Kindle QD film, the sandwiched film was further divided into three layers of equal size, all of which were used for the leaching test to obtain an upper boundary of leaching potential. To obtain the metal background in the rest of LCD assembly, the unit including front glass, film components, and back panel were cut into ~1 by 2 inches pieces with bolt cutters and a box cutter for the TCLP test. In comparison, the film in the Samsung TV could not be separated without employing aggressive chemical agents, so the film was tested in its original structure. Each QD film sample was leached at ~1.5 g of dry weight to 30-mL extraction fluid, while display assembly was leached at ~ 34 g dry weight to ~680 mL fluid following 1:20 mass-to-leaching ratio. TCLP extraction fluid (pH 4.93 ± 0.05) was prepared with 5.7-mL glacial acetic acid, and 64.3 mL of 1-M NaOH added to 1-L Milli-Q water. The mixtures were tumbled end over end at 30 ± 2 RPM for 18 hours and then centrifuged at 4000 RPM for 10 min. The supernatant was filtered through a 0.45-µm nylon syringe filter and measured for pH. The filtrate was parsed and preserved in 2% nitric acid for ICP-MS analysis. All TCLP tests were run in triplicate. A total of 30 common elements, including Cd, In, and Zn, were analyzed for assessing the potential metal leaching in TCLP tests (**Table S1**).

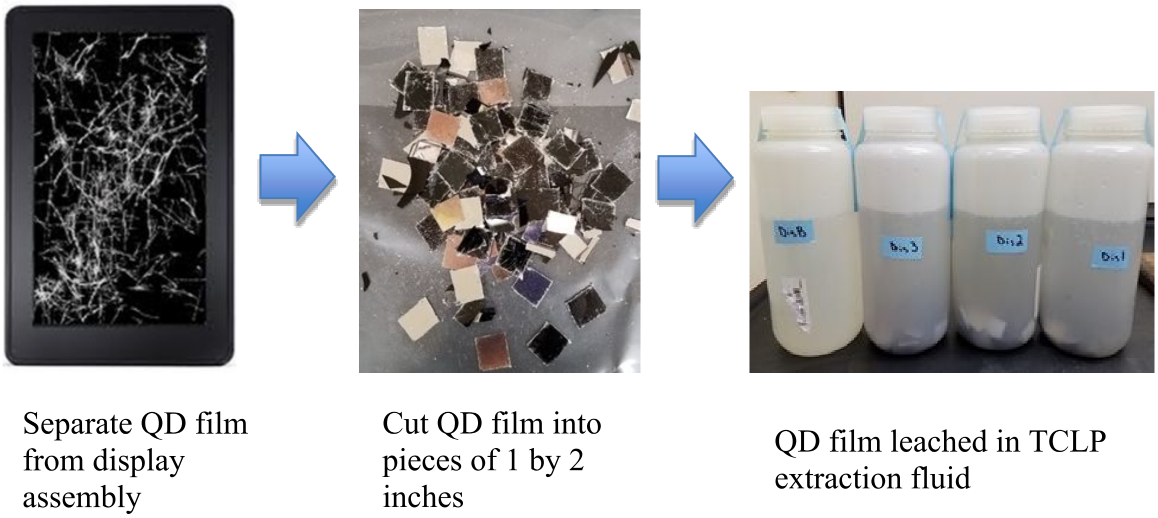

Fig. 3 Toxicity Characteristic Leaching Procedure (TCLP) for QD leaching.

5. Experimental results and Discussion

The amount of CdSe and InP incorporated in the two commercial QD-enabled displays are summarized in Table 2. The concentration of InP (3.56 ± 0.24 μg/cm^2) in the QDEF film of Samsung SUHD TV is comparable with the concentration of CdSe (3.92 ± 0.32 μg/cm^2) in the QDEF film of Kindle Fire Tablet, with a ratio of InP concentration to CdSe concentration is 0.91. However, compared with the assumption in the first traversal, i.e., 40 times more InP QD than CdSe QD is needed for a comparable picture quality in LCD display, the experimental results of CdSe and InP concentrations revealed the improvement of InP quality after several years of development. However, the total amount of InP in Samsung SUHD TV is significantly larger than that of CdSe in Kindle Fire Tablet due to the larger display area. The incorporated amount of CdSe and InP is the input data of the second traversal of *dLCA* for QD-enabled displays. The amount of CdSe and InP in displays represents the maximum heavy metal release potential during the EOL disposition, which is an active area of research for experimentalists.

Table 2 Amount of CdSe and InP incorporated in the two sample QD-enabled displays normalized to film area (cm^2).

