

# Additive Manufacturing of Quantum Dot Nano-Inks

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## ABSTRACT

In this work, we describe our approach for characterizing a nanocomposite material to judge its suitability for 3D printing. We have successfully synthesized CdSe quantum dots (QDs) and introduced them (in liquid and in solid form) into photopolymer printing media. Suspensions prepared with addition of QDs in a solvent-based solution showed a decrease in viscosity with an increase in the volume of QDs added. When solid QDs were used, the viscosity of the resulting nanosuspensions remained similar to the pure photopolymer. Moreover, we have demonstrated feasibility of “printing” the suspension by manually curing the photopolymer with UV light. Our results demonstrate that the cure depth of the resulting samples does not depend on the loading of the QDs at the low concentrations tested. We have also studied the stability of these nanosuspensions over time by evaluating their physical properties such as surface tension, viscosity, and cure depth.

**Keywords:** Additive Manufacturing, Quantum Dots, Polymer Nanosuspensions

## 1 INTRODUCTION

Additive Manufacturing (AM) pertains to technologies that fabricate 3D artifacts through the successive addition of 2D cross-sectional layers. Due to this layer-by-layer fabrication process, AM allows a designer to create geometrically complex artifacts with designed topologies and meso-structures that cannot be fabricated by any other means. As a process that only uses the material needed, AM is an inherently low-waste, environmentally friendly manufacturing approach. However, the narrow choice of materials used in AM remains a key limitation of this technology [1].

In order to advance AM material selection, we look to introduce nanomaterials into AM printing media as a means of modifying their fundamental material properties. The

goal of our research is to introduce a nanosuspension into a Jetted Photopolymer AM system, thereby creating an inkjettable liquid for 3D printing of parts. Jetted Photopolymer is an AM process that combines principles of ink-jet printing and stereolithography. Briefly, tiny drops of photosensitive acrylic polymer are deposited using the array of inkjet print heads and the build material is UV cured after the deposition of each individual layer, thus creating a 3D object. Printability of the inks can be evaluated using Ohnesorge number:

$$Oh = \frac{\mu}{\sqrt{\gamma \rho d}} \quad (1)$$

where  $\mu$  is the viscosity,  $\gamma$  is the surface tension,  $\rho$  is the density, and  $d$  is the nozzle diameter. If the inverse of the  $Oh$  of an ink has a value between 1 and 10, then it is likely that the ink will be successfully jetted [2]. Therefore, it is important to measure these parameters prior to printing.

We chose QDs as a potential nanomaterial to use in AM systems due to their unique optical signatures that can bring new properties to 3D parts. QDs have been incorporated in both inkjet and photopolymer systems [3-6]. However, no attempts have been made to combine inkjet with QDs in photopolymers, and also not in any AM applications. Therefore, the primary research question for this is work is: *What effects do Quantum Dots have on printability of commercially available photopolymer resins?* As a variety of nano-inks can be deposited simultaneously to create graded materials, the presence of nanoparticles will offer the AM designer greater flexibility in the final design of material properties.

## 2 MATERIALS AND METHODS

### 2.1 Chemicals and materials

Cadmium Oxide (CdO) (99.95%), Selenium powder

(200 mesh, 99.999%), Tri-n-octylphosphine (TOP) (90%), Tri-n-octylphosphine oxide (TOPO) (98%), and 1-Tetradecylphosphonic acid (TDPA) (98%) were purchased from Alfa Aesar and used as received. Objet® Vero White and Vero Clear resin was purchased from Objet and used as received.

## 2.2 Synthesis of CdSe quantum dots

Synthesis of CdSe QDs was performed by a colloidal chemistry route described previously [7]. Briefly, 0.53 mmol of Se was dissolved in 2.4 mL of TOP at 150°C and constant stirring. Se/TOP solution was left on a hot plate under constant magnetic stirring and 40°C temperature. Separately, 0.4 mmol of CdO, 0.8 mmol of TDPA, and 9.77 mmol of TOPO were loaded in 50 mL three-neck round-bottom flask and heated to 270°C. It took ~30 min for solution of CdO to become optically clear. Se/TOP mixture was then injected into the hot solution of CdO/TOPO/TDPA. The reaction was continued at ~260°C. The color change from yellow to orange to red indicates the formation and growth of CdSe QDs. The heating source was removed ~10 min after injection of Se/TOP, and the QDs were transferred to the toluene.

