Video Article

Generation of Zerovalent Metal Core Nanoparticles Using n-(2-aminoethyl)-3-aminosilanetriol

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Abstract

In this work, a facile one-pot reaction for the formation of metal nanoparticles in a water solution through the use of n-(2-aminoethyl)-3-aminosilanetriol is presented. This compound can be used to effectively reduce and complex metal salts into metal core nanoparticles coated with the compound. By controlling the concentrations of salt and silane one is able to control reaction rates, particle size, and nanoparticle coating. The effects of these changes were characterized through transmission electron microscopy (TEM), UV-Vis spectrometry (UV-Vis), Nuclear Magnetic Resonance spectroscopy (NMR) and Fourier Transform Infrared spectroscopy (FTIR). A unique aspect to this reaction is that usually silanes hydrolyze and cross-link in water; however, in this system the silane is water-soluble and stable. It is known that silicon and amino moieties can form complexes with metal salts. The silicon is known to extend its coordination sphere to form penta- or hexa-coordinated species. Furthermore, the silanol group can undergo hydrolysis to form a Si-O-Si silica network, thereby transforming the metal nanoparticles into a functionalized nanocomposites.

Video Link

The video component of this article can be found at http://www.jove.com/video/53507/

Introduction

As the demand and applications of designer nanomaterials increases, so do the various methods of synthesis. The "top-down" methods, such as laser ablation or chemical etching have been employed for their excellent controllability and capability of resolving materials reliably down to the sub-micron level. These methods rely on bulk materials being processed into finer components, which typically increase the cost of production as the desired nanostructure size decreases. An alternative method of synthesis to this is the "bottom-up" approach, which controls synthesis at the molecular level and builds up to the desired nanostructure. This imparts a significant degree of control on the desired self-assembly, functionality, passivity, and stability in the generation of these nanostructured materials[1]. By working from the molecular level, hybrid nanocomposites can be generated providing the benefits of both materials within the same structure.

As nanomaterials are synthesized through the bottom-up strategy, methods need to be employed to control particle size, shape, texture, hydrophobicity, porosity, charge, and functionality[2]. In metal core nanoparticle synthesis, the initial metal salt is reduced in an autocatalytic process to generate zero-valent particles, which in turn direct the nucleation of other particle. This leads to clustering and finally nanoparticle production[3]. In an effort to control the size of nanoparticles created and prevent them from precipitating out of solution, stabilizers such as ligands, surfactants, ionic charge, and large polymers are exploited for their ability to block nanoparticles from further agglomeration[4-10]. These materials inhibit the van der Waals attraction of the nanoparticles, either through steric hindrance due to the presence of bulky groups or through Coulombic repulsions[3].

In this work, a facile, one pot, synthetic strategy for the generation of various metal core nanoparticles using the silane, n-(2-aminoethyl)-3-aminosilanetriol (2-AST) is presented (**Figure 1**). Ligands on this compound are capable of reducing metal precursors and stabilizing metal nanoparticles with a relatively high efficacy. The three silanol moieties present are also capable of crosslinking and this forms an interconnected network of organosilane polymer impregnated with nanoparticles within its matrix (**Figure 2**). Unlike most silanes, which readily undergo hydrolysis in the presence of water, this compound is stabilized in water, which is beneficial for hydrophobicity purposes, stability, and control.

Protocol

Note: All reagents are used as is from manufacturer with no further purification. Reactions were monitored for up to one week via UV-Vis spectroscopy to ensure complete reduction. All reactions are carried out under a vent hood and appropriate safety attire is worn at all times, including gloves, eye goggles, and lab coats.

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1. Synthesis of Silver Nanoparticles

1. Weigh out 0.0169 g (0.1 mmol) of silver nitrate directly into a 50 ml Erlenmeyer flask.
2. Add in 20 ml of 18.2 MΩ of ultrapure water and a magnetic stirrer bar. Cover flask with stopper to prevent evaporation.
3. Place flask in an oil bath situated on a stirrer/hot plate and ensure that temperature is maintained at 60 °C.
4. Slowly add 144 µl (0.2 mmol) of 2-AST using a precision micropipette. Flush pipette several times in solution to ensure all silane is transferred into the solution.
5. Take UV-Vis spectroscopy readings according to protocol listed in Section 5.
6. After 6 hr, remove sample from the oil bath and transfer to a 20 ml sample vial for storage, TEM, FTIR and further analysis.
   Note: Synthesis of gold and palladium nanoparticles follows the same method and stoichiometric amounts with the exception of gold nanoparticles requiring 216 µl (0.3 mmol) 2-AST. The reaction may continue to produce nanoparticles for up to 2 weeks, but the rate is not significant compared to initial rate.

