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Stability and Redispersion of Platinum Nanoparticle Suspensions for Attachment to Dyes in Low-Cost Solar Cells

Honors Thesis

University of Connecticut

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Introduction

As fossil fuel resources are depleted and continue to pollute the atmosphere, there will be growing demand for sustainable and renewable energy. One of the most promising of these renewable sources which has been rapidly developing over the past 50 years is solar energy harnessed and converted into electricity by the solar cell. The most common method to fabricate solar cells utilizes high purity silicon substrate to absorb photons from sunlight. Silicon is a semiconductor which allows incoming photons to transfer energy to loose electrons. The cell is engineered so that there is an electrical imbalance between two silicon interfaces. The n-type has excess electrons and the p-type is electron depleted so that incoming photons transfer energy to the excess electrons of the n-type silicon, which then jump to fill the gaps in the p-type silicon, thus creating an electric current.

Although silicon based solar cells have achieved high efficiencies over recent years, the highly purified silicon is very costly to produce. It is therefore necessary to find a more economical method for producing solar cells which can still yield relatively high efficiencies. Current research has shown that dye-sensitized solar cells (figure 1) may be able to achieve similar efficiencies to silicon based cells at a much lower cost. This type of cell uses a sensitizer to absorb light, which is then anchored to the surface of a wide band semiconductor. Charge separation occurs at the interface through photo-induced electron injection from the dye to the conduction band of the solid. The semiconductor then transports electrons in the conduction band to the charge collector. The large absorption band of the sensitizers and the nanocrystalline morphology of the oxide film substrate allows the cell to absorb a wide spectral range (Gratzel et al. 2003). The use of oxide substrates such as TiO_2 reduces the cost of the cell because it is much cheaper to produce than silicon substrates. Figure 1 depicts the structure of the dye sensitized solar cells where the anode is comprised of a monolayer of molecular sensitizing dye adsorbed onto the nanocrystalline TiO_2 electrode surface coated on a piece of glass.

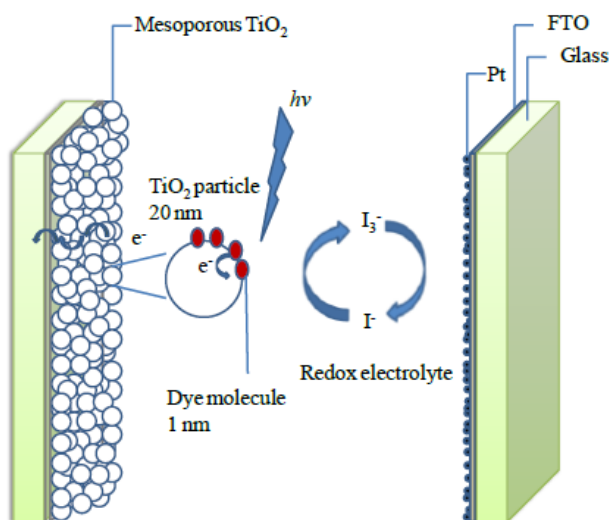
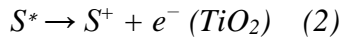


Figure 1. Structure of the Dye Sensitized solar cell (Liu et al. 2013)

The cathode or counter electrode is a platinum coated fluorine doped tin oxide (FTO) layer on a second piece of glass. In between, is a liquid electrolyte containing a redox couple (I^-/I_3^-) that permeates the TiO_2 film to allow the transfer of electrons from the oxidized dye to the electrolyte solution and the counter electrode. Where silicon in traditional cells acts in both charge separation and transport, in the dye sensitized solar cell the charge separation occurs at the surfaces between the dye, semiconductor, and electrolyte (Liu et al. 2013).

Figure 2 shows the energy diagram of the dye sensitized solar cell in which incoming photons pass through the transparent electrode and excite the dye molecules from ground state (S^0) to excited state (S^*) which causes them to transfer electrons to the conduction band of TiO_2 , oxidizing the dye (S^+).



Next, electrons travel between TiO_2 nanoparticles to the counter electrode. The I^-/I_3^- redox couple regenerates the oxidized dye to its ground state by donating electrons from the I^- ion which is oxidized to I_3^- .



I_3^- diffuses to the counter electrode where it recovers electrons which have returned from the external circuit of the cell and is reduced back to I^- .

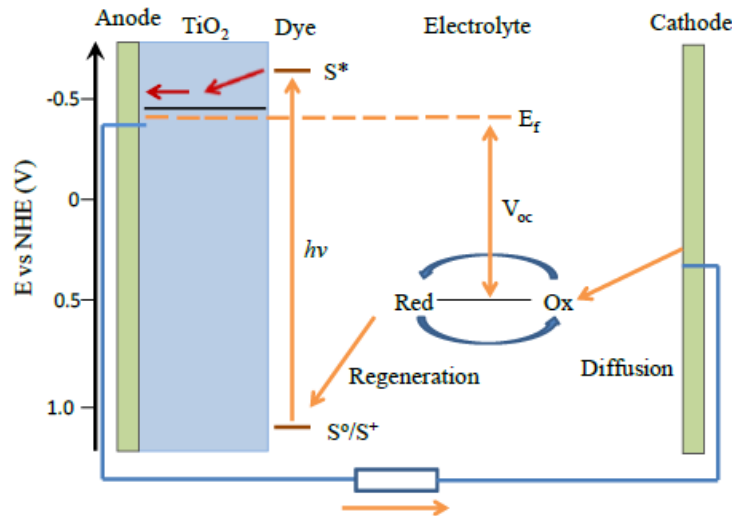
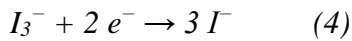


Figure 2. Energy Diagram of Dye Sensitized solar cell (Liu et al. 2013)

This regeneration of the oxidized dye and reduction of I_3^- to I^- causes a potential loss of about 0.5-0.6 V due to the formation of diiodide radicals. This voltage loss can be reduced by using a platinum nanocatalyst attached on the working electrode at the site where the dye reacts with the iodide/triiodide redox couple (Miyazaki et al. 2003)

The objective of this research is to develop a process based on a pure or mixed solvent that will maintain a stable dispersion of the nanoparticles without interfering with their ability to bond with the dye molecules in the solar cell. In order to do so, different synthesis, cleaning, and redispersion methods were performed and their effectiveness was analyzed.