## 2.3 Purification of CdSe nanocrystals

CdSe QDs were transferred to 50 mL centrifuge tubes. Anhydrous ethanol was added to the solution of QDs, and the mixture was shaken to form an emulsion. Mixtures were then centrifuged at 4,000 rpm for 5 min. The ethanol layer was carefully removed from the tubes and a second wash was added. This procedure was repeated at least 10 times to purify the CdSe QDs. Then nano-pure water was added to the samples and the purification procedure was repeated with water at least 5 times to remove ethanol from the system. Water was carefully removed from the CdSe QD precipitate. Centrifuge tubes with precipitate were frozen at -80°C for 24 hours. Then the samples were transferred to a freeze-dry system and allowed to dry under vacuum for ~10 days. CdSe QD powder was produced.

## 2.4 Preparation of nanosuspensions

Two sets of polymer nanosuspension were prepared. The first contained Objet Vero White® photosensitive resin and CdSe QDs in toluene. The second contained Vero Clear® resin and CdSe QD powder.

To prepare Vero White/QDs nanocomposites, a solution of CdSe QDs in toluene was added to the resin and stirred for 1 hour in a dark space. Table 1 shows the volumes of resin and QDs in toluene used to prepare different nanosuspensions with Vero White resin.

A second set was prepared by adding CdSe QD powder to Vero Clear® resin. Samples were sonicated for 20 minutes and stirred for 30 minutes before characterization.

Volume of Vero White® Resin, mL	Volume of CdSe QDs in toluene, mL	Ratio (v/v)
5	0	1:0
5	0.05	100:1
5	0.10	50:1
5	0.25	20:1
5	0.50	10:1

## 2.5 Characterization

Viscosity measurements were performed with an AR-2000 rheometer using 40 mm diameter, 2° angle rheometric cone. Surface tension was measured using the Wilhelmy Plate Method with KSV Sigma 70 Tensiometer using a 20 mm-length aluminum plate.

## 3 RESULTS AND DISCUSSION

### 3.1 Quantum dots in toluene

We first used CdSe QDs in toluene solution and prepared nanosuspensions by mixing them with Vero White resin. Photographs of the resulting suspensions are shown in Figure 1. QDs are well-dispersed in the photopolymer media, and no visible aggregation or precipitation of particles is observed in freshly prepared suspensions.

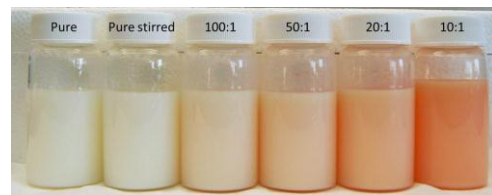


Figure 1. Photographs of Vero White® resin and nanosuspensions (fresh) with different volumes of CdSe QDs as indicated.

The inkjet process requires low viscosity inks with a printing viscosity depending on the print head. Figure 2 shows the dependence of Shear Stress on Shear Rate for fresh nanosuspension (3 measurements for each solution). Shear Stress is related to Shear Rate by the following equation:

$$\tau = \gamma \times \mu \quad (2)$$

where  $\tau$  is the shear stress,  $\gamma$  is the shear rate, and  $\mu$  is the viscosity. Linear dependence of Shear Stress on Shear Rate indicates that nanosuspensions and pure resin act as Newtonian liquids (viscosity is independent of rate). Newtonian behavior is mandatory for inkjet applications.

It is clear that viscosity of the suspensions decreased with increase of CdSe QDs volume in comparison with

pure resin. The viscosity of pure polymer that was stirred decreased in comparison with pure resin that did not undergo any procedures, indicating changes in polymer properties in contact with air.