2. Transmission Electron Microscope (TEM) Sample Preparation

1. Ensure that sample has cooled to RT.
2. Place a 200 carbon-mesh formvar-coated copper grid onto a clean piece of filter paper.
3. Using a 1 ml plastic Pasteur pipette, cast-drop approximately 60 µl of the nanoparticle sample directly onto the grid.
4. Allow grid to dry for 24 hr before imaging.
5. Take high-resolution TEM images with the following conditions: 10 µA current and 100 kV accelerating voltage[22].

3. Nuclear Magnetic Resonance (NMR) Sample Preparation

Note: Perform NMR at RT. At high temperatures signals may coalesce, which degrades the quality of spectra obtained.

1. Using a precision pipette, pipette 50 µl of deuterium dioxide (D_2O) into a clean NMR tube.
2. With another clean precision pipette, pipette 400 µl of nanoparticle sample into the same NMR tube.
   1. As samples may adhere to the inner walls of the NMR tube, slowly add solutions into the NMR tube. If sample does adhere, cap the tube and shake the top of the tube to force the solution to the bottom.
3. Mix the sample by shaking and repeatedly inverting the NMR tube.
4. Place sample tube into the NMR following directions set by NMR protocol provided by manufacturer. An upwards of 1,000 scans may be necessary for proper resolution in a ^1H proton NMR pulse program.
   Note: NMR tube walls should be clean. It is recommended that the outer wall of the tube is wiped with a microfiber or lint free cloth prior to analysis for spectra clarity.
5. Discard sample when finished. Do not return sample to parent solution.

4. Fourier Transform Infrared (FTIR) Spectroscopy Sample Preparation

1. Place 2 ml of nanoparticle sample into a small glass container. A 3 ml tube or 1 dram glass vial works well.
2. Dry the samples by placing the glass container in a vacuum desiccator fitted with a stopcock.
3. Attach desiccator to vacuum pump apparatus. Drying of samples may take a few hours depending on vacuum strength. Consider samples dry after there is no visible liquid in container.
4. Scrape down the sample using a clean spatula and collect solid materials.
5. Place solid material onto ATR-FTIR spectroscope fitted with a ZnSe crystal diode laser.
6. Obtain FTIR spectra integrating 32 scans between 4,000-500 cm^{-1} with a spectral resolution of 2.0. Use the air background[23].

5. UV-Vis Spectroscopy Sample Preparation

1. Conduct UV-Vis spectroscopy on nanoparticle samples that are in a one to ten dilution of nanoparticle sample to water so that saturation does not occur in spectrometer analysis.
2. Remove nanoparticle samples for UV-Vis while reaction is running at half hour intervals.
3. Using a precision pipette, remove 100 µl of nanoparticle material and place into a plastic cuvette.
4. Add 1 ml of ultrapure water to the same cuvette and mix thoroughly by flushing the pipette several times.
5. Record UV-Vis absorbance spectrum between 250-800 nm.
6. After analysis, do not return sample to reaction. Dispose of analyte in an appropriate manner.

Representative Results

The reaction was monitored via UV-Vis spectrometry as nanoparticle formation should produce peaks characteristic for each individual metal nanoparticle. The final analysis of synthesized materials was accomplished through TEM and FTIR. The FTIR spectra was obtained from dried powder of samples. The particle size analysis can be accomplished by measuring nanoparticle diameter from images obtained via TEM and averaging results.

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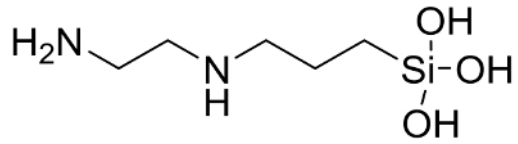
Complexation of nanoparticles with 2-AST silane can be verified with FTIR by the presence of characteristic peaks for silane and amine functionalities (**Figure 3C**, **5C**, & **6C**). Literature suggests the presence of Si-O-Si linkages can produce strong infrared absorption around 1,000 cm^{-1} with branching and extended polymer chains broadening this peak[20]. Peaks in the range of 1,550-1,650 cm^{-1} are attributed to NH_2 deformation. A moderate NH_2 stretch and NH wag can be seen at 3,000-2,750 cm^{-1} and 910-770 cm^{-1} respectively[19].