	2011 Kindle Fire Tablet (7'')	2016 Samsung SUHD TV (60'')
CdSe ($\mu g/cm^2$)	3.92±0.32	n/a
InP ($\mu g/cm^2$)	n/a	3.56±0.24
Theoretical concentration assumed in the 1st Traversal ($\mu g/cm^2$)	~3 – 5	> 120
QDEF film size (cm^2)	224	10065
*Total CdSe amount (μg)	877.3	n/a
*Total InP amount (μg)	n/a	35836.5
Product year	2011	2016

Note: *The value was estimated based on the area of the QD film in each product.

Table 3 summarizes the amount of leached Cd or In from the TCLP tests for the two commercial QD-enabled displays. The QD matrix layer in Kindle display was separated from the sandwich-structured QDEF for direct contact with TCLP fluid, which shows that the leached Cd concentration was relatively high at 1.34 μg/L, accounting for 0.021% of total embedded QD material. In contrast, the leached In concentration is substantially lower at 0.077 μg/L since the InP embedded matrix layer could not be separated from the TV QDEF. Both Kindle and TV QD films leached very low concentrations that were orders of magnitude below the maximum Cd limit (1.0 mg/L) for the toxicity characteristic regulated by Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDR). The result is not surprising considering that QDs are dispersed in a strong PET matrix, which is sandwiched between two barrier layers that protect QDs from decomposition. However, with the widespread use of QD in displays, the Cd and In release have to be monitored to ensure that the disposal of the QD-enabled display complies with requirements of relevant waste management regulations.

In this study, we used the film-only TCLP results to quantify the upper limit of QD release in the EOL stage. Depending on the film structure, the leaching potential appears to be mainly affected by the barrier layers. It was reported that the barrier layer could reduce the water vapor transfer rate to less than 1×10^{-3} grams per square meter per day at 20°C.[59] In comparison, the remaining components of the LCD assembly leached a much lower Cd concentration at 0.079 μg/L (Table 3). However, due to the large amount of non-QD film components in the display unit, the total mass of leached Cd (~0.04 μg) from the background is comparable with that from the QD film (~0.05 μg) in the TCLP test. Since the QDEF is only a small component in the entire display assembly, its contribution to the overall hazardous waste leaching is probably not significant.

Table 3 Release of Cd and In from QD films in TCLP tests

		Upper limit	Background
Kindle Fire Tablet (7'')	Leached Cd (μg/L)	1.344	0.079
	Leached Cd (%)	0.021	<0.01
Samsung SUHD TV (60'')	Leached In (μg/L)	0.077	Negligible
	Leached In (%)	0.003	Negligible

Note: 'Upper limit: the leaching of heavy metal contaminants from QD film only; 'Background': the leaching of heavy metal contaminants from the rest of LCD display components.

6. *dLCA* modeling: The second traversal for QD-enabled displays

The second traversal of the *dLCA* framework will leverage the revised estimates for the QD incorporated in the two devices based on acid digestion followed by ICP-MS. This information is integrated into the life cycle model for the synthesis of CdSe and InP QD enabled displays from the first traversal. Note that the functional unit of the second traversal of the *dLCA* is the *amount of QDs required per unit area of the display*, and is consistent with the first traversal.

The results for cumulative energy demand (CED) for the production of CdSe (red and green) QD (30.3 MJ/g) and InP (red and green) QD (658.2 MJ/g) were computed in the first traversal and published in a previous paper.[29] These estimates are directly used in the second traversal of the *dLCA* for the estimation of life cycle impacts associated with the different device types with QD-enabled displays such as TV, PC monitors, notebooks, tablets and smartphones based on the size of the display. The display sizes of different devices (e.g. TV, PC monitors, notebooks, tablets and smartphones) are surveyed based on the market capitalization. Combined with the unit amount of CdSe (3.92 ± 0.32 μg/cm^2) and InP (3.56 ± 0.24 μg/cm^2) QD obtained from experimental work presented in Table 2, the amount of QD embedded in different devices are calculated and summarized in Table 4. Here the lower bound and the upper bound is calculated based on the smallest and the largest display size of each device type, respectively. For both the first and second traversals, it was assumed that the CED per unit gram of QD is independent of device types and depends on the size of the screen, thus ignoring the influence of the types of sample devices on the results. Note that the CED impact category only accounts for the production of QDs needed in a display type, and does not include the energy cost to produce, operate and dispose of the display device itself.