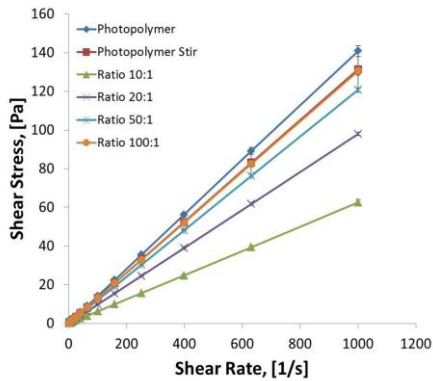


Figure 2. Shear Stress as a function of Shear Rate for Vero White® resin and nanosuspensions with different volumes of CdSe QDs in toluene.

We monitored the stability of the prepared suspensions over time. Figure 3(A) and (B) shows photographs of fresh 1:10 by volume ratio and 1 month old suspensions. It is clear that the nanoparticles are not stable and that they precipitate from the resin. Moreover, the resin itself changes its appearance from a milky-white to an almost clear solution—Figure 3(C). This indicates that the presence of toluene and QDs affects the properties of the Vero White® resin.

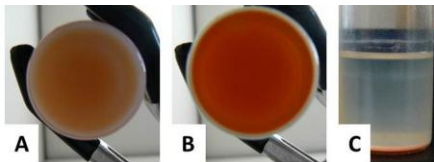


Figure 3. 1:10 by volume ratio nanosuspensions: (A) fresh, bottom view; (B) 1-month old, bottom view; and (C) 1 month old, side view.

Since the addition of QD solution into the resin decreased viscosity and changed the properties of the resin over time, we used powder QDs for further experiments.

### 3.2 Quantum dots in powder

Different loadings of QDs powder were added to the Vero Clear® resin to form nanosuspensions (0%, 0.005%, 0.01%, and 0.02%; where the ratio is QD to photopolymer by weight percent). Figure 4 shows photographs of the nanosuspensions. QDs dispersed well in a Vero Clear® resin without visible aggregation in freshly prepared solutions. Figure 5 shows the Shear Stress vs. Shear Strain plot for prepared nanosuspensions. It is seen that curves overlap, demonstrating that small QDs loadings do not

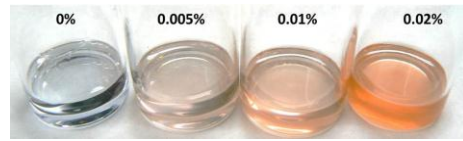


Figure 4. Vero Clear® photopolymer nanosuspensions with different loadings of CdSe QDs as indicated.

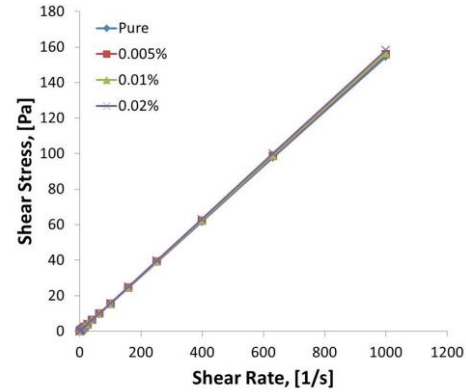


Figure 5. Shear stress as a function of strain for nanosuspensions with different CdSe QDs loadings.

affect significantly the viscosity of nanosuspensions compared to pure resin. Thus, the nanosuspensions are within a printable range of viscosity.

Surface tension of the ink effects droplet formation. Ten data points were taken the same day suspensions were prepared for the surface tension measurements. The results of these measurements are summarized in Figure 6. It appears that surface tension slightly decreases with increase of the QDs concentration.

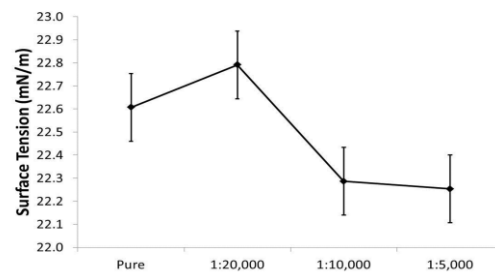


Figure 6. Surface tension of photopolymer with different CdSe QDs loadings as indicated.