For silver nanoparticle synthesis, the starting materials were added to a preheated solution and the reaction was monitored until reduction was complete. The UV-Vis spectroscopic analysis of the product showed the formation of silver nanoparticles with an increasing peak at approximately 414 nm (**Figure 3A**), which followed the literature values of the surface plasmon resonance of silver nanoparticles formation[11, 12]. The concentration of silver nanoparticles increased until the reduction of the metal salt was complete. After 6 hr of the reaction, TEM analysis (**Figure 3B**) confirmed the presence of silver nanoparticles. The particle size analysis showed that the majority of the nanoparticles were in the 10 ± 2.3 nm size range. In order to better understand the role of our silane compound, a RT ^{1}H NMR of the silver nanoparticle solution was conducted (**Figure 4B**). It is believed that the coordination of the amine to nanoparticles gives rise to the new peaks between 2.73 to 3.40 δ. Furthermore, the samples were re-analyzed again after one year and retained the same characteristics, verifying the stability of the particles.

The reaction with gold chloride was carried out in the same manner as the silver nitrate nanoparticle synthesis. In the gold samples, an increasing peak in the 533 nm range over the course of 6 hr (**Figure 5A**) was observed, which is characteristic of the surface plasmon resonance band for gold nanoparticles[13, 14]. The particle size analysis calculated the average size to be approximately 24 ± 5.4 nm in diameter (**Figure 5B**). A ^{1}H NMR sample was prepared for the gold samples in the same manner as the silver (**Figure 4C**). The coordination of amines with the generated gold nanoparticles can be seen by the additional splitting peaks between 2.45-3.26 δ. These samples were also re-analyzed after one year and have been found to retain the same characteristics as the initial sample, which indicated that they too had good colloidal stability.

Palladium nanoparticles were synthesized in the same manner as the silver and gold reactions. It is well-known that a featureless spectra is obtained upon the production of Pd-nanoparticles; there is no observable λ_{max} increase in UV-Vis spectrometry from surface plasmon resonance (**Figure 6A**) as Pd^0 nanoparticles are produced[15, 16, 17]. However, TEM imaging and particle size analysis indicated that palladium nanoparticles, sized at 1.8 ± 0.56 nm in diameter (**Figure 6B**), were synthesized. A ^{1}H NMR sample was prepared for this sample following the same preparative methods as the previous nanoparticles (**Figure 4D**). In the samples, the coordination of amines with Pd^0 nanoparticles can be observed via the additional peaks between 2.81-3.26 δ.

N-(2-aminoethyl)-3-aminosilanetriol



Empirical Formula	$C_5H_{16}N_2O_3Si$
Molecular Weight	180.28
Specific Gravity	1.00
Flash Point	>110 °C
pH	10.0-10.5

Stable aqueous solutions due to internal hydrogen bonding.

Figure 1. Properties of n-(2-aminoethyl)-3-aminosilanetriol (2-AST). Please click here to view a larger version of this figure.

