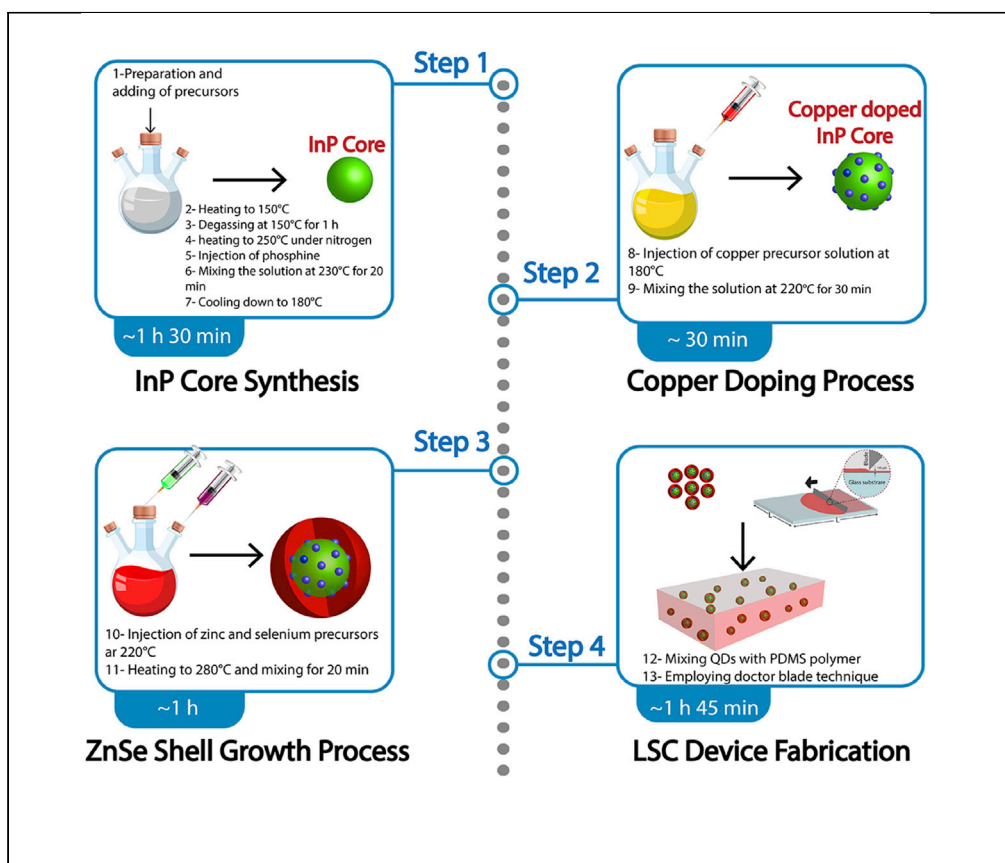# STAR Protocols

Protocol

Protocol on synthesis and characterization of copper-doped InP/ZnSe quantum dots as ecofriendly luminescent solar concentrators with high performance and large area

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Highlights

Detailed methods for preparation of copper-doped InP/ZnSe core/shell structure

Integration of QDs into polydimethylsiloxane polymeric host material

Large-scale fabrication of LSC devices

Characterization techniques of QD-LSC devices

Luminescent solar concentrators (LSCs) are simple and cost-effective solar energy harvesting devices. Indium phosphide (InP)-based colloidal quantum dots (QDs) are promising QDs for efficient LSC devices due to their environmentally benign nature. One major challenge in LSC devices is reabsorption losses. To minimize the reabsorption, Stokes shift engineering is a critical process to designing the QD material. Here, we present a protocol that contains the preparation of structurally engineered copper-doped InP/ZnSe QDs and their LSC application.

Protocol

Protocol on synthesis and characterization of copper-doped InP/ZnSe quantum dots as ecofriendly luminescent solar concentrators with high performance and large area

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SUMMARY

Luminescent solar concentrators (LSCs) are simple and cost-effective solar energy-harvesting devices. Indium phosphide (InP)-based colloidal quantum dots (QDs) are promising QDs for efficient LSC devices due to their environmentally benign nature. One major challenge in LSC devices is reabsorption losses. To minimize the reabsorption, Stokes shift engineering is a critical process to designing the QD material. Here, we present a protocol that contains the preparation of structurally engineered copper-doped InP/ZnSe QDs and their LSC application. For complete details on the use and execution of this protocol, please refer to Sadeghi et al. (2020).

BEFORE YOU BEGIN

Preparation of solutions and reagent (for synthesis of copper-doped InP QDs)

⏱ Timing: 1 h 45 min

1. Measure 22 mg of Indium Chloride ($InCl_3$) carefully with a clean lab spoon on an analytical balance and put into the 50 mL three-neck round bottom flask. Add 3 mL of 1-Octadecene (ODE) carefully with a syringe into flask which contains 22 mg of $InCl_3$ in glovebox.

   △ CRITICAL: $InCl_3$ should be measured in glovebox to avoid interaction with oxygen environment.

2. Measure 48 mg (0.2 mmol) of hexadecylamine (HDA) carefully in the glovebox by using analytical balance and add it into the flask which contains $InCl_3$-ODE solution.

3. Measure 28 mg (0.1 mmol) of stearic acid (SA) and put it into the vial. Label the vial and put it into the glovebox.

4. Measure 43 mg of zinc undecylenate carefully and put it accurately into the vial. Label the vial and put it into the glovebox.

5. Add the pre-measured SA and zinc undecylenate precursors into the flask which contains $InCl_3$-ODE-HDA.

   △ CRITICAL: Such hazardous chemicals ($InCl_3$ and HDA) must be measured in glovebox to avoid any burning, fumes, or interaction with environment.

Figure 1. Schlenk line synthesis setup
(A) 50 mL three-neck round bottom flask and heating mantle.
(B) Hot-plate.
(C) Schlenk line and vacuum pump system (backside).

6. Prepare 3×10^{-4} mol stock phosphine solution by mixing 1 gr tris(trimethylsilyl)phosphine with 17.8 mL ODE in glovebox.

7. Add 0.5 mL of (0.02 M) tris(trimethylsilyl)phosphine-ODE solution with micro syringe in a vial in glovebox.

⚠ CRITICAL: Phosphine stock solution (ODE- P(TMS)$_3$) is pyrophoric (air-sensitive), therefore it should be handled with particular attention in glovebox. For storage it must be kept in glovebox to avoid any reaction with air. Moreover, due to its temperature-sensitive property it should be kept below zero degrees in glovebox.

8. Prepare the setup in fume hood with 50 mL three-neck round bottom flask, Schlenk line for nitrogen (N$_2$) purge and vacuum pump, and heating mantle with magnetic stirring. N$_2$ gas flow should be checked and confirmed for further synthesis (Figure 1).

9. To prepare copper stearate stock solution, add 91 mg (0.5 mmol) of copper (II) acetate ($Cu(Ac)_2$) and 284 mg (1 mmol) of SA in 5 mL of 1-octadecene in three-neck round bottom flask, heat the solution at 150°C with N_2 purge under continuous stirring for 60 min. Cool down the copper solution to 60°C under N_2 atmosphere.

Preparation of solutions and reagent (for multiple ZnSe shelling on Cu-doped InP QDs)

⏱ Timing: 45 min

10. Measure 62 mg selenium (Se) in glove box to avoid moisture and air with a clean lab spoon and put in a vial with label.
11. Add 7.9 mL trioctylphosphine (TOP) with syringe into 62 mg Se carefully without splitting, put a magnet before mixing on a magnetic stirrer. This should be done in glove box carefully.