Background

Colloidal metal nanoparticles have recently received much attention and research due to their unique electronic structure and extremely large surface area. Platinum nanoparticles with a diameter of 2 nanometers for example, have a surface area of 140 m²/g (Kraynov et al. 2015). These well dispersed, stable colloidal metal nanoparticles can be used in catalyst applications for oxidation and reduction reactions in fuel cells, biosensors, carbon monoxide oxidation in catalytic converters, nitric acid production, petroleum cracking, and many other important applications (Dai et al. 2010).

Platinum is the material used as the catalyst in dye sensitized solar cells due to its high conductivity, chemical and electrochemical stability, as well as its high catalytic activity for oxidation of iodide to triiodide. In contrast, other metals such as silver, iron, gold, etc. are corroded by I^-/I_3^- and are thus unfit for use (Naresh et al. 2013). Carbon conductive polymer, graphene, graphene oxide, molybdenum sulfide, etc. have also been studied in order to replace the more expensive platinum catalyst but are unable to achieve the catalytic efficiency of platinum.

The use of platinum nanoparticles in order to catalyze the iodide/triiodide redox couple on the counter electrode in dye sensitized solar cells (DSSC's) has been accepted as a viable method to increase their efficiency. The counter electrode transfers electrons to complete the circuit in the cell, regenerates triiodide in the interface of the electrolyte and counter electrode, and reduces the iodide/triiodide redox couple to keep potential low and minimize energy losses (Wei et al. 2015). By the same concept, it should be theoretically possible to achieve further catalysis by utilizing platinum nanoparticles binded to the dye molecules on the working electrode of the cell. Liu et al. 2013 tested this catalysis by using cyclic voltammetry measurements in order to find the oxidation potential of plain FTO glass vs. platinized FTO for oxidation of I^- to I_3^- . It was found that the platinized glass had a peak current of oxidation that was about one volt less than that of the plain glass. Ma et al. 2015 also highlighted platinum's electrocatalytic activity for I^-/I_3^- redox, noting its high cathodic current density in CV electrochemical analyses as well as its low resistance found from EIS test. These findings show that a platinum catalyst is able to oxidize I^- to I_3^- near its Nernstain redox potential and thus should be able to reduce the overpotential of dye regeneration in the cell. In order to effectively utilize a platinum catalyst on the working electrode of the cell it is necessary to develop a process to maintain a stable dispersion of platinum nanoparticles without interfering with their ability to bond with the dye molecules (Liu et al. 2013).

There are two approaches to consider for the wet chemical preparation of metal nanoparticles. They are called either top down, or bottom up methods. Top down methods are achieved by mechanical grinding of metals and stabilization by the addition of colloidal protecting agents. Bottom up methods are achieved by chemical reduction of metal salts, electrochemical pathways, or controlled decomposition of metastable or ganometallic compounds. Some examples of different methods for the synthesis of nanoparticles include using excess reducing agents such as sodium citrate, reduction of metallic salts in dry ethanol, air saturated aqueous solutions of poly (ethylene glycol), as well as common sugars such as glucose, fructose and sucrose (Panigrahi et al. 2004).

One of the most widely used and effective methods for liquid phase preparation of nanoparticles is the chemical reduction of transition metal salts in the presence of stabilizing agents in aqueous or organic media. Figure 3 depicts the formation of nanostructured metal colloids and shows that the metal salt gets reduced or thermally decomposed in order to generate highly unstable zerovalent metal atoms which can then collide with further metal ions, atoms, and clusters to form an irreversible stable nucleus (Bonnemann et al. 2001).

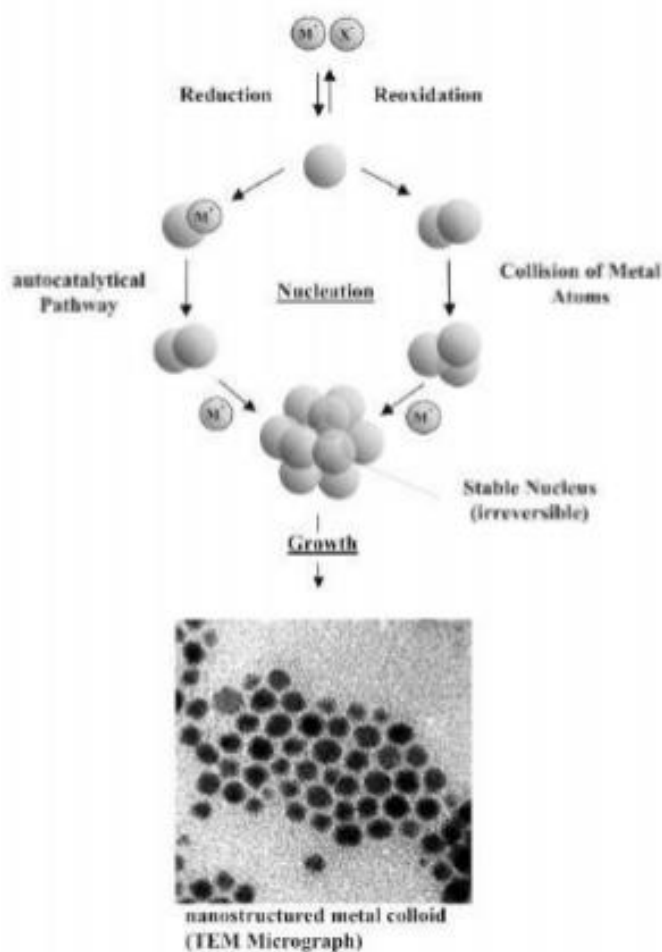


Figure 3. Salt Reduction Method for Formation of Nanostructured Metal Colloids (Bonnemann et al. 2001)

This method is ideal because it allows nanoparticles to be produced in the liquid phase with a narrow size distribution and appropriate concentration for catalyst purposes. The stabilizer, metal precursor, reducing agent, and solvent must all be carefully chosen to serve the purposes required of the nanocatalyst. Temperature is another extremely important parameter to consider for nanoparticle synthesis and particle stability. The time it takes for a sorbate molecule to desorb from the surface of the nanoparticle significantly decreases with increasing temperature. This residence time can also be decreased if the suspension is exposed to an external electric field which could be brought on by polar solvent molecules. (Kraynov et al. 2015)