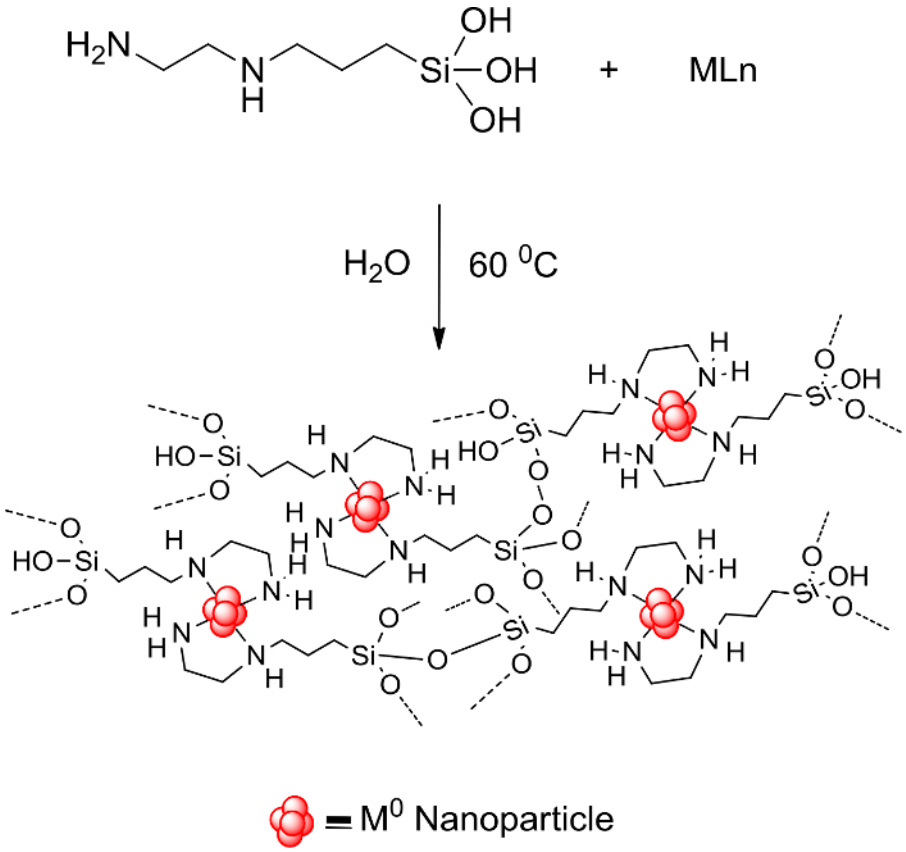


Figure 2. General scheme of the synthesis of 2-AST stabilized metal nanoparticles. Please click here to view a larger version of this figure.