⚠ CRITICAL: Syringe should be carefully handled without any puncture the gloves or touch on the skin.

12. Measure 499 mg of zinc stearate ($Zn(St)_2$) carefully and put in a vial, inject 7.9 mL of 1-Octadecene (ODE) into measured zinc stearate in glove box. Label the vial.

⚠ CRITICAL: Labelled vials of Se and ($Zn(St)_2$) solutions must be taken out of glove box carefully; trash such as used syringes, tissue papers, or anything used must be taken out of glove box. Otherwise, these things can harm the glove box and its atmosphere.

13. Slightly heat zinc stearate solution to mix with ODE completely for 5 min at 50°C on a hot-plate (Figure 1B), solution must have milky appearance without any precipitates after heating.
14. Slightly heat Se solution to dissolve in TOP completely for 10 min at 80°C on a magnetic stirrer, solution must be transparent without any precipitates after heating.

⏸ Pause point: Store the prepared solutions at a temperature range between 20°C–25°C in an inert atmosphere. Use paraffin around the cap of vial so that air must not interact with solutions.

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Indium chloride ($InCl_3$)	Sigma-Aldrich	334065
1-Octadecene (ODE)	Sigma-Aldrich	74740
Zinc undecylenate	Sigma-Aldrich	329584
Stearic acid (SA)	Sigma-Aldrich	175366
Hexadecylamine (HDA)	Sigma-Aldrich	445312
Copper (II) acetate ($Cu(Ac)_2$) powder, 99.99% trace metals basis	Sigma-Aldrich	517453
Selenium (Se) powder, −100 mesh, 99.99% trace metals basis	Sigma-Aldrich	229865
Trioctylphosphine (TOP)	Sigma-Aldrich	718165
Zinc stearate ($Zn(St)_2$)	Sigma-Aldrich	307564
Tris(trimethylsilyl)phosphine ($P(TMS)_3$)	Sigma-Aldrich	333670
Toluene (anhydrous)	Sigma-Aldrich	244511
Hexane (anhydrous)	Sigma-Aldrich	296090
Ethanol absolute for analysis EMSURE® ACS,ISO,Reag. Ph Eur	Sigma-Aldrich	1009831011
SYLGARD 184-Kit: Silicon Elastomer and Curing Agent	Sigma-Aldrich	761036

(Continued on next page)

Continued

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Other		
FEI Talos F200S 200 k microscope	Thermo Fisher Scientific	N/A
Bruker D2 phase X-ray diffractometer	Bruker	N/A
Sigma 3-18KS centrifuge	Sigma	N/A
BYK Instruments- Film Casting Knife 4"	BYK Instruments	N/A
Edinburgh Instruments spectrofluorometer FLS1000	Edinburgh Instruments	N/A
PicoQuant MicroTime 100 time-resolved confocal fluorescence microscope	PicoQuant	N/A
Femtosecond pump-probe spectrometer (Helios, Ultrafast Systems)	Helios, Ultrafast Systems	N/A
Newport Oriel LCS-100 solar simulator AM 1.5G.	Newport Corporation	N/A
A picosecond pulsed diode laser (EPL) from Edinburgh Instruments	Edinburgh Instruments	N/A
Continuous-wave Ti:sapphire laser	ALPHALAS	N/A

MATERIALS AND EQUIPMENT

Alternative sources for reagents

Reagent or resource	Alternate sources
Chemicals, peptides, and recombinant proteins	
Indium Chloride (InCl$_3$)	TCI Chemicals, Product Number: I0778 (Purity: >99.0%)
1-Octadecene (ODE)	TCI Chemicals, Product Number: O0008 (Purity: >90.0%)
Zinc Undecylenate	N/A
Stearic acid (SA)	TCI Chemicals, Product Number: S0163 >98.0%(T)
Hexadecylamine (HDA)	TCI Chemicals, Product Number: H0074 >95.0%(GC)
Copper (II) acetate (Cu(Ac)$_2$) powder, 99.99% trace metals basis	N/A
Selenium (Se) powder, −100 mesh, 99.99% trace metals basis	Alfa Aesar Product Number: A12592 Selenium, powder, 99+%
Trioctylphosphine (TOP)	TCI Chemicals, Product Number: T0503 Purity: >85.0%(GC)
Zinc Stearate (Zn(St)$_2$)	N/A
Tris(trimethylsilyl)phosphine (P(TMS)$_3$)	N/A
Toluene (anhydrous)	TCI Chemicals, Product Number: T0260 >99.5%(GC) [for Spectrophotometry]
Hexane (anhydrous)	TCI Chemicals, Product Number: H1197 Purity: >96.0%(GC)
Ethanol absolute for analysis EMSURE® ACS,ISO,Reag. Ph Eur	N/A
SYLGARD 184-Kit: Silicon Elastomer and Curing Agent	Dow Chemical Company Product Number: 1673921

Stock solutions

Reagent	Solvent amount	Reagent concentrations	Storage CONDITIONS
Zinc undecylenate, HDA, SA and InCl$_3$ dissolved in ODE	3 mL ODE	Zinc undecylenate: 0.033 M HDA: 0.066 M SA: 0.033 M InCl$_3$: 0.039 M	Temperature: 20°C–25°C Environment: Under inert atmosphere It should be freshly prepared
Tris(trimethylsilyl)phosphine (P(TMS)$_3$) dissolved in ODE (stock solution)	17.8 mL ODE	Tris(trimethylsilyl)phosphine (P(TMS)$_3$): 0.02 M	Temperature: ⁻30°C Environment: Under inert atmosphere Storage Duration: ∼ 6 months
Copper (II) acetate (Cu(Ac)$_2$) and SA dissolved in ODE (stock solution)	5 mL ODE	Cu(Ac)$_2$: 0.1 M SA: 0.2 M	Temperature: 20°C–25°C Environment: Under inert atmosphere Storage Duration: ∼ 2 weeks
Zinc Stearate (Zn(St)$_2$) dissolved in ODE (stock solution)	7.9 mL ODE	Zn(St)$_2$: 0.1 M	Temperature: 20°C–25°C Environment: Under inert atmosphere It should be freshly prepared
Se dissolved in TOP (stock solution)	7.9 mL TOP	Se: 0.1 M	Temperature: 20°C–25°C Environment: Under inert atmosphere It should be freshly prepared

Instruments (for Structural Characterization):

Technique	Instrument	Condition
Transmission electron microscopy (TEM)	FEI Talos F200S 200 k microscope	Accelerating voltage 200 keV
X-Ray Diffraction	Bruker D2 Phase X-ray diffractometer	Cu Kα radiation (λ = 1.541 Å)
Centrifuge	Sigma 3-18KS Centrifuge	max. speed [min^{-1}]:18.000 max. RCF [× g]:30.070 Temperature setting range [°C]:$^{-}$20–+40
Doctor Blade	BYK Instruments- Film Casting Knife 4"	Gap Clearance: 0–150 mils Blade Width: 4 in