In order to stabilize metal nanoparticles and prevent their agglomeration, the presence of some protective or stabilizing agent is usually necessary. Both electrostatic and steric properties influence the attraction/repulsion and thus stability of particles in solution. Electrostatic stabilization is achieved through the coulombic repulsion between colloidal particles due to their electrical double layer formed by adsorbed ions on their surface. Steric stabilization relies on organic molecules bonded to the colloidal particle which creates a layer of molecules acting as a buffer to prevent contact and agglomeration between particles (Bonnemann et al. 2001). Thermodynamically, nanoparticles tend to lower their extremely high surface energy, which along with attractive dipole-dipole interactions between metal nanoparticles, leads to their instability. Monodispersed nanoparticles will stabilize themselves through the sorption of molecules surrounding them or by lowering surface area by coagulation and agglomeration. In order to maintain a desirably small particle size (1 to 3 nanometers) for catalyst purposes, coagulation and agglomeration must be avoided (Kraynov et al. 2015). The addition of a stabilizing agent with the nanoparticle suspension can arrest particle growth from the reduction of excess platinum ions and help to form colloidal nanoparticles without significant agglomeration (Liu et al. 2013). The best stabilizers are ionic, with strong adsorptive properties and steric/electrostatic stabilization. Large molecules with chemical groups that have a free electron lone pair such as aromatic systems can adsorb strongly on metal surfaces providing stabilization for the suspension (Kraynov et al. 2015). Stabilizers used in platinum nanoparticle synthesis often employ thiol and amine groups and may be organic ligands, polymers, and surfactants. Some examples include simple hydrocarbon chains or dendrimers, proteins, triblock copolymers, polyvinyl pyrrolidone (PVP), acetate, and often employ thiol and amine groups (Liu et al. 2013; Wang et al. 2000).

Although stabilization is imperative to synthesizing a suspension of nanoparticles for catalyst purposes, it is ideal to create a suspension without the use of capping agents in order to avoid unwanted excess molecules in solution so that active surface sites of the nanoparticle are not blocked from their desired catalytic activity. "Unprotected" nanoscopic metal colloids can be produced in organic media without the addition of capping agents. According to Wang et al (2000), their stability comes from the solvent and/or simple adsorbed anions. Unprotected copper nanoparticles with mean diameter of 13.3 nanometers have been synthesized in methanol by reducing copper salts with hydrazine hydrate (Curtis et al. 1988). Palladium nanoparticles between 6 and 10 nanometers have also been made with atom clustering processes (Cardenas-Trivino et al. 1987), as well as thermal decomposition in methyl isobutyl ketone (Esumi et al. 1989). Wang et

al (2000) used a modified polyol process in which an ethylene glycol solvent containing NaOH was added to another glycol solution with H_2PtCl_6 in order to form a platinum hydroxide colloidal solution. This solution was then heated at $160^\circ C$ for 3 hours with argon gas flowing through the system in order to remove organic biproducts. The reaction yielded a dark brown colloidal suspension of platinum metal nanoclusters with an average diameter of 1-2 nm with observed stability after several months of storage. During the first stage, metal hydroxide crystallizes and then precipitation occurs by progressive dissolution of the hydroxide and evolution of water. In the second stage, dissolution of the intermediate phase leads to reduction and evolution of volatile products of the reaction which spurs homogeneous nucleation and growth of metal particles (Komarneni et al. 2002). It is further noted in Wang et al (2000) that the initial pH of the the platinum hydroxide solution must be about 12 or greater in order to prevent precipitation during the heating process. After the reaction is complete, the solution is stable at a pH higher than 7. Observations in this study showed that changes in platinum precursor concentration had a very minimal effect on resulting average particle size. The ability to yield such small particle sizes at higher metal concentrations was justified by the small size, narrow distribution of the metal hydroxide colloids that are formed prior to the reaction.

Three methods for synthesizing platinum nanoparticles were compared in Liu et al. (2013).

Table 1. Parameters Used to Prepare Platinum Nanoparticles and Resulting Particle Size Distribution (Liu et al. 2013)

PS	Method	Precursor	Stabilizer	[Stabilizer] ^a	PTC	[PTC] ^a	Solvent	Particle diameter, mean \pm SD (nm)
1	1	H_2PtCl_6	None	None	None	None	EG	1.5 ± 0.3
2	1	$PtCl_4$	None	None	None	None	EG	1.6 ± 0.4
3	2	H_2PtCl_6	DA	22	TDAB	2.5	Toluene	1.9 ± 0.3
4	2	H_2PtCl_6	DA	22	TDAB	2.5	Hexane	1.9 ± 0.2
5	2	H_2PtCl_6	DA	22	TOAB	2.5	Hexane	1.9 ± 0.2
6	2	$PtCl_4$	DA	22	TDAB	2.5	Hexane	1.9 ± 0.4
7	2	$PtCl_4$	DA	22	TOAB	2.5	Hexane	1.8 ± 0.3
8	2	H_2PtCl_6	DA	22	TOAB	4	Hexane	1.7 ± 0.3
9	2	H_2PtCl_6	DA	2	TOAB	4	Hexane	1.8 ± 0.2
10	3	H_2PtCl_6	DT	2	TOAB	4	Toluene	1.6 ± 0.4
11	3	$PtCl_4$	DT	2	TOAB	4	Toluene	1.6 ± 0.4
12	3	H_2PtCl_6	DT	2	TOAB	2.5	Hexane	1.7 ± 0.4
13	3	H_2PtCl_6	DT	2	TDAB	2.5	Hexane	1.8 ± 0.5
14	3	H_2PtCl_6	DT	2	TOAB	4	Hexane	1.6 ± 0.4
15	3	H_2PtCl_6	DT	22	TOAB	4	Hexane	1.7 ± 0.5
16	3	H_2PtCl_6	DA	22	TOAB	2.5	Hexane	2.1 ± 0.3
17	3	H_2PtCl_6	DA	22	TDAB	2.5	Hexane	2.2 ± 0.3
18	3	H_2PtCl_6	DA	2	TOAB	4	Hexane	2.2 ± 0.4
19	3	H_2PtCl_6	DA	22	TOAB	4	Hexane	2.2 ± 0.4

PS parameter set, PTC phase-transfer catalyst, EG ethylene glycol, TOAB tetra-n-octylammonium bromide, TDAB tetradecylammonium bromide, DA dodecylamine, DT dodecylthiol, SD standard deviation

^aThe number given is the ratio of the molar concentration to that of Pt

The first was similar to the method used in Wang et al (2000) in which a platinum precursor solution was mixed and stirred with a NaOH solution in ethylene glycol. In Liu's first method, the solution was heated at 160°C for 2 hours with nitrogen flow passing through the system in order to obtain a homogeneous colloidal suspension of platinum nanoparticles. The second method was a phase transfer method in which a platinum precursor was mixed with toluene containing a PTC. With the introduction of an alkylamine stabilizer, and then the NaBH₄ reducing agent, nanoparticle formation proceeded with effective stabilization by the capping molecules. The third method was similar to method 2 except a dodecanethiol stabilizer was added to the system after the reducing agent. The parameters of each method tested as well as their resulting particle size results are shown in table 1. The smallest mean particle size of about 1.5 nm was achieved by the reaction of the H₂PtCl₆ precursor using the first method. For this reason, along with the absence of excess capping agents that may hinder the ability of platinum to bond with dye molecules in DSSC's, this is the method that is focused upon in the remainder of this paper. TEM imagery of the resulting platinum nanoparticles synthesized using method 1 and the H₂PtCl₆ precursor is shown in figure 4.