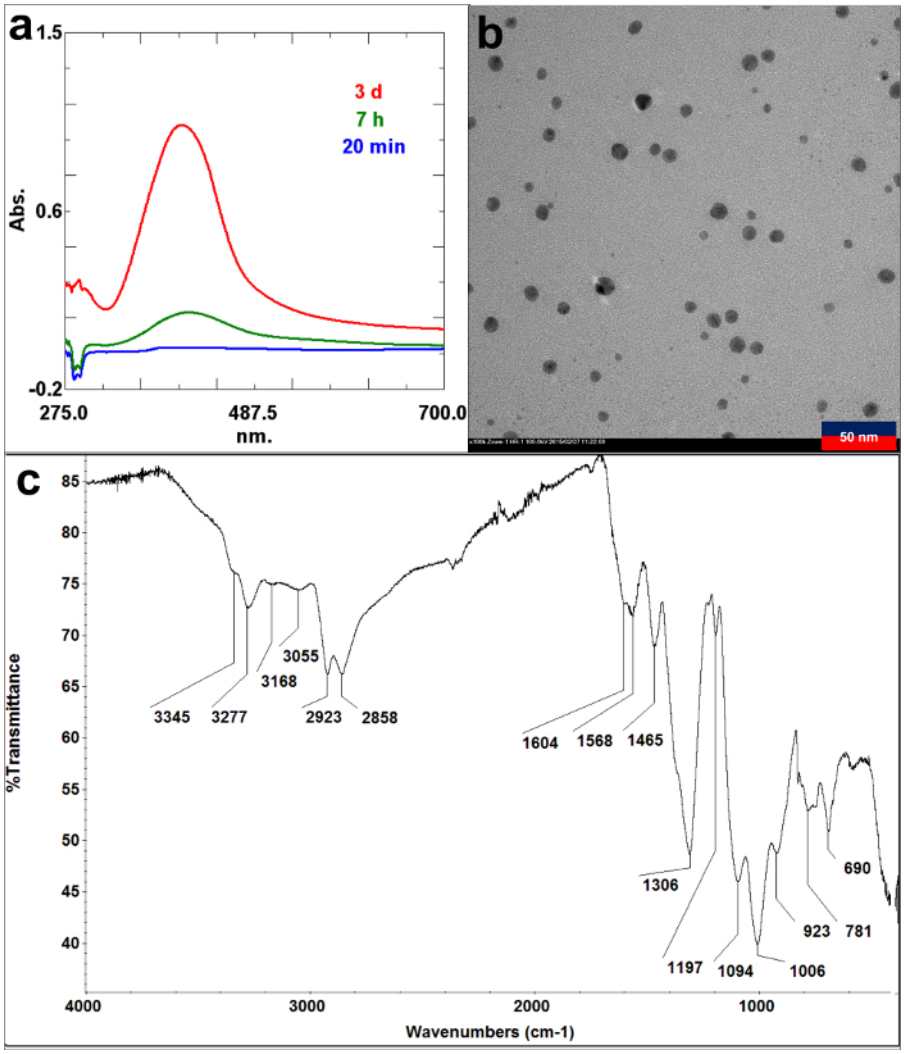


Figure 3. Silver Nanoparticles. (**A**) UV-Vis spectral analysis of silver nanoparticle reaction mixture at a 1-10 dilution was monitored over time. (**B**) TEM imaging of silver nanoparticle. (**C**) FTIR of dried silver nanoparticle solution. Please click here to view a larger version of this figure.

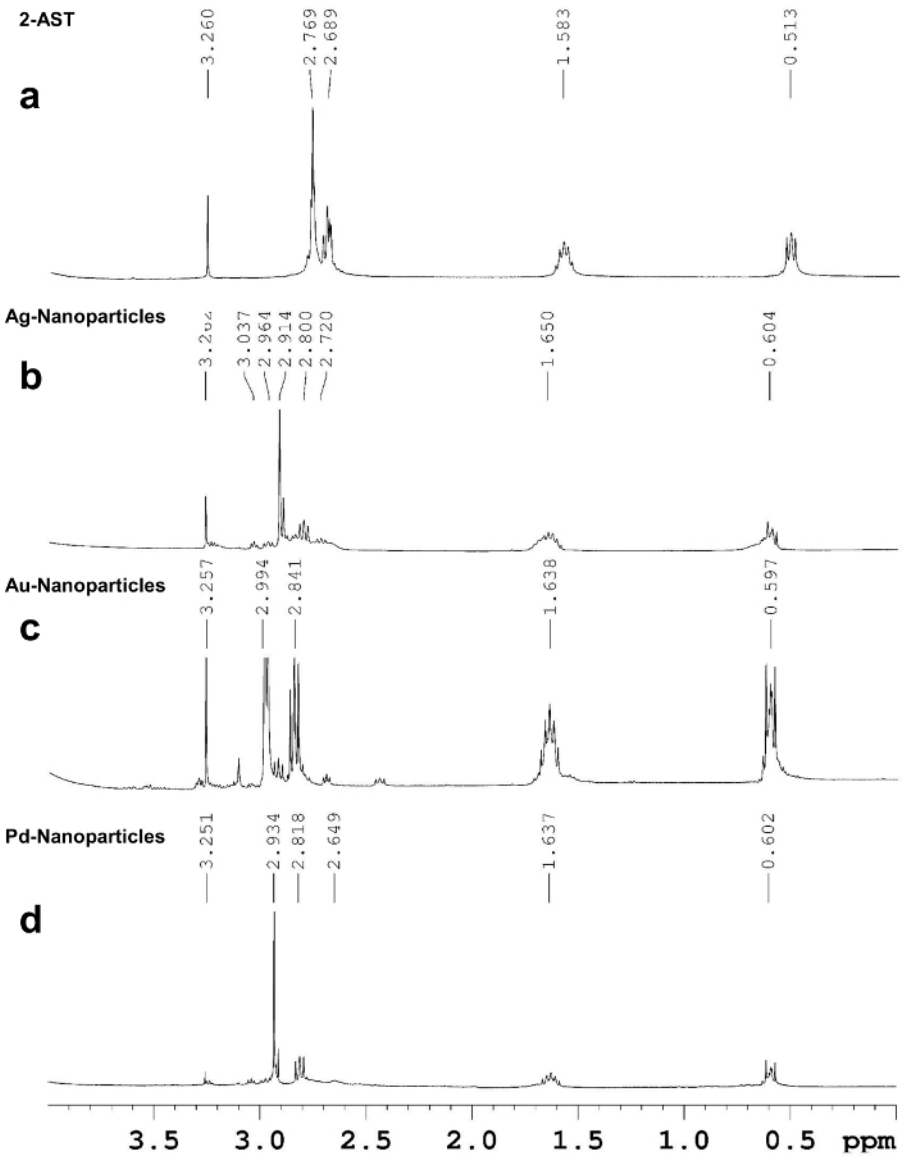


Figure 4. NMR Spectrometry. ^{1}H NMR of solution sample in D_2O. (**A**) n-(2-aminoethyl)-3-aminosilanetriol; (**B**) silver nanoparticles; (**C**) gold nanoparticles; (**D**) palladium nanoparticles. Please click here to view a larger version of this figure.