Instruments (for Optical Properties Measurement):

| Property	Instrument	Condition
Photoluminescence	Edinburgh instruments spectrofluorometer FLS1000	325 mm focal length monochromator, Xe Lamp. The excitation source was 450 W ozone free xenon arc lamp that covers a range of 230 nm to >1000 nm for steady-state measurements
UV-Visible Absorbance	Edinburgh instruments spectrofluorometer FLS1000	325 mm focal length monochromator, Xe Lamp. The excitation source was 450 W ozone free xenon arc lamp that covers a range of 230 nm to >1000 nm for steady-state measurements
Photoluminescence Quantum Yield (PLQY)	Edinburgh instruments spectrofluorometer FLS1000	325 mm focal length monochromator, Xe Lamp. The excitation source was 450 W ozone free xenon arc lamp that covers a range of 230 nm to >1000 nm for steady-state measurements
Time resolved spectroscopy	Picoquant Micro time 100 time resolved confocal fluorescence microscope	8 mW picosecond diode laser (λ_{ex}= 375 nm) pulsed at 250 KHz repetition rate to 40× objective lens
Transient Absorption Spectroscopy	Femtosecond pump-probe spectrometer (Helios, Ultrafast Systems)	Fourth-harmonic output of a tunable, femtosecond optical parametric amplifier (OPA, TOPAS Prime, Spectra-Physics), which was pumped with a 2-mJ, 800-nm Ti^{3+}: sapphire regenerative amplifier (pulse duration: 120 fs, pulse repetition rate: 1 kHz, Spitfire Ace, Spectra-Physics
Electro-optical measurement of QD-LSC device	Newport Oriel LCS-100 solar simulator AM 1.5G.	The output power of the Xe lamp was 100 mW.cm^{-2}.
Reabsorption measurement of QD-LSC device	A picosecond pulsed diode laser (EPL) from Edinburgh Instruments	Operation wavelength of 365 nm and pulse width of 65 ps, repetition rate of 20 MHz, average output power of 5 mW
Scattering measurements of QD-LSC device	Continuous-wave Ti:sapphire laser	Operation wavelength of 780 nm with the power of 900 mW

STEP-BY-STEP METHOD DETAILS
Synthesis of InP QDs

⏱ Timing: 1 h 30 min

The initial step for the synthesis of copper doped InP/ZnSe core/shell QDs requires the preparation of InP QDs as core structure, following steps include copper doping and ZnSe shell growth on InP core, respectively. In terms of precursors, to synthesize InP core QDs, InCl$_3$ and P(TMS)$_3$ are used as source of indium and phosphorus, respectively. 1-Octadecene (ODE) plays a role as solvent during synthesis procedure. In addition, hexadecylamine (HDA), stearic acid (SA), and zinc undecylenate are used as ligands to control the growth kinetics of InP core QDs.

1. Measure 22 mg of InCl$_3$ and 48 mg of HDA by using precision balance which is inside the glovebox (Figure 2A) and add into a 50 mL three-neck round bottom flask. Afterward, add 3 mL of ODE into the flask.
2. Measure 43 mg of Zinc undecylenate and 28 mg of SA by using precision balance (Figure 2B) and add into vials. Label the vials carefully and put them into the glovebox.
3. Add 43 mg of Zinc undecylenate and 28 mg of SA into the three-neck round bottom flask which contains 3 mL ODE, 48 mg of HDA, and 22 mg InCl$_3$.
4. Take the reaction flask back to fume hood setup, fit it for N$_2$ purging, and place the flask into heating mantle for heating and stirring (Figure 2C).
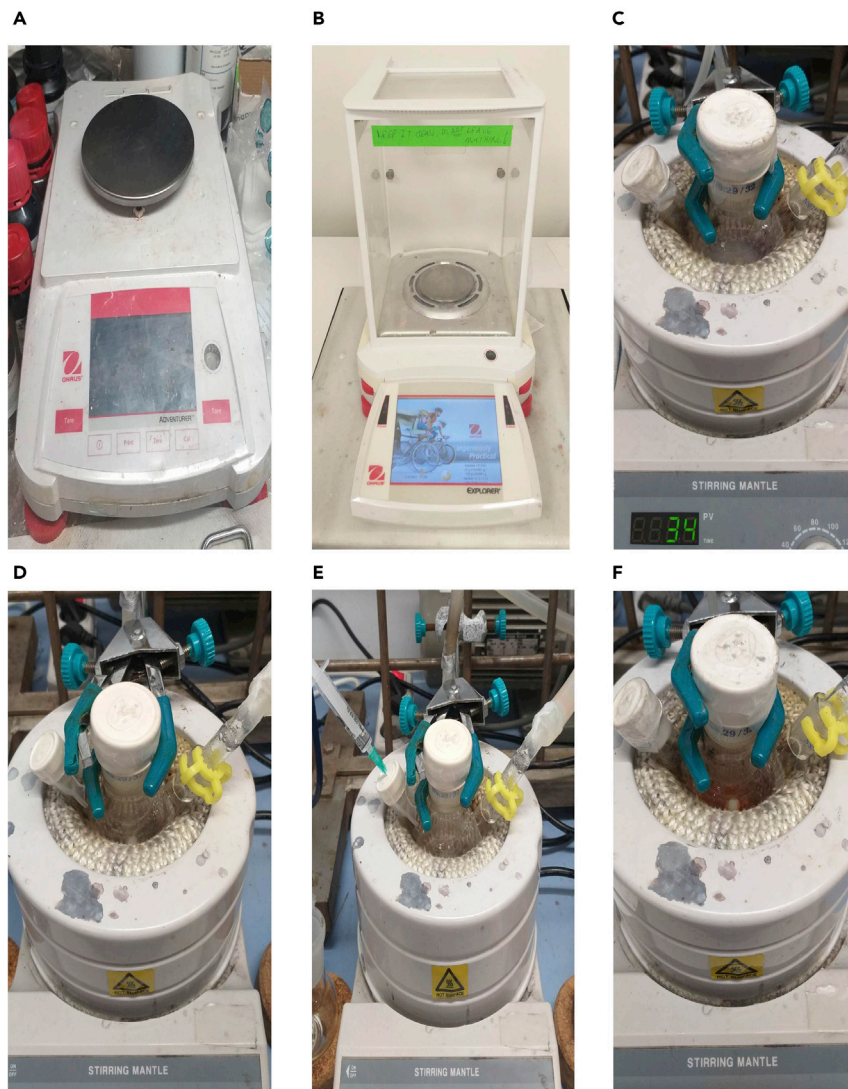
Figure 2. Equipment used for synthesis of QDs
(A) Precision balance, which is inside the glovebox.
(B) Precision balance, which is outside the glovebox.
(C) Flask and heating mantle
(D) In-based solution before phosphine injection.
(E) Phosphine injection by using syringe.
(F) After the phosphine injection, solution color changes to orange as a result of nucleation of InP QDs.

5. Cover the caps with parafilm to avoid interaction with atmosphere.
6. Increase the temperature of the solution up to 150°C. In the meantime, start degassing process. Keep the solution under vacuum 1 h at 150°C.

   Note: Vacuum pressure that is used during degassing is around 133.3 pascal (Pa) (1 Torr). Close N_2 before opening the vacuum; to make sure if N_2 is close, there must be no bubbles. Meanwhile presence of bubbles in reaction flask indicates N_2 is open.

7. After 1 h, turn off the vacuum and start N_2 purging with constant speed.
8. Keep the solution at 150°C under N_2 atmosphere 10 min.
9. Increase the temperature up to 250°C to initiate the nucleation and growth under N_2 atmosphere.

⚠ CRITICAL: The solution must turn transparent and colorless while the temperature is increasing (Figure 2D). Before initiating nucleation and growth steps, if solution color does not turn into transparent, it shows the presence of oxygen, which can result in oxidation of QDs. To avoid reacting solution with oxygen, the reaction must be performed in inert atmosphere. Moreover, to prevent any leakage, covering the septa caps with parafilm can be performed as an additional option.

10. Inject the 0.5 mL stock phosphine solution (Figure 2E) quickly injected into the solution at 250°C (for the mass production it is injected with an injection speed of 5 mL/min). After injection, nucleation and growth steps take place, as a result solution's color should change to orange instantaneously (Figure 2F).
11. After injection, cool down the temperature to 230°C, mix the solution for 20 min.
12. After 20 min, cool down the solution temperature to 180°C for adding copper solution.