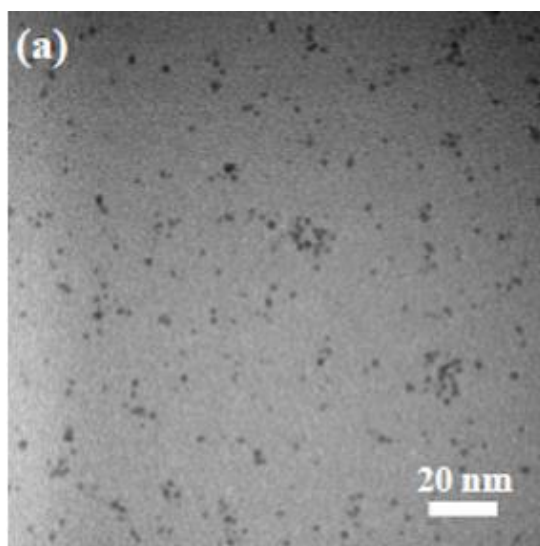


Figure 4. TEM Imagery of Platinum Nanoparticles Dispersed in Ethylene Glycol Prepared by Method 1 with H₂PtCl₆ Precursor (Liu et al. 2013)

From DLS measurement, Liu et al. (2013) found that as soon as the temperature of the reaction reached 160°C, the particle size reached its minimum value and did not change. Particle size testing after two years of dark storage showed that the size distribution was only about 0.1 nm larger with no observed aggregation or precipitation.

Although Wang et al (2000) pointed to the metal hydroxide colloids as the reason for their small particle size and highly stable results, other research has pointed to the formation of acetate

as the stabilizing mechanism in polyol nanoparticle synthesis (Liu et al. 2013; Yang et al. 2004; Komarneni et al. 2002). When heated, ethylene glycol rearranges to form acetaldehyde, which is then oxidized by the metal cation (platinum) to form acetic acid. At the high pH induced by the addition of hydroxide, acetic acid deprotonates to form the acetate ion which acts as a stabilizing molecule for the nanoparticle suspension. The reaction is given as follows:



The acetate formed from the reaction stabilizes the Pt suspension through the formation of chelate-type complexes via its carboxyl group (Liu et al. 2013).

With acetate ligands binding to, and thus stabilizing platinum nanoparticles, it should be possible to neutralize hydroxide ions within the suspension, and redisperse the stable particles in ethylene glycol. Liu et al. (2013) tested this hypothesis by acidifying the suspension to pH 3, centrifuging the solution, disposing of supernatant, and redispersing in ethanol three times. The resulting cleaned particles were then dispersed in ethylene glycol and testing results showed that particle size was still stable.

Wang et al. (2000) also stated that the platinum nanoparticles can be separated by adjusting the pH of the solution below 4 using dilute aqueous HCl. After centrifugation and disposal of supernatant, they found that the platinum could be redissolved in organic solvents such as alcohol, ketone, THF, DMF, and DMSO. The size of the nanoparticles as well as their stability is not mentioned for these redispersions. They do however, mention that redispersion in cyclohexanone or cyclopentanone with average diameter of 1-2 nm did not form any precipitate after several months. Liu et al. (2013) performed similar testing in which the platinum nanoparticles were separated and redispersed into ethanol, hexane, acetone, acetonitrile, 2-propanol and cyclopentanone. It was found that particles could be redispersed in ethanol, acetone, acetonitrile, 2-propanol and cyclopentanone, however testing results showed rapid aggregation of platinum. Reproducing the results found in these studies, and looking deeper into the production, acidification, cleaning, and redispersion of the Pt nanoparticles is important in order to assess their compatibility for bonding with dye molecules in dye sensitized solar cells.

Methods

Materials

Hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), sodium hydroxide, 37% hydrochloric acid and ethylene glycol were purchased from Sigma-Aldrich. Acetone was purchased from Fisher Scientific. All chemicals were used without further purification. Deionized water was produced by a PURELAB Ultra water purification system.

Preparation of Platinum Nanoparticle Suspensions

Platinum nanoparticle suspensions were produced using the polyol process in which an ethylene glycol solvent containing NaOH is added to another ethylene glycol solution with H_2PtCl_6 and is heated in order to form a colloidal platinum nanoclusters. Suspensions are made and results are compared based on parameters from both Wang et al (2000) and Liu et al. (2013). A solution of NaOH (0.1 g for Liu, 0.5 g for Wang) in ethylene glycol (20 mL for Liu, 25 mL for Wang) was prepared the day before testing and stirred overnight at 400 rpm. The NaOH solution was then added dropwise to a flask containing the Pt precursor (0.1036 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ for Liu, 0.5 g for Wang) dissolved in ethylene glycol (20 mL for Liu, 25 mL for Wang) and stirred at 400 rpm throughout the procedure. Nitrogen gas was set up to flow through the system in order to remove oxygen water, and organic biproducts. The system was then heated at 160°C for 2 hours to obtain a dark brown homogenous colloidal Pt nanoparticle suspension. The color of the solution observably changed from a yellow-orange hue to a transparent dark brown between 88 and 94°C . After cooling, the suspension was transferred to a 100 mL beaker for further testing and analysis.

pH adjustment

In order to separate the Pt nanoparticles for cleaning and redispersion, the pH was adjusted by adding 0.5 M aqueous HCl. According to Liu et al. (2013) and Wang et al (2000), the solution should be adjusted to pH ca. 3 or 4 respectively. Since pH readings of the colloidal metal suspension proved difficult, the required volume of HCl was calculated stoichiometrically. To test the effectiveness of this theoretical value, different amounts of HCl adjustment were performed. Different volumetric ratios of HCl were pipetted into a glass test tube containing small amounts of Pt suspension. After shaking the test tubes to mix the solution, they were centrifuged at 4,000 rpm for 20 minutes. If the platinum was not effectively separated from solution, more acid would be added followed by another round of centrifugation at 4,000 rpm. Once separated, nanoparticles would begin the cleaning phase or be redispersed by sonication and tested for size.