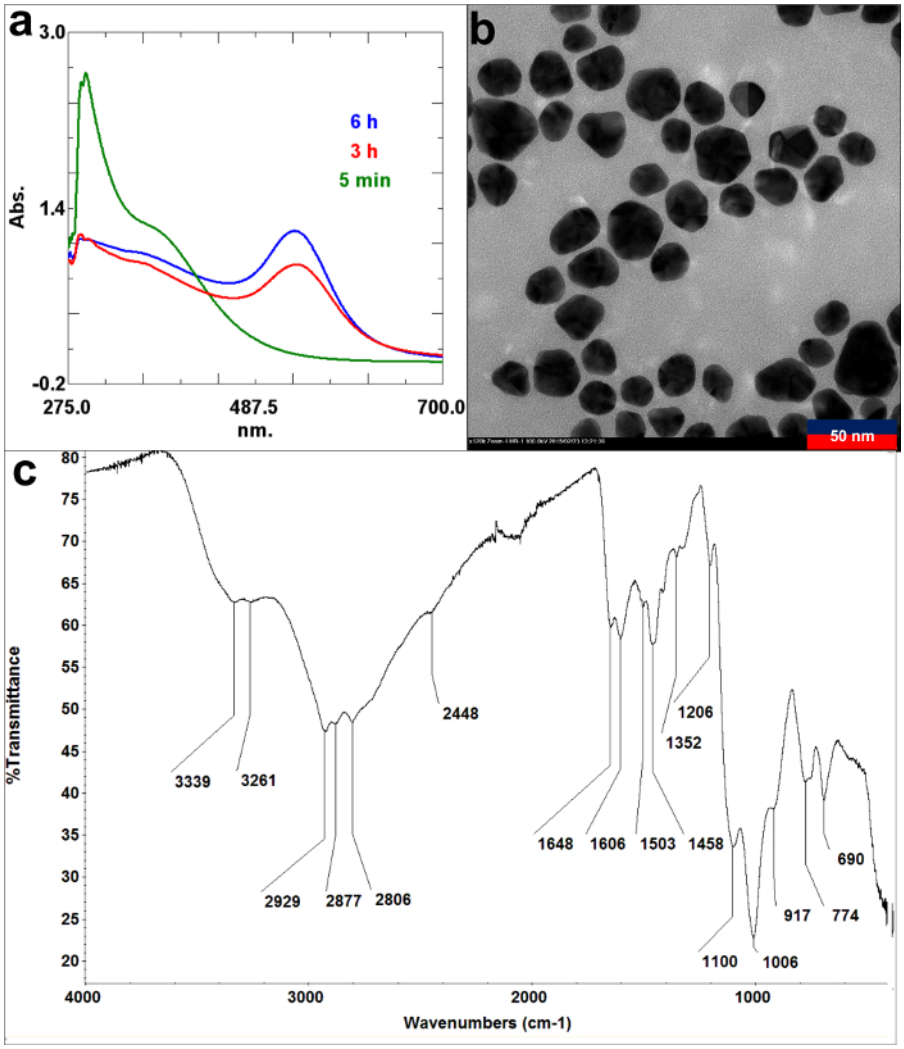


Figure 5. Gold Nanoparticles. (**A**) UV-Vis spectral analysis of gold nanoparticle reaction mixture at a 1-10 dilution was monitored over time. (**B**) TEM imaging of gold nanoparticles. (**C**) FTIR of dried gold nanoparticle solution. Please click here to view a larger version of this figure.