Copper (Cu) doping and ZnSe shell growth process

⏱ Timing: 1–4 h (depending on multiple ZnSe shell growth)

13. Inject 10 μL of prepared copper solution which is at 60°C into a vial using micro syringe, add 990 μL of ODE with pipette into it. In case of any leakage degas the vial 10 min before and after adding precursors. As alternative approach, mixing of copper solution and ODE can be performed in glovebox. Shake the vial until it turns homogenous solution.
14. Add copper-ODE solution into the reaction flask which already contain InP QDs, adjust the temperature as 220°C and mix the solution for 30 min at 220°C.
15. After 30 min, color of the solution becomes darker due to copper doping.
16. For the first ZnSe shell growth inject 600 μL of prepared Zn stearate stock solution and mix 10 min at 220°C. After 10 min, inject 600 μL of prepared Se stock solution and mix 10 min.
17. Increase the solution temperature to 280°C and keep at that temperature for 20 min.
18. For additional ZnSe shell growth, cool down the temperature to 220°C and inject the Zn and Se precursors as mentioned above. Afterward, increase the temperature of the solution up to 280°C again. For the second, third, fourth, fifth, and sixth shell growth 825 μL, 1050 μL, 1400 μL, 1750 μL, and 2275 μL of stock solution were used, respectively.
19. In this regard, as a first step, after synthesis process add the QD solution into 50 mL of falcon tubes and centrifuge them at 8227 × g for 15 min at a temperature range between 20°C-–25°C. At the end of centrifugation process the byproducts occurred during reaction will aggregate due to gravitational force. Supernatant part will be QD solution.
20. Take the falcon tubes after centrifugation process and pour the QD solution (supernatant part) to a new falcon tube to separate from the aggregates of byproducts.
21. Add 1 mL of toluene to each tube and centrifuge again at 8227 × g for 15 min to aggregate the additional byproducts.
22. Separate the supernatant part (QD solution) by pouring it into another falcon tube.
23. Add ethanol (until 50 mL volume) and mix the QD solution vigorously.
24. Centrifuge the QD solution at 8227 × g for 15 min at a temperature range between 20°C–25°C. Due to presence of ethanol QDs will aggregate.
25. Pour the supernatant part into the waste and add 2 mL of toluene to dissolve the QDs. Afterward, add ethanol (until 50 mL volume) and mix vigorously. Centrifuge the solution again with the same parameters.

⚠ CRITICAL: It is recommended that the centrifugation process has to be repeated multiple times. Mostly, the centrifugation process with two cycles is not enough to remove the byproducts that form during the synthesis of QDs. Thus, as a first step, it is important to centrifuge the as-synthesized QD solution two times to precipitate the byproducts and separate the supernatant part, which contains the QDs, from the byproducts. Afterwards,

adding ethanol into the supernatant part and performing the centrifugation will precipitate the QDs. It is important to centrifuge the QDs by using ethanol a minimum two times to effectively purify.

26. At the final step of centrifugation process add 500 μL of hexane to dissolve the QDs.
27. For storage keep the QDs in hexane solvent.

Large-scale synthesis of Cu-dopped InP/ZnSe QDs

⏱ Timing: ∼3–4 h

28. To get large scale of QDs, multiply above quantities 10 times and perform the reaction in 100 mL three neck round bottom flask.

⏸ **Pause point:** Store the prepared QDs in a vial, you can use parafilm to avoid its interaction with atmosphere, keep it at a temperature range between 20°C–25°C.

Optical properties of QDs

⏱ Timing: 45 min

To confirm the high efficiency and low absorption of nanostructures for LSC applications, optical properties of as-synthesized QDs must be determined accurately. All measurements are performed in oxygen atmosphere at a temperature range between 20°C–25°C. Hexane is used as solvent during measurements. As an alternative solvent to hexane toluene can be used for optical measurement.

29. Measure the photoluminescence and UV-Visible absorbance spectra (Figure 3A) of synthesized QDs by Edinburgh instruments spectrofluorometer FLS1000. Excitation source must be Xenon arc lamp which covers the range pf 230 nm–1000 nm.
30. Measure the photoluminescence, UV-Visible absorbance and PLQY by using the standard quartz cuvettes with 1×1 cm^2 dimensions (Figure 3B). Fill the cuvette with quantum dot solution and place in the module.

⚠ CRITICAL: It is important to minimize the reabsorption effect. To this end, dilute the QD solution until the absorbance reaches a maximum value of 0.1 at the longest wavelength absorption band (Würth et al., 2013).

31. To measure the optical properties of solid sample, use another sample holder which is specific for solid-state sample.
32. Excite QD solution with 375 nm and set wavelength 400 nm for PL intensity and PLQY measurement (Figure 3C and 3D).
33. Set the scatter range between 370 nm to 440 nm and set the emission range between 560 nm to 975 nm for copper doped samples.
34. Number of recorded signal photons must be adjusted to 1 million photons per second.
35. Time resolved measurements must be performed on QD solutions at first excitonic peak at a temperature range between 20°C–25°C with density 0.1 (Figure 3E).

⚠ CRITICAL: If the record signal photons are not adjusted to 1 million photons per second, then PLQY of QDs could be affected by the instrumental factor.

36. Acceleration factor must be calculated by the absorbance of QDs to perform the accelerating aging test, the illumination wavelength must be 365 nm. After finding absorbance, multiply it with the power density of the UV lamp to find absorbed power (Figure 3F).
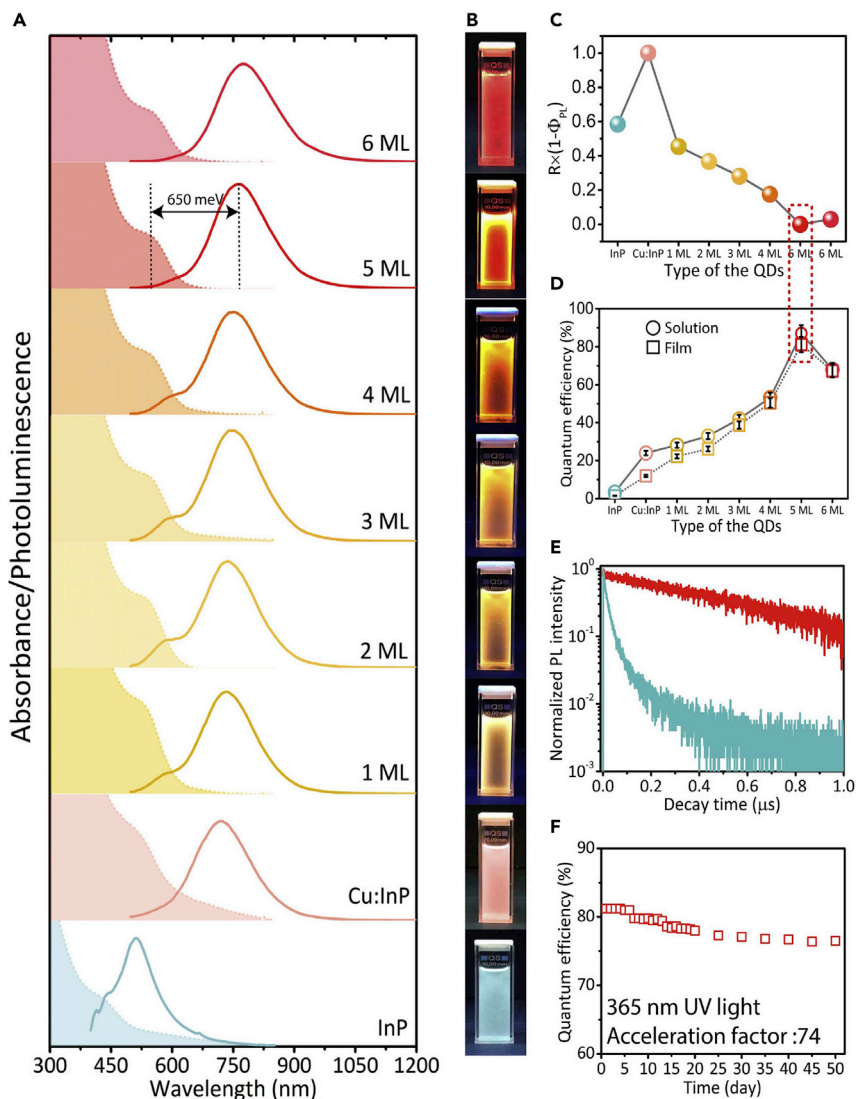
Figure 3. The optical properties of copper-doped InP/ZnSe QDs