To measure the effect of the QD loading on the cure depth of the Vero Clear® resin, a volume of each sample was exposed to ultraviolet (UV) light (wavelength 365 nm) for 15 seconds and the thickness of the resulting films was measured with a micrometer. The UV dose that each sample received was measured as 26 mJ/cm<sup>2</sup> using a calibration dosimeter. Preliminary tests revealed that the glassware holding the sample volume conveys a portion of the UV light to the sides and the bottom of the sample volume, creating a hollow shape instead of a film. For that reason, black plastic fixtures were used to shield the sample

from the glass walls and the outside of the beaker from UV light. The beaker was completely shielded from the UV light, and the desired disc-shaped films were created. Figure 7 shows the schematic of the beaker set-up and a photograph of the fabricated photopolymer film. For each ratio of QDs in photopolymer, three samples were exposed to UV light for cure depth measurements. Each film was measured in three different locations: two side measurements and one center measurement. Bubbles on the surface of the cured films were avoided to ensure the quality of the measurements. Results showed that QD loadings did not affect significantly the cure depth. Table 2 shows the average values of cure depth with standard deviations for different nanosuspensions.

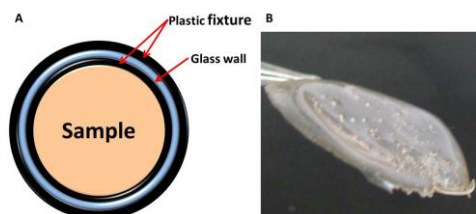


Figure 7. (A) Schematic of the beaker set-up for the cure depth experiments; (B) Cured photopolymer film.

Composition of nanosuspension (% of QDs)	Cure depth, [ $\mu\text{m}$ ]
0%	211 $\pm$ 25
0.005%	196 $\pm$ 14
0.01%	206 $\pm$ 24
0.02%	202 $\pm$ 18

Cured samples were examined under UV light for a fluorescence signature. Unfortunately, no fluorescence was detectable with the naked eye in all samples. This indicates that either the photopolymer blocks emission of light from the QDs or the concentration of the QDs is not high enough for detection. To further test fluorescence, we imaged the cured samples under a fluorescent microscope (Leica CTR 6500). Results showed that we can detect QDs with concentrations as low as 0.005% in the photopolymer.

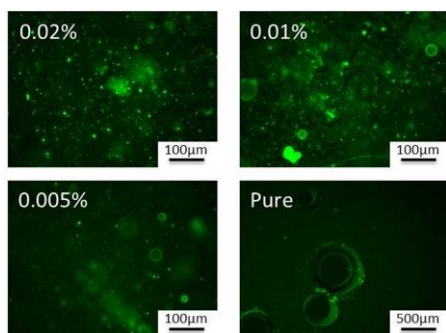


Figure 9. Fluorescence images of cured samples with different loadings of QDs as indicated.

## 4 CONCLUSIONS

The purpose of this work was to study the effects of the addition of QDs in liquid and solid states to commercially available photosensitive resin on the resin's physical properties. We studied two types of nanosuspensions: 1) Vero White® with CdSe QDs in toluene, and 2) Vero Clear® with CdSe QDs powder. In both cases QDs were well dispersed in the photopolymer without visible aggregation or precipitation in fresh solutions. The addition of QD toluene solution to the resins led to a significant decrease of viscosity of the photopolymer and its appearance, thus making it impossible to use as a printing media. QDs in powder form did not significantly affect the viscosity, surface tension, or cure depth of the photopolymer, thus making them viable candidates for use in a polyjet process. However, QDs precipitate from the resin within a week. Although we could not detect the fluorescence signature from QDs in the cured samples via the naked eye, fluorescence was detectable with a fluorescence microscope in photopolymers with QD concentrations as low as 0.005%. Thus, we demonstrated the feasibility of curing the nanosuspension and therefore the feasibility of selectively printing the resultant resin and make 3D objects with embedded quantum dots. Future work will demonstrate printing functionality.

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