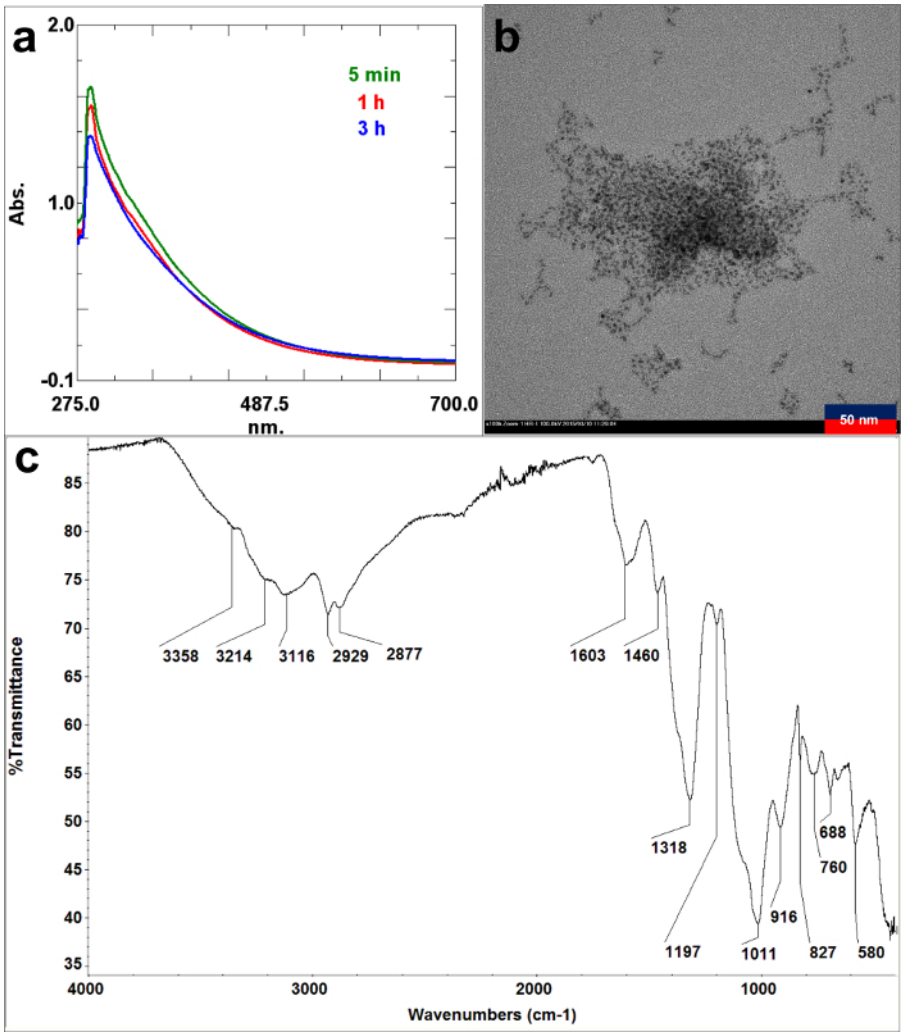


Figure 6. Palladium Nanoparticles. (**A**) UV-Vis spectral analysis of palladium nanoparticle reaction mixture at a 1-10 dilution was monitored over time. (**B**) TEM imaging of palladium nanoparticles. (**C**) FTIR of dried palladium nanoparticle solution. Please click here to view a larger version of this figure.

Discussion

Salts reported in this paper are the only salts that were tested of that metal. As a result, it is uncertain that this reaction strategy would work with all salts of the metals, particularly gold. The solubility of these salts in water may also affect the outcome of the reaction in terms of reaction time, morphology, and yields. In all reactions, the silane was added to an already dissolved metal salt solution.

It is worth noting that care must be taken to ensure accuracy for these reactions require a small concentration of metal salts, which may be hygroscopic or deliquescent[18]. This issue was experienced in the gold chloride nanoparticle synthesis as gold complexes are air sensitive and may decompose when left exposed to air. In an effort to alleviate this, gold chloride salt was stored in a refrigerator until needed and then removed, quickly measured and returned to refrigeration when complete. Also, since a condenser is not used with the reaction vessel, care should be taken that the solvent does not evaporate during the heating phase. Water used as the solvent should be of high purity. Contaminates in solvent and pH variations may affect nanoparticle formation.

The production of gold and silver nanoparticles takes place under mild reaction conditions, which bodes well for this protocol in industrial applications. This method allows one to produce noble metal nanoparticles in aqueous medium with high yields. A major advantage of this method is that it does not require any additional reducing agent, which is known to complicate the isolation of resulting nanoparticles as additional purification steps may be needed. It is expected that this protocol will extend to other metals as well. This method can also provide an avenue where the particles can be rendered heterogeneous via sol gel methods.

Moreover, most of the materials can be converted to gels via copolymerization with other gelation agents[21]. Research is already underway to prepare and analyze such gels. Ongoing research is directed towards generating such a nanocomposite, which will be interesting for applications in recoverable heterogeneous catalysis.

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Disclosures

There are no conflicting financial interests.

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