(A) Absorbance and photoluminescence spectra of all synthesized QDs such as core InP, copper doped InP and copper doped InP/ZnSe core/shell QDs having different shell thickness of ZnSe.

(B) QDs under 365 nm UV irradiation.

(C) Normalized Quantum factor of copper doped InP QDs.

(D) Evaluation of PLQY by increase in thickness of ZnSe shell. The error bars were calculated by the standard error of the mean of three samples.

(E) Time resolved PL measurements of core InP and copper dopped InP QDs in solvent hexane.

(F) Accelerating aging test performance of synthesized QDs at UV irradiation of 365 nm (Figure reprinted with permission from Sadeghi et al., 2020).

37. Divide the absorbed power with the ratio of absorbed photons by the film under 1 sun condition will give acceleration factor (Figure 3F).

38. The brightness of quantum dots used for LSC application is an important parameter. In this regard, to calculate the brightness ($B = PLQY \times \epsilon$) equation was used as mentioned before (Lim et al., 2015). PLQY is the ratio of emitted photon number to the absorbed photon number. Molar extinction coefficient (ϵ) is defined as how strongly a substance absorbs light at a given wavelength per molar concentration. (ϵ) value was calculated according to Xie et al., 2009. The resulting brightness value is calculated as 3.56×10^5 cm^{-1}M^{-1}.

LSC device fabrication

🕐 Timing: 1 h 45 min

39. To fabricate LSCs device, the polymeric host PDMS elastomer which possess the quality of highly transparent in near Infrared and visible region is selected. PDMS also offers large-scale production which is not expensive.
40. In order to use in LSC device fabrication, QD solution with different concentrations of 13 mg.mL^{-1}, 26 mg.mL^{-1}, and 52 mg.mL^{-1} are prepared in hexane.

⚠ CRITICAL: Hexane has lower boiling point comparing to toluene. Therefore, hexane is preferred to remove organic solvent easier. As an alternative solvent, chloroform can be used to dissolve QDs.

41. Mix the silicon elastomer (SYLGARD 184) with curing agent. Adjust the mass ratio of curing agent to the elastomer as 1/10. Add QD solutions with concentrations of 13 mg.mL^{-1}, 26 mg.mL^{-1}, and 52 mg.mL^{-1}. Final QD concentrations in elastomer are 13 mg.mL^{-1}, 26 mg.mL^{-1}, and 52 mg.mL^{-1}, respectively.
42. For concentration of 26 mg.mL^{-1}, the picture of PDMS-QD mixture is given in (Figure 4A).
43. Stir the mixture vigorously using a lab spoon 5 min in a glass petri dish until the bubbles appear (Figure 4B).

⚠ CRITICAL: It is important to use glass petri dish compared to polymer petri dish because curing process is performed around 70°C.

44. Place the petri dish into a desiccator and 133.3 Pa (1 Torr) vacuum pressure is used to degas the sample 1 h until all bubbles are completely removed. At the final stage, a homogenous mixture is obtained (Figure 4C).
45. Under UV irradiation emission of homogenous mixture is given in Figure 4D.
46. In order to produce films with different thicknesses on 10 × 10 cm^2 glass substrates doctor-blade method can be adjusted Figure 4E.
47. After degassing process, pour the mixture on commercial glass substrates, which have 2 mm thickness with different dimensions and perform the doctor-blade method (Figure 4F). The transmission of glass substrates between 400–800 nm is measured by Edinburgh Instruments FS5 spectrofluorometer (Figure 5).
48. To control the film thickness, adjust the size of the gap between the blade and the substrate.
49. The doctor-blade is translated over the LSC length to form a thin QD-polymer composite layer Figure 6A.
50. Cure the substrate in the oven at 70°C to remove hexane solvent for 45 min.
51. The final thickness of QD-polymer composite is 100 μm (Figures 6B and 6C).

Optical measurements of QD-LSC device

🕐 Timing: 2–3 h

Optical properties of QD-LSC device are important to understand and examine the stability of Cu-doped InP/ZnSe QDs, and the efficiency of the LSC device.

52. The absorbance (Abs) and photoluminescence (PL) of the QD solution and small-size QD-LSC devices (10 cm × 10 cm) (Figure 6D) are measured by using Edinburgh instruments spectrofluorometer FLS1000 with a different sample holder which is specific for solid-state sample. As reference use glass samples with same size.
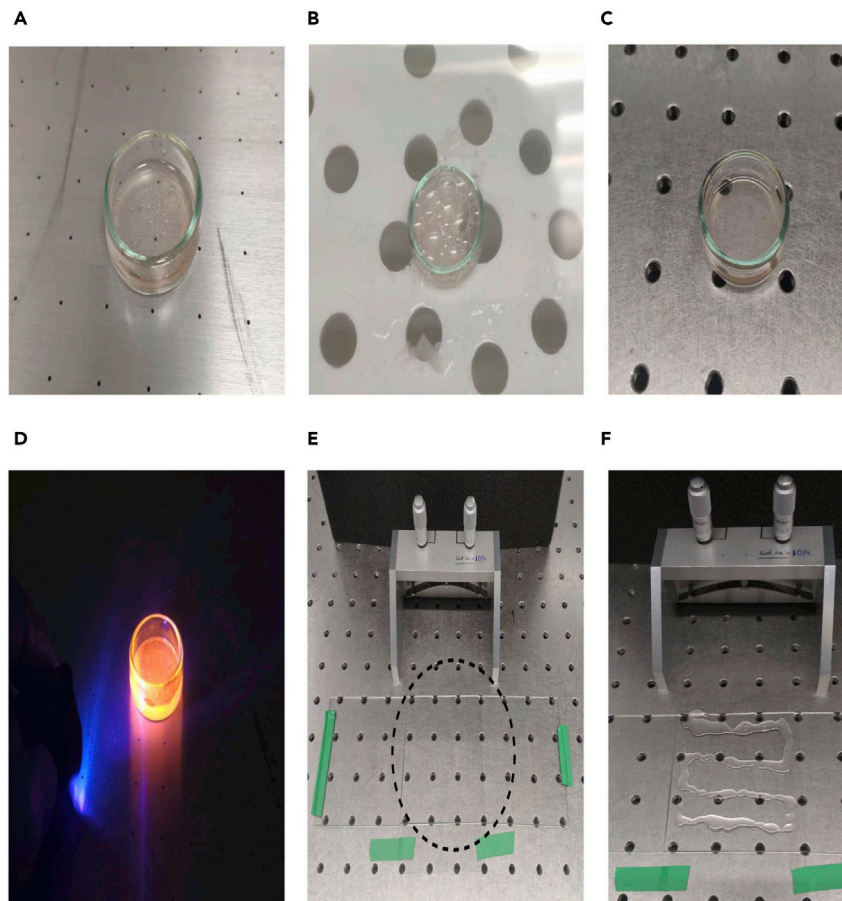
Figure 4. Preparation procedure of QD-PDMS film
(A) Photograph of QD-PDMS mixture
(B) QD-PDMS mixture is placed under vacuum chamber.
(C) After degassing 1 h, all bubbles are disappeared.
(D) Photograph of QD-PDMS mixture under UV irradiation.
(E) The 10 × 10 cm^2 glass substrate (shown in black dashed circle) is immobilized for doctor-blade method by using other glass samples with same thickness. The outer glasses are taped.
(F) QD-PDMS sample is poured on glass sample for doctor-blade technique.