Platinum cleaning

For the cleaning step, ethanol, DI water, and acetone were added to the separated nanoparticles. Both with and without sonication to disperse the particles with the cleaning agent, the samples were centrifuged at 4,000 rpm. The supernatant was then disposed of and cleaned particles were redispersed in ethylene glycol by sonication for further size testing.

Dynamic Light Scattering (DLS) size measurement

DLS measurements were carried out using a Malvern Zetasizer Nano-ZS instrument with a nominal detection from 0.3 to 1000 nm. A 1 mL diluted sample of about 1.2×10^{-5} mol/L Pt in ethylene glycol was prepared and filtered into a clean DLS cuvette using 0.22 micron filters. The measurement was performed for four runs with 11 cycles.

Results

Using the parameters from Liu et al. (2013), two stable suspensions of platinum nanoparticles suspended in ethylene glycol with a small particle size distribution were synthesized. Figure 5a-b shows the frequency plots for the size distribution of both suspensions obtained from DLS testing.

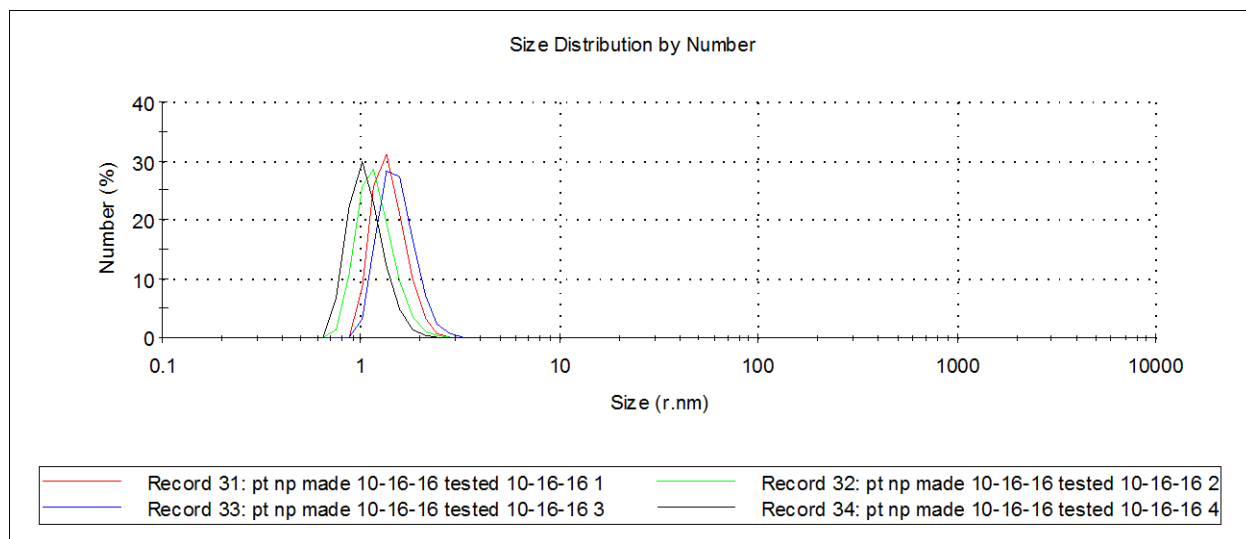


Figure 5a. DLS size distribution for suspension 1

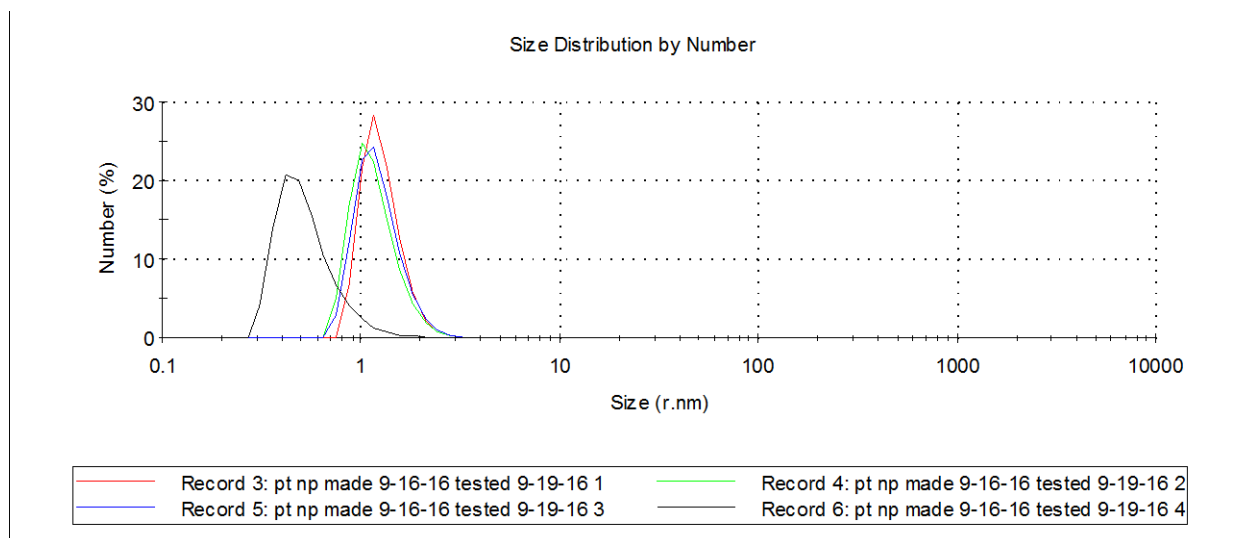


Figure 5b. DLS size distribution for suspension 2

The mean particle size was found to be 0.94 ± 0.36 r.nm (with the error value denoted by the standard deviation of four runs of testing) for suspension 1 and 1.23 ± 0.18 r.nm for suspension 2. This result compares closely to the results found by Liu of about 1.5 nm and speaks to the

compatibility of this synthesis method for reproduction in addition to the small particle size achieved. (Raw data can be found in appendix A)

In order to test the stability of the suspension, the particle size of suspension 1 was retested after 10 days of storage (Figure 6).