Table 4 Amount of QD embedded in different display devices assuming they use QDEF technology

Devices	Amount of QD (g)			
	CdSe QD ($\times 10^{-3}$)		InP QD ($\times 10^{-3}$)	
	Lower bound	Upper bound	Lower bound	Upper bound
TV *(32"-60")	19.1	38.9	10.0	35.3
PC Monitors *(15"-25")	2.4	6.2	5.7	2.2
Notebooks *(10"-17")	1.1	3.1	1.0	2.8
Tablets *(7"-10")	0.5	1.1	0.5	1.0
Smartphones	0.1	0.5	0.1	0.5

*(3.5"-6.9")

Note: *Display size in inches

The CED attributed to QDs in different devices for the first and second traversal is shown in Fig. 4. Firstly, the comparison of the results for the two traversals highlight a significant reduction in the CED estimates for both CdSe and InP QD based displays. The use of experimentally generated empirical data in the second traversal significantly reduces the estimates by numerous orders of magnitude. Secondly, a significant reduction in the CED on a per device basis in observed for InP QD enabled display devices. This is due to the much lower empirical loading of InP QDs in commercially available devices in comparison to the assumption made in the first traversal. Even in comparison to the CdSe QD loading, InP QD incorporated in sample device is lower, which is the reason for an overall greater reduction in the CED associated with InP QDs than the CdSe QDs. This is evident also if we consider the difference between the life cycle energetics per unit area of InP QD-enabled displays (first traversal: 2.59 x 10^{1} MJ/cm^2, second traversal: 5.28 x 10^{-3} MJ/cm^2) with CdSe QD-enabled displays (first traversal: 4.32 x 10^{-2} MJ/cm^2, second traversal: 3.92 x 10^{-4} MJ/cm^2).

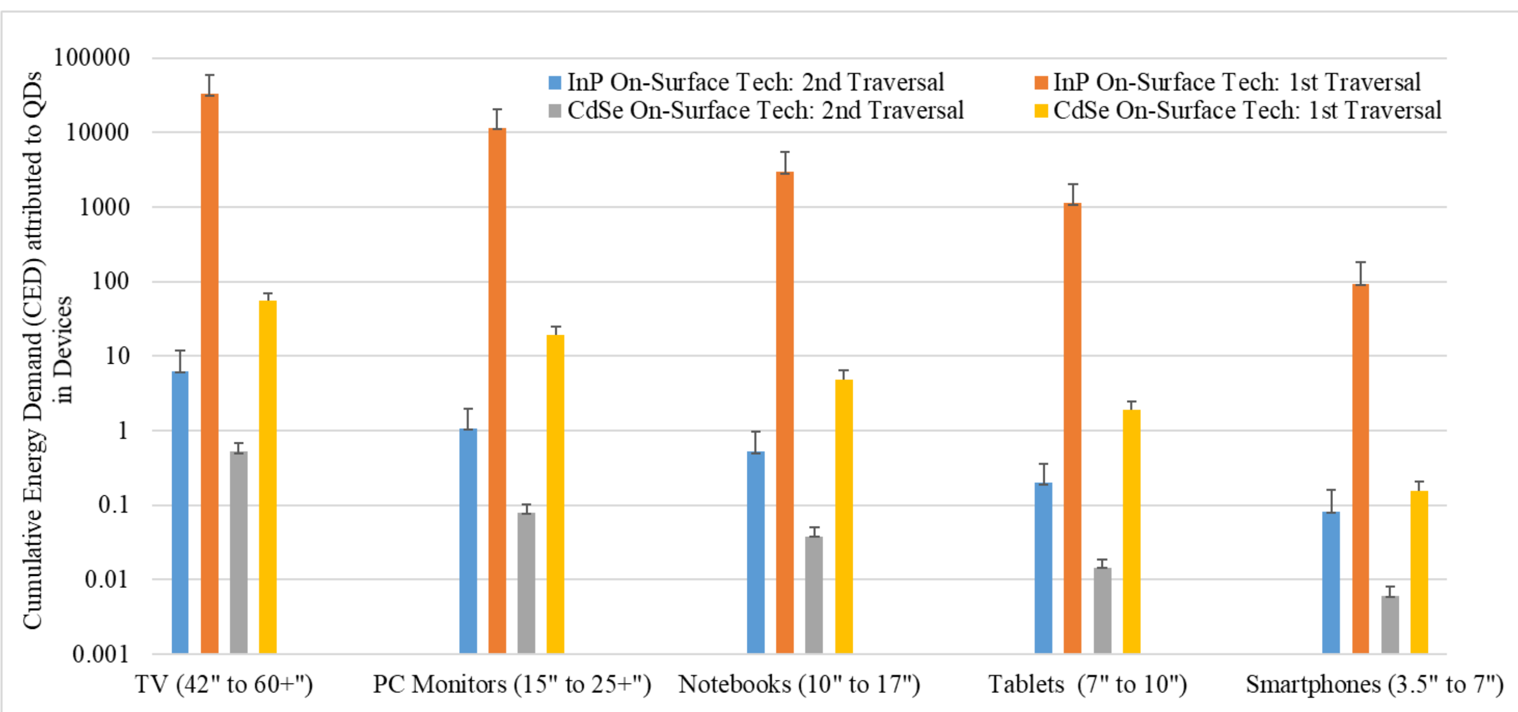

Fig. 4 CED results attributed to QDs in different devices for 1st and 2nd traversal. Significant changes are noted in results between the two traversals.