53. To evaluate the optical output intensity of the QD-LSC device, UV lamp is used. To simulate the situations, in which the solar window panels are illuminated partially by sunlight irradiation on the different hours of the day the portion of the QD-LSC can be altered (LSC size is 10 × 10 cm). While changing the illumination area black mask can be used to cover the QD-LSC device partially. When the illumination area changes from 0 to 100 cm^2 optical output intensity increases (Figures 6E and 6F).

54. To measure the reabsorption in the fabricated QD-LSC, apply laser beam excitation at 365 nm perpendicular to the surface with different optical distances and record the output intensity from the edge at different optical distances from the excitation spot in fabricated QD-LSC. The decrease in normalized integrated PL intensity demonstrates the reabsorption and scattering losses (Figures 6G and 6H).

55. To investigate the scattering losses of QD-LSC device, propagate a laser beam at the wavelength of 780 nm through edge of the LSC device. Collect the output light at different optical distances (Figures 7A and 7B).

56. To measure the efficiency of the QD-LSC devices, mask the excessive area of solar cell with a black tape.
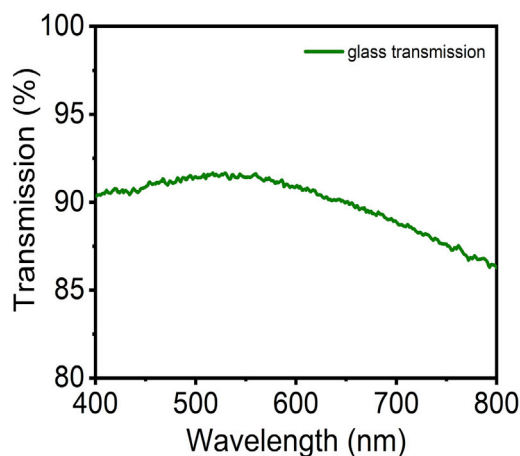
Figure 5. The transmission of glass substrates is measured between 400-800 nm by Edinburgh Instruments FS5 spectrofluorometer

57. The solar cell was coupled to the LSC when LSC is illuminated by the solar simulator as shown in Figure 8A as referenced before (Sadeghi et al., 2018.; Sadeghi et al., 2019).

   ⚠ CRITICAL: As an alternative approach to using black tape, reflective ink can be used as shown by Meinardi et al. (2014).

58. Illuminate the surface of the QD-LSC using AM 1.5G Solar Spectrum. To obtain *I-V* curve of the silicon solar cell we used Keithley two-probe source meter device. The set-up is shown in Figure 8B.

Structural characterization of QDs

⏲ Timing: 4–6 h

To evaluate and understand the structural properties of copper doped InP/ZnSe QDs, X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) are important.

59. Prepare the samples with different ZnSe shells for transmission electron microscopy (TEM) to evaluate the monolayer thickness and for X-ray diffraction (XRD) techniques.
60. To obtain a good quality of image, the centrifugation process plays a critical role in removing the byproducts that formed during the process.
61. In this regard, as a first step, after synthesis process add the QD solution into 50 mL of falcon tubes and centrifuge them at 8227 × g for 20 min at a temperature range between 20°C–25°C. At the end of centrifugation process, the byproducts occurred during reaction will aggregate due to gravitational force. Supernatant part will be QD solution.
62. Take the falcon tubes after centrifugation process and pour the QD solution (supernatant part) to a new falcon tube to separate from the aggregates of byproducts.
63. Add 1 mL of toluene to each tube and centrifuge again at 8227 × g for 20 min to aggregate the additional byproducts.
64. Separate the supernatant part (QD solution) by pouring it into another falcon tube.
65. Add ethanol (until 50 mL volume) and mix the QD solution vigorously.
66. Centrifuge the QD solution at 8227 × g for 20 min at a temperature range between 20°C–25°C. Due to presence of ethanol QDs aggregate.
67. Pour the supernatant part into the waste and add 2 mL of toluene to dissolve the QDs. Afterward, add ethanol (until 50 mL volume) and mix vigorously. Centrifuge the solution again with the same parameters.
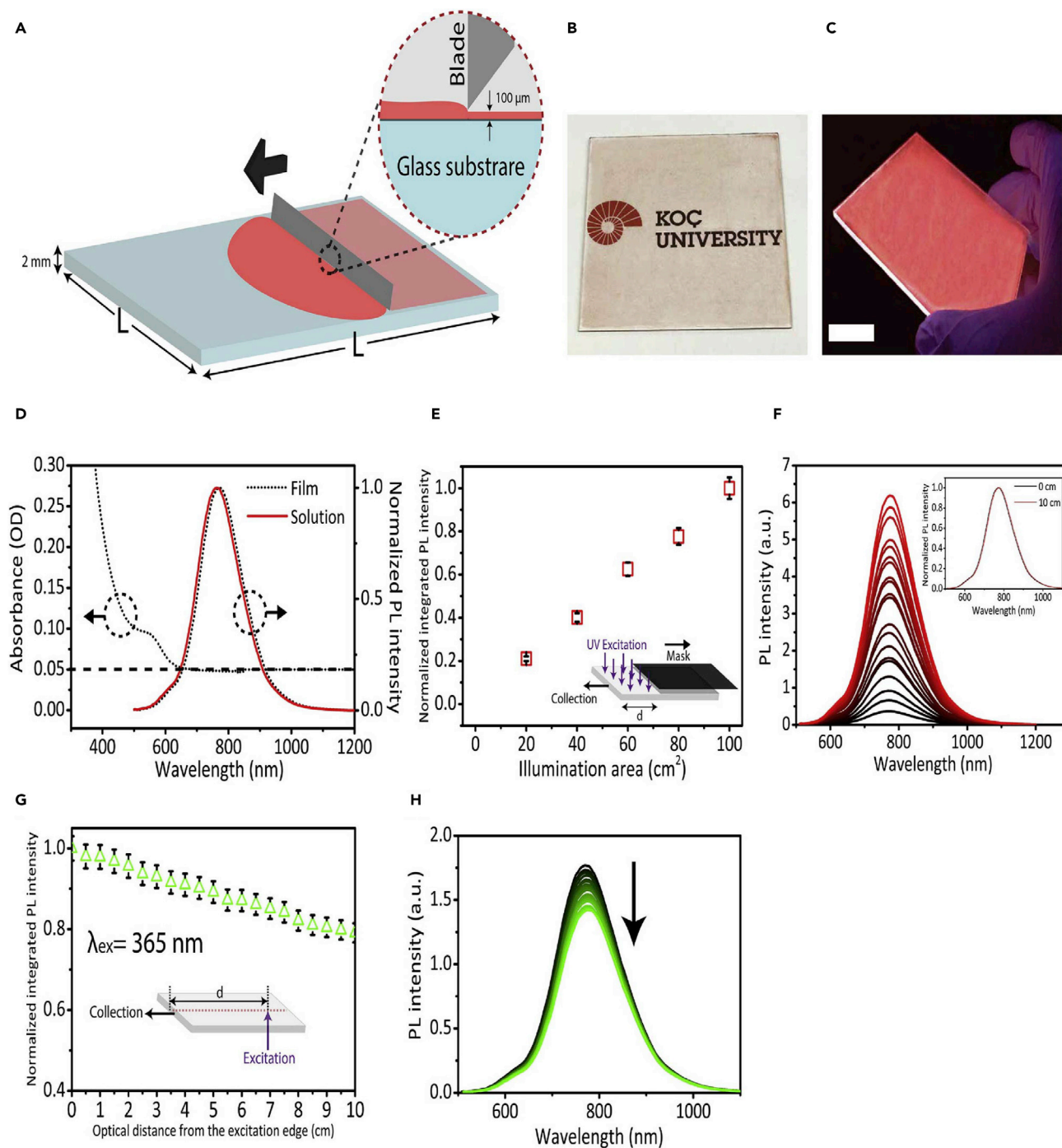
Figure 6. Copper-doped InP/ZnSe QD-based LSCs