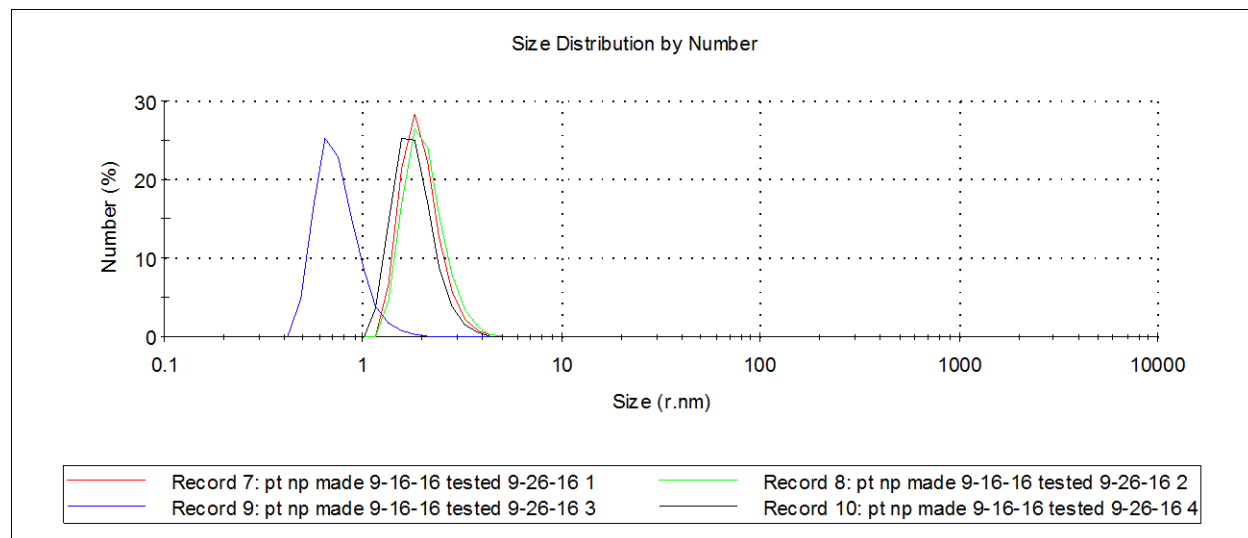


Figure 6. DLS size distribution for suspension 1 after 10 days storage

The mean particle size was found to be 1.46 ± 0.55 r.nm which indicates some aggregation of platinum nanoclusters. Although no precipitate was observed and the size is still very small, the size increase of about 0.5 nm is greater than the 0.1 nm increase observed by Liu et al. (2013) after 2 years of storage. This discrepancy may be due to a number of reasons such as sample contamination due to dust or other outside factors, or differences in storage methods not specified by Liu. If their samples were stored at a temperature other than room temperature the adsorption and aggregation of particles could be influenced.

Two suspensions of platinum nanoparticles suspended in ethylene glycol with a small particle size distribution were also synthesized using the parameters from Wang et al. (2000) Figure 7a-b shows the size distributions of both suspensions obtained from DLS testing. Particle size for suspension 3 was tested five days after synthesis and suspension 4 was tested two days after synthesis.