7. Conclusions

Life cycle assessment (LCA) is a powerful tool used for evaluating impact of established products and processes, however, its application on emerging technologies is limited as data scarcity due to proprietary design contributes to uncertainty in the LCI. This study proposed a *dLCA* framework, which emphasizes the collaborative iterative evaluation to tackle challenges associated with the retrospective (traditional) LCA of emerging technologies, i.e. quantum dot (QD)-enabled displays in this study.

This paper reports on an experimental study of two sample QD-enabled displays, a 2011 Kindle Fire Tablet with CdSe QD-enabled display, and a 2016 Samsung TV with InP QD-enabled display. Data were collected on the amount of QD incorporated in displays. The experimental result showed that the concentration of InP (3.56 ± 0.24 μg/cm^2) in the QDEF film of Samsung SUHD TV is comparable with the concentration of CdSe (3.92 ± 0.32 μg/cm^2) in the QDEF film of Kindle Fire Tablet, with a ratio of InP concentration to CdSe concentration is 0.91. This is marked reduction in comparison to the first traversal of the *dLCA* that assumed 40 times more InP QD than CdSe QD were required based on a report presented by industry representatives to the ROHS. The value of acquiring experimental data on the CdSe and InP concentrations is that it reveals a decrease in InP QD loading, which in turn translates into an improvement in terms of environmental impacts, resulting from years of development of Cd-free QD displays.

In order to estimate the end-of-life release of QDs, simulated landfill disposal of the two sample (Kindle tablet and Samsung TV) was performed. The leached Cd and In from the US EPA TCLP test for the two commercial QD-enabled displays were 1.34 μg/L and 0.077 μg/L, respectively. While the results highlight the release of Cd below the RCRA limits, the widespread adoption of Cd-based QDs in different types of display devices may result in an increase in the number of devices making their way to the landfills. This study presents the first estimates of Cd and In release from QD-enabled displays, which represents baseline data to generate InP and CdSe QD-specific characterization factors for human and ecological toxicity in the subsequent *dLCA* traversal. In addition, more work is still needed to monitor release through other end-of-life pathways such as incineration to ensure that the disposal of QD-enabled display follows RCRA's LDR requirements.

Using the experimental results on the loading of CdSe and InP QDs in displays, the second traversal of *dLCA* was performed and cumulative energy demand (CED) attributed to QDs in different devices (i.e. TV, PC monitors, notebooks, tablets and smartphones) was calculated. While we find that the CED of InP QD based displays is still higher than that of CdSe QDs in the second traversal, the reduction in overall life cycle emissions was due to the lower amounts of InP QDs incorporated than that was previously assumed based on prior reports. In addition to the reduction of life cycle impacts due to improvements in QD loading levels, we expect that improvements in the synthesis process of Cd-free QDs may further reduce the associated life cycle emissions. For instance, one of the primary reasons behind the higher CED associated with the production of InP QDs using the hot-injection method is that it requires solvents and specialized chemicals that tend to be energy-intensive. However, there are other relatively new approaches such as the heating-up method that may provide environmental benefits.[60] There is a need to continue to evaluate the life cycle environmental profile of the state-of-the-art techniques for ENM synthesis in the subsequent traversals of the *dLCA* of QD-enabled displays.

Lastly, this study demonstrated the role of collaborative research between life cycle modelers and experimentalists to address uncertainty in the LCA of nano-enabled technologies. LCA practitioners working on emerging technologies are often faced with data scarcity and quality issues due to the proprietary nature of industrial data, which requires them to make certain assumptions based on previous scientific literature and industry reports. Even though these assumptions are not incorrect and a common strategy in LCA, they are likely to contribute an unknown amount of uncertainty to the results. For this reason, we present the *dLCA* framework that promotes the development of collaborative research across the life cycle for the creation of new datasets. In this way, the experimentally obtained results are fed into the LCA model, thus reducing the uncertainty associated with different stages of LCAwith every iteration, while simultaneously guiding future research questions for experimentalists. Although the study presented here considers the case of QD-enabled displays, the proposed *dLCA* framework and the interdisciplinary collaborations promoted by it are applicable for improving estimates of life cycle environmental impacts for other emerging technologies.

Conflicts of interest

There are no conflicts to declare.

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