(A) Schematic representation of fabrication process of QD-LSCs.

(B) Transparency of fabricated QD-LSC shown under an ambient light with loading concentration of 26 mg.mL^{-1}.

(C) Total internal reflection is visible on edges and seems brighter in photograph of QD-LSC under 365 nm UV radiation (scale bar, 1 cm).

(D) PL and Absorbance of QDs in the film (black dashed line) and in the solution (red line).

(E) Optical output intensity of QD based LSC with changing the illumination area. The error bars were calculated by the standard error of the mean of three samples.

(F) The output emission spectra of the LSC, when illumination area increased as in (e). Inset: Normalized output spectra at the optical distances of 0 and 10 cm from the collection edge.

68. Repeat the centrifugation process in the presence of ethanol 3 times by using the same parameters.
69. At the final step of centrifugation process add 500 μL of hexane to dissolve the QDs.
70. Take 50 μL of QD-hexane solution and complete the solution volume to 1 mL by adding 950 μL of hexane for TEM samples.
71. Using the micropipette, a fraction of solution (about one third) is dropped on TEM grid coated with carbon.
72. Let it dry and it is ready for TEM measurements.
73. After the sample is ready, it is fixed on the sample holder and the sample holder is inserted in the TEM microscope (TALOS F200S). All measurements were carried out under high tension of 200 kV.
74. TEM analyses indicate the average particle size of InP core (2.5 nm $\pm$ 0.2 nm) (Figure 9A).
75. Average particle size can be increased after copper doping (2.7 nm $\pm$ 0.2 nm) (Figure 9B).
76. 3 ML ZnSe shelling can enlarge the QDs up to 6.3 nm $\pm$ 0.2 nm, while the 5 ML ZnSe shelling can increase the size up to 8.5 nm $\pm$ 0.3 nm (Figures 9C and 9D).
77. Each monolayer of ZnSe shell represents the cubic crystal structure of 0.57 nm.
78. To prepare XRD samples of InP core and copper doped InP/ZnSe QDs, add the concentrated QD solution on silicon wafer by drop-casting. Increase the temperature to 60°C evaporate the hexane solution.
79. In Figure 10 top and bottom panels of patterns show the XRD peak of InP and copper doped InP/ZnSe core/shell QDs, respectively.
80. A clear intensity peak around 25-degree theta will be observed for InP, with a small peak around 40-degree theta (Figure 10A).
81. While the clear intensity peak around 25-degree theta is observed for Cu InP/5ML ZnSe, with two other peaks around 40 and 50-degree theta (Figure 10B).
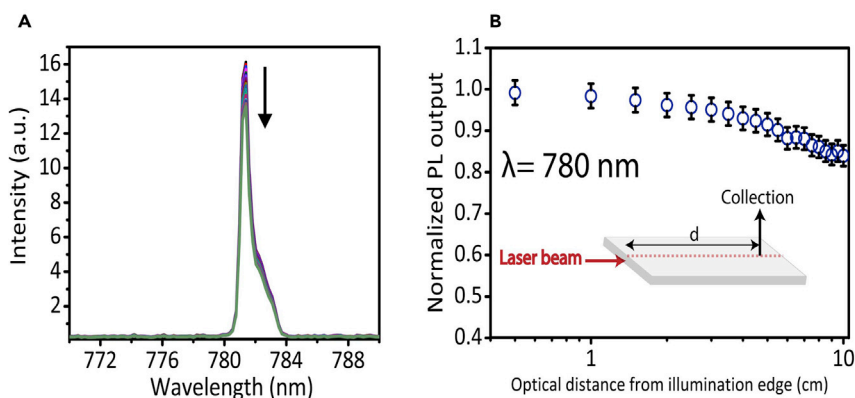
Figure 7. The scattering measurements of the fabricated QD-based LSC
(A) The PL output was shown at different optical distances ranging from 0 to 10 cm in the arrow direction when the laser beam with the wavelength of 780 nm was propagated inside the slab based on the setup schematic demonstrated at (b)-inset.
(B) The normalized PL output was shown at different optical distances ranging from 0 to 10 cm when the laser beam with the wavelength of 780 nm was propagated inside the slab. Inset: The schematic demonstrates the setup, in which the QD-based LSC illuminated by the laser beam at the edge and the optical output was collected from the face by using an optical fiber. The error bars were calculated by the standard error of the mean of three samples.
(Figure reprinted with permission from Sadeghi et al., 2020).
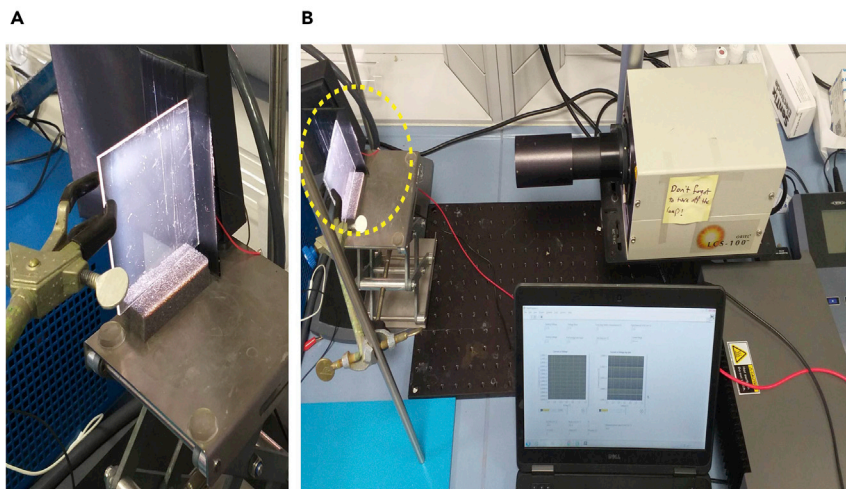
Figure 8. Images of the solar simulator setup
(A) QD-LSC which is coupled to solar cell from LSC edge.
(B) Illuminated QD-LSC by AM 1.5G Solar Spectrum is shown inside the yellow dashed circle. Measurement is performed by Keithley two-probe source meter device.