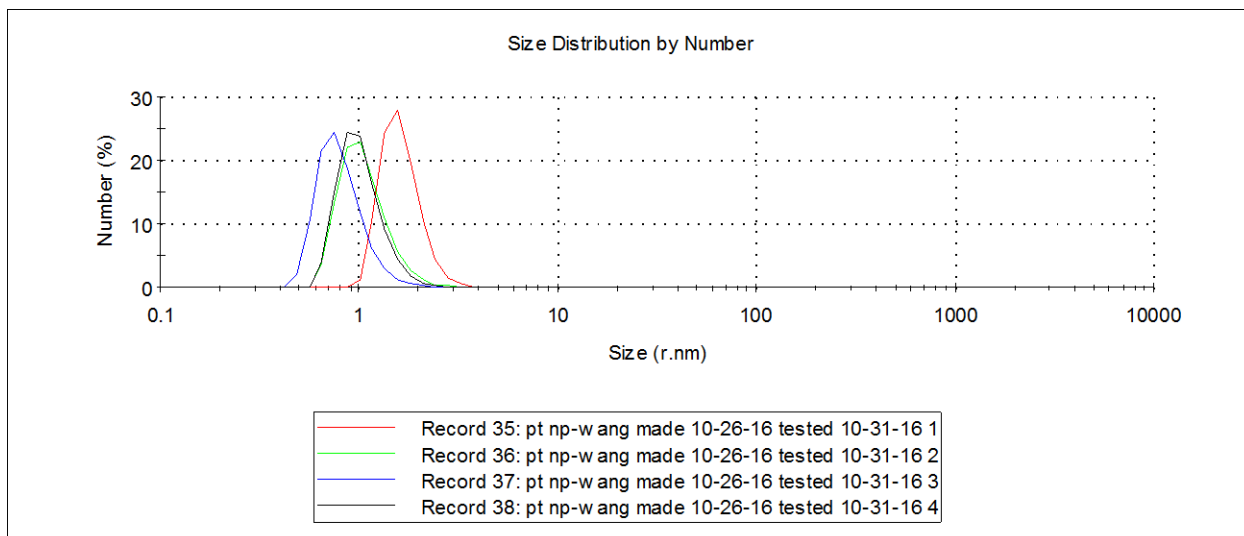


Figure 7a. DLS size distribution for suspension 3

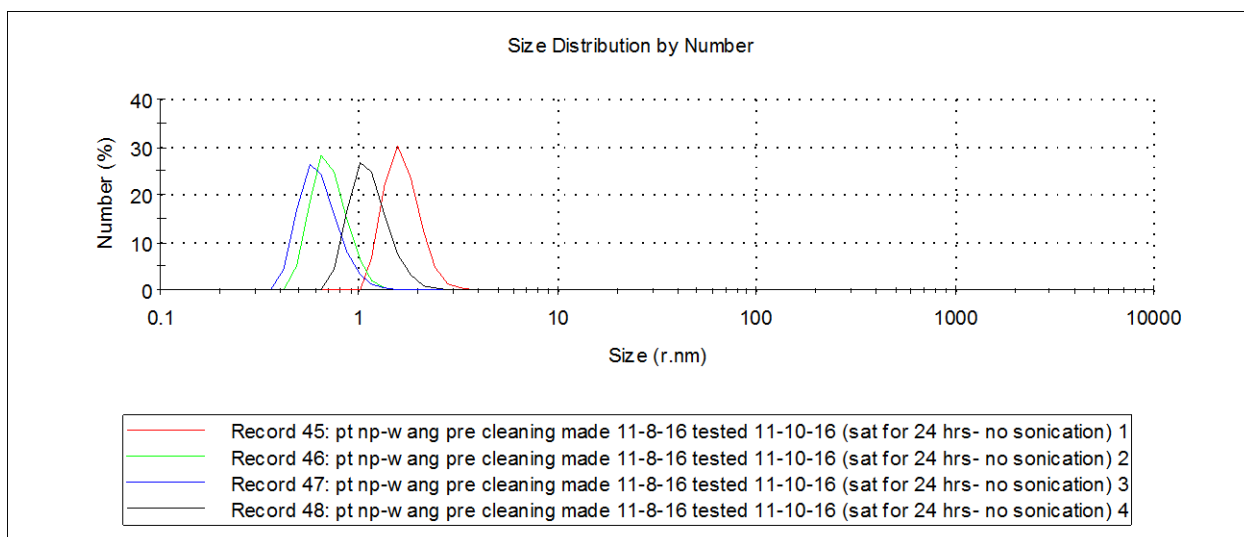


Figure 7b. DLS size distribution for suspension 4

The mean particle size was found to be 1.05 ± 0.35 r.nm for suspension 3 and 0.98 ± 0.46 r.nm for the suspension 3. This result compares closely to the results found by Wang of about 1-2 nm and indicates that this may be another compatible synthesis method for reproducible small platinum nanoparticles.

In order to test the stability of the suspension, the particle size of suspension 4 was retested after 8 days of storage. Figure 8 shows the size distribution of suspension 4 obtained from DLS testing after 8 days of storage.

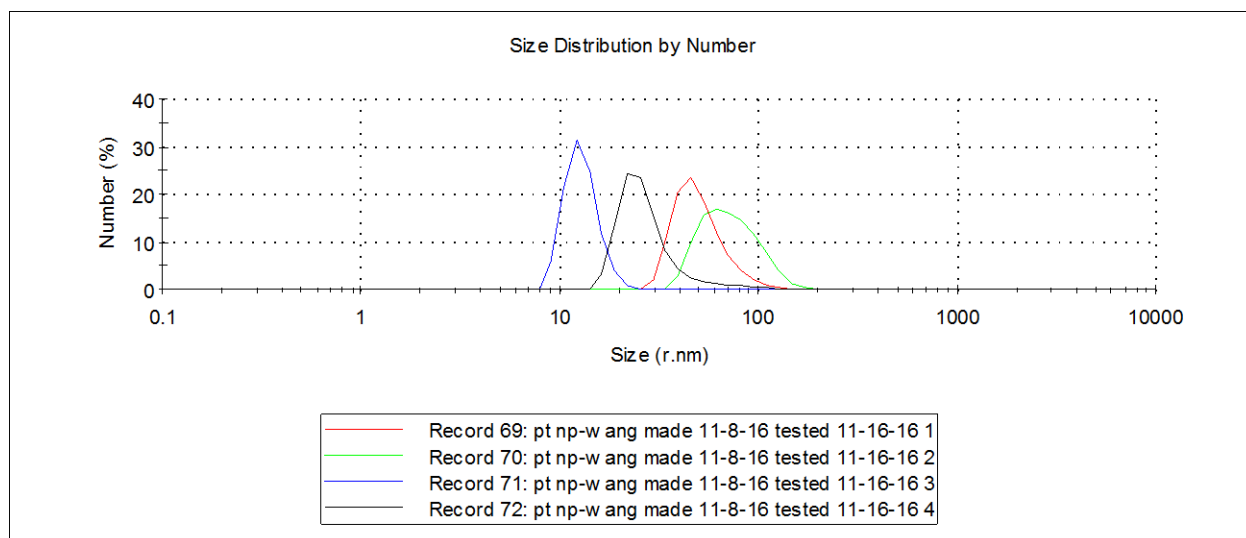


Figure 8. DLS size distribution for suspension 4 after 8 days of storage

As can be seen from the plot, the particles significantly aggregated after only 8 days. The mean particle size was found to be 35.2 ± 22.3 r.nm which indicates that platinum nanoparticles adsorbed to each other to form larger clusters over time. This may be due to the higher concentration of platinum used in the synthesis process. The Wang method used a concentration of 40 mmol/L $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ versus the Liu method which used a concentration of 5 mmol/L. This higher concentration may have caused an increase in interactive adsorptive forces between Pt particles which could overcome the stabilizing effects of the acetate ligands. Another possibility is that a malfunctioned occurred in the DLS testing process. In order to check for human error, the test was carefully conducted three more times all yielding similar results. Suspension 3 was also tested 22 days after its synthesis and a similarly aggregated particle size was found. From this point forward in experimentation multiple batches of platinum suspensions made using the same methods, as well as previously stored suspensions 1 and 2, all yielded similarly high particle size results from DLS testing. This points to the possibility that the DLS equipment may need to be calibrated, there is a contamination of lab equipment/chemical agents, or there is another unforeseen error causing these testing results.

The HCl adjustment of the platinum suspension proved to be more complicated than described by Liu and Wang. They did not go into a great deal of detail concerning the procedure for acidification, stating only that the solution was acidified to pH 3 (4 for Wang) by adding dilute 0.5 M HCl to the platinum suspension, followed by centrifugation. Because the platinum suspension consists of metal nanoparticles in ethylene glycol, the pH meter and pH paper were unable to provide accurate readings of pH. Therefore, the HCl to Pt suspension ratio for Liu's method was calculated stoichiometrically to be 1.34 mL 0.5 M HCl per 20 mL suspension based on the balanced reaction of the platinum precursor with ethylene glycol and hydroxide (equation 6). In order to test the validity of this theoretical calculation different ratios of acid to suspension were mixed and the resulting separation of platinum was observed. The theoretical ratio was found to be an underestimate as only higher ratios of HCl to Pt yielded significant separation of platinum

and supernatant. The best separation occurred with a ratio of 3.1 mL 0.5 M HCl per 20 mL suspension for the Pt nanoparticles produced from Liu's method and 7.33 mL 0.5 M HCl per 20 mL suspension for Wang's method. This discrepancy between theoretical and experimental values for pH adjustment may be due to the strong bonding and adsorption energy of suspended Pt nanoparticles, acetate, and hydroxide ions which is not easily overcome by acid base kinetic reactions. It may be beneficial to leave the solution for a period of time before centrifugation in order to allow the reaction to come to a more stable equilibrium. This way enough time may have passed in order for the acid to effectively neutralize hydroxide ions so that excess HCl does not have to be added.

The cleaning step performed by Liu et al. (2013) used ethanol as the cleaning agent while other research has identified DI water or acetone as other potential solvents (Chen et al. 2006). To find which cleaning solvent was most effective three 3 mL samples of platinum suspension were separated after pH adjustment and dissolved in 40 mL of DI water, ethanol, and acetone respectively. After centrifugation Pt particles had not been effectively separated from any of the solvents, although ethanol showed the most significant separation. The cleaning step was then repeated using 15 mL of ethanol, which yielded slightly better separation, but still not ideal. Interestingly, after storing this sample for two days room temperature, the Pt was completely separated from the ethanol. The Pt was then redispersed in 20 mL ethylene glycol and its particle size distribution was tested (Figure 9).

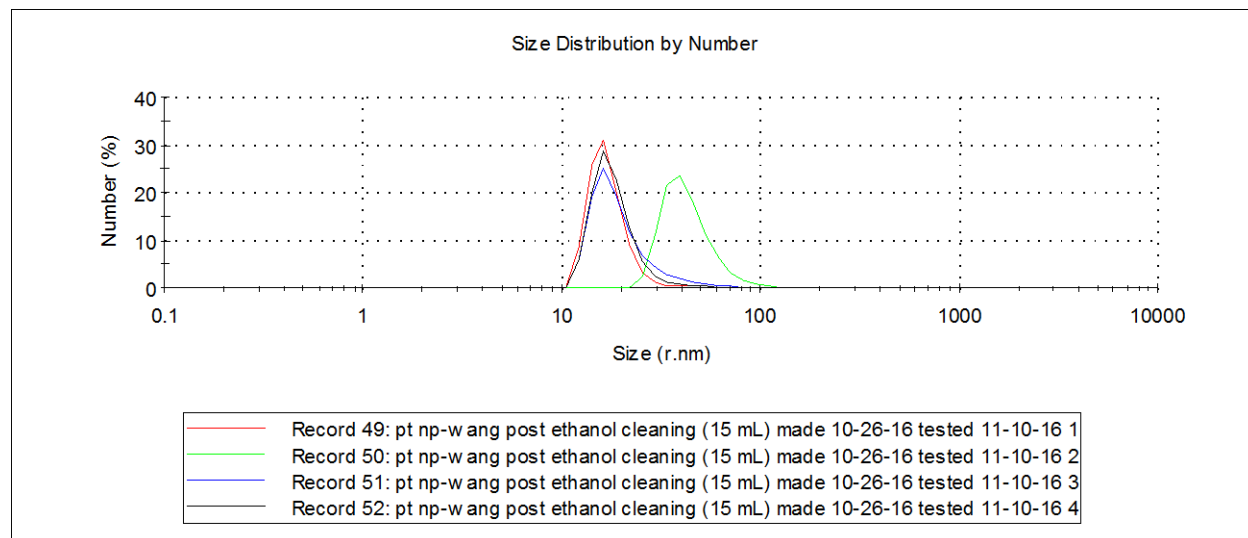


Figure 9. DLS size distribution for Pt redispersion after ethanol cleaning

DLS results yielded a mean particle size of 22.1 ± 11.5 r.nm indicating significant aggregation of pt nanoparticles. This ethanol cleaning step was repeated four more times using 20 mL of ethanol and similarly large particles between 10 and 40 r.nm were found. This aggregation may be due to the removal of stabilizing surfactant ions during the acidification and cleaning, simply due to the separation of Pt nanoparticles which caused them to aggregate because of the close proximity, or

due to the force of centrifugation which caused them to collide with one another to form larger clusters.

Unfortunately, non-aggregated platinum suspensions with particle size distributions close to those initially produced during experimentation were unable to be reproduced during the last phase of testing. Since the same procedure was used and DLS testing results showed that particles were 10 to 100 times larger than those initially produced, some error or equipment malfunction must have occurred preventing the reproduction of similar results. Due to time constraints this error could not be identified although as mentioned previously possible errors include calibration of DLS equipment, contamination of lab equipment/ chemicals, or another unforeseen error. Because of this the testing of dispersions in other solvents such as cyclopentanone or ethanol could not be completed. It is likely that these solvents would have failed to produce stable small sized nanoparticles due to the lack of acetate stabilizing ligands present from the ethylene glycol although it may be possible to that they could maintain the suspension long enough for the Pt particles to bond with dye molecules.

Conclusion

Due to time constraints and experimental hindrances, further research and testing is needed to effectively assess the compatibility of Pt nanoparticles synthesized by the methods used in this study with the dye molecules in dye sensitized solar cells. Raman spectroscopy should be performed on Pt suspensions with and without the cleaning step in order to test whether Pt is effectively bonded to the dye molecule. Although Raman spectroscopy was not performed important conclusions can still be made. This research shows that the thermal reduction in ethylene glycol of the H_2PtCl_6 precursor with NaOH can be an effective method for producing nanoscopic platinum colloid suspensions. Small particle size distributions were achieved using parameters based on methods described by both Liu et al. (2013) and Wang et al. (2000) Separation of Pt nanoparticles can be achieved using the experimental volumetric ratios for acidification found in this study. Ethanol was observed to be the most effective solvent for cleaning, although the resulting Pt redispersion was aggregated beyond desirable size distributions. These findings, along with future research into dye sensitized solar cell technology will pave the way for a cleaner, more sustainable, and more efficient energy source.

Appendices

Appendix A. Raw Particle Size Data from DLS Testing

Suspension Run	1	2	1 (10 days)	3	4	4 (8 days)	Ethanol 1
1	1.164	1.348	1.808	1.561	1.561	45.64	16.34
2	1.005	1.164	1.808	0.986	0.6846	61.21	39.41
3	1.164	1.412	0.647	0.7493	0.5587	12.18	16.34
4	0.4166	1.005	1.561	0.912	1.134	21.91	16.34
Mean	0.937	1.232	1.456	1.052	0.985	35.235	22.108
St. Dev.	0.355	0.184	0.552	0.353	0.457	22.301	11.535

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