EXPECTED OUTCOMES

This protocol allows for the synthesis of biocompatible and efficient copper doped InP/ZnSe core/shell QDs and their LSC application as a promising candidate. In this regard, to engineer the Stokes shift and to reduce the reabsorption of the QDs we doped the InP QDs with copper as transition metal ion (Xie and Peng, 2009; Erickson et al., 2014; Viswanatha et al., 2011). After copper doping, InP QDs experienced a prominent PL red shift around infrared region with 650 meV which decreased its reabsorption property. Moreover, by passivation of the surface trap states via ZnSe shell growth (Lim et al., 2011; Sharma et al., 2017) and strong electron-hole pair confinement the core/shell QDs possessed high PLQY of 87% in the Near-Infrared region.

For the LSC application, copper doped InP/ZnSe core/shell QDs were mixed with PDMS polymer. Gram scale synthesis of Cu-doped InP Zn/Se QDs can lead to the fabrication of mass production of LSC device. Therefore, to demonstrate the applicability for the solar window application large-area QD-based LSC (3,000 cm^2) was fabricated by using the doctor-blade technique (Li et al., 2016). The resulting QD-based LSC devices exhibited power conversion efficiency (PCE) and external quantum efficiency levels (EQE) of 3.4% and 5.9%, respectively, under 365 nm. The PLQY of the QDs can be lower while they are pumped under lower energy photons instead of UV.

LIMITATIONS

Take care of the chemicals and solutions which are used throughout the protocol, because reagents and solutions must not interact with oxygen environment. Otherwise, oxidation might take place resulting in undesired nanostructures because atmospheric oxygen can create unfavorable reactions during the synthesis process. Furthermore, this study falls to reach out the more than 10% of EQE value due to using low efficient silicon solar cells during electrical-optical measurements. The optical properties of the QD-LSC device were tested only under UV light. Therefore, it is highly important to evaluate the efficiency of the QD-LSC device under simulated or real AM1.5G irradiation. Moreover, the high costs of chemicals limit the large-scale production.

TROUBLESHOOTING
Problem 1
The bubbles in the syringes during injections (steps 10 and 13)
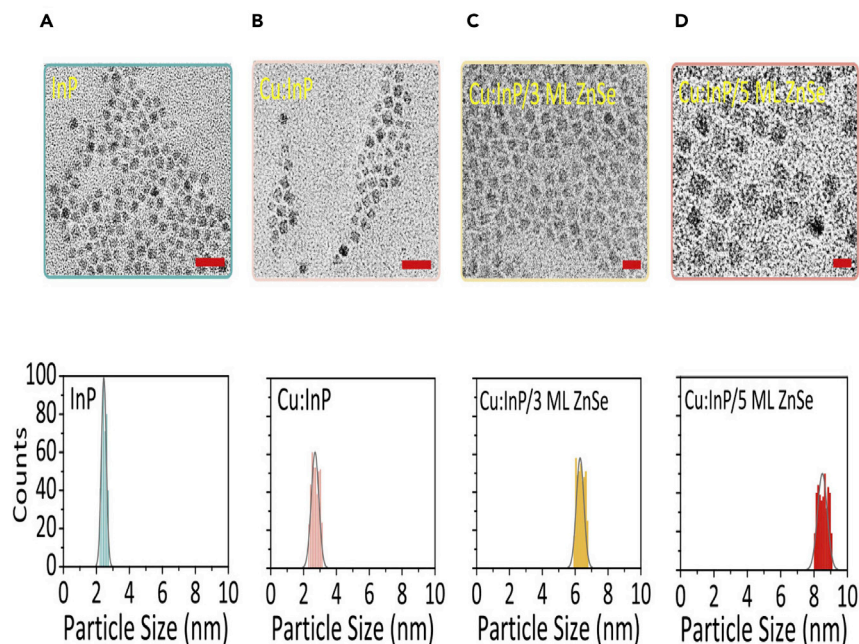
Figure 9. Size distribution and TEM images of synthesized QDs by increasing the shell thickness
Scale bar for InP and Cu-doped InP is 5 nm, and scale bar for Cu-doped InP/ZnSe (with 3 ML and 5 ML) is 10 nm.
(A) Average particle size of InP is 2.5 nm $\pm$ 0.2 nm.
(B) Average particle size of Cu-doped InP is 2.7 nm $\pm$ 0.2 nm.
(C) Average particle size of Cu-doped InP/ZnSe (with 3ML) QDs is 6.3 nm $\pm$ 0.2 nm.
(D) Average particle size of Cu-doped InP/ZnSe (with 5 ML) is 8.5 nm $\pm$ 0.3 nm. (Figure reprinted with permission from Sadeghi et al., 2020).

Potential solution
Many chemicals in liquid form are measured with help of syringes throughout the protocol. In this regard syringes must contain no air and must be used accurately; otherwise air inside the syringes can form bubbles which will give inaccurate amount of reagent.

Problem 2
Possible oxygen effects (steps 10 and 13)

Potential solution
No atmospheric oxygen should interact with reaction; this can result in unwanted reactions in solution which will later affect the size and efficiency of QDs. During the precursor preparation, use oxygen-free N_2 environment. Use glovebox and hood for the reagents which may interact with environment fast and absorb the moisture. Cover the septa with parafilm. In addition, while taking aliquot it is critical that the syringe does not contain any oxygen.
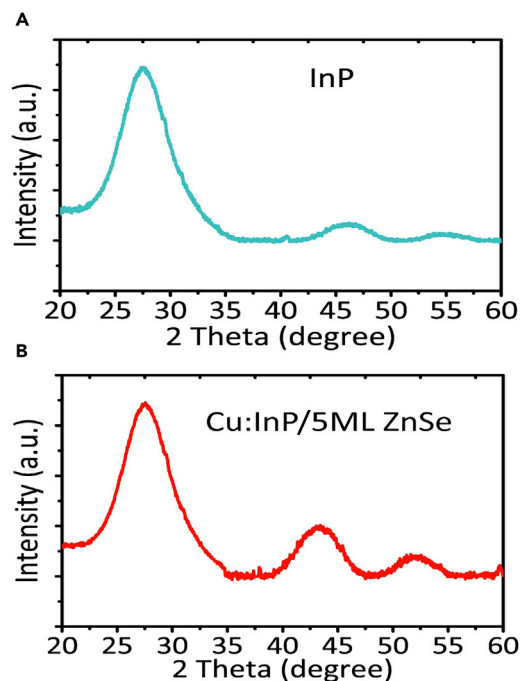
Problem 3
Not well distributed QDs in PDMS polymer matrix (step 41)

Potential solution
Mix the QD-hexane solution with PDMS polymer vigorously to distribute the QDs as good as possible until the bubbles clearly appear.

Problem 4
In case of non-cured QD-PDMS LSC device (step 50).

Figure 10. The XRD patterns of InP and Cu-InP/5ML ZnSe QDs

(A) InP core QDs

(B) Cu-InP/5ML ZnSe QDs (Figure reprinted with permission from Sadeghi et al., 2020).

Potential solution

If the QD-PDMS LSC device does not cure, increase the curing agent ratio.

Problem 5

The stability of fabricated QD-LSCs has only been tested under UV light (step 53).

Potential solution

Additionally, evaluate them under sun irradiation or other broadband light sources under different humidity levels.

RESOURCE AVAILABILITY

Lead contact

Further information and request for reagent and sources should be fulfilled by the lead contact, Sedat Nizamoglu (snizamoglu@ku.edu.tr)

Materials availability

No unique reagents were generated during this study.

Data and code availability

The published article includes all datasets/code generated or analyzed during this study.

ACKNOWLEDGMENTS

AUTHOR CONTRIBUTIONS

G.O.E. and S.S. performed both experiments and analysis. S.N. planned and supervised the entire study, and G.O.E., S.S., M.S., and S.N. wrote the manuscript. All the authors read and accepted the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interest.

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