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# Continuous Synthesis of Monodisperse Ag Nanocubes

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**ABSTRACT:** The precise control of both the size and shape of Ag nanoparticles strongly influences their optical properties. Although the synthesis of Ag nanocubes with sharp corners and edges has been demonstrated, the ability to scale these approaches with high selectivity remains elusive. In this study, a continuous flow microwave-assisted reactor was used to separate nucleation from growth events, which provides a method to synthesize very uniform single crystalline Ag nanocubes. Nucleation in the microwave zone was enhanced through seed-mediated processes by sulfide formation, and a



chemical regulator was used in the growth zone to further improve the sharpness of the edges of the nanocubes. Transmission electron microscopy and optical properties were used to optimize the reaction conditions and Ag nanocubes with edge lengths of 28 and 45 nm were readily synthesized with narrow particle size distributions and high selectivities (>70%). Nanocubes with 28 nm edge lengths were used to prepare films to demonstrate the detection of Rhodamine 6G with concentrations down to 10 nM using surface enhanced Raman spectroscopy. These results indicate that continuous flow approaches have the potential to produce large quantities of uniform Ag nanocubes that can be used for sensing or other applications.

## INTRODUCTION

The ability to synthesize nanoparticles with fine control over particle size, shape, and composition is of scientific and technical interest since these parameters have a strong correlation with optical, electronic, physical, and chemical properties.<sup>1-4</sup> Recent studies have indicated that continuous flow methods can provide excellent control over the synthesis of nanoparticles with highly uniform sizes and shapes, and have the potential to scale to industrial quantities.<sup>5-9</sup> A benefit of continuous flow methods is that very precise control over temporal, thermal, and chemical conditions can be obtained. Ag nanoparticles have been widely studied due to their shape dependent properties, which provide unique control for applications including plasmonics, catalysis, and sensing via surface enhanced Raman scattering (SERS). These characteristics make Ag nanoparticles suitable to studies involving facet-selective catalysis,<sup>10,11</sup> high sensitivity sensing devices,<sup>12</sup> and light trapping in photovoltaics.<sup>13</sup>

There has been considerable interest in developing approaches that can synthesize Ag nanoparticles with well-controlled shapes and particle sizes. This includes using different silver precursors, reducing agents, solvents, and dispersants in order to achieve smaller particles with high uniformity and shape selectivity.<sup>14–20</sup> However, most of these approaches only allow small quantities of nanoparticles to be synthesized, and have limited scalability to larger quantities. Recent results have shown that biphasic-liquid segmented continuous flow methods can synthesize both Ag nanocubes and nanospheres, and are readily scalable in regard to production rates.<sup>8</sup> The potential benefits of using microwave radiation have been proposed for the scalable synthesis of

nanoparticles since microwave radiation can rapidly and uniformly heat reactants to high temperatures allowing fast nucleation rates, shorter reaction times, and increased conversion rates. Furthermore, the combination of microwave heating with continuous flow approaches can further improve scalability and allow the synthesis of highly uniform nanomaterials.<sup>21</sup> Recently, continuous flow microwave-assisted methods have been used in the synthesis of a range of nanomaterials, where improvements in reagent utilization, a significant reduction in reaction times, and a decrease in particle size distributions have all been demonstrated.<sup>9,22–25</sup>

Ag nanocubes have been shown to have superior sensing performance by SERS compared to Ag nanoparticles with random shapes or nanoparticles that are spherical.<sup>26</sup> This is due to resonance modes that are enhanced with specific particle sizes and shapes,<sup>27</sup> where oriented particles with truncated crystallographic facets exposing sets of (1 0 0) planes can increase the local electric fields due to charge accumulation on their sharp edges. This effect enhances the Raman signal, which significantly increases the detection sensitivity.<sup>28</sup> Colloidal nanoparticles synthesized using wet chemistry with defined surface chemistries can be easily modified and used for integrated SERS sensing measurements.<sup>29</sup> However, the shape-specific enhancement of Raman scattering signal depends strongly on the nanoparticle shape and size uniformity, which makes the synthetic approach crucial to optimizing sensing performance.

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In this study, a continuous flow microwave-assisted approach was used to synthesize Ag nanocubes. We have evaluated how reaction parameters allow control over Ag nanoparticle size and shape. Optimization of the reaction parameters allows us to demonstrate the scalable synthesis of Ag nanoparticles with excellent control over size and with high selectivity for nanocube shapes. Small Ag nanocubes, with sharp edges, were obtained by using a post reaction sodium bromide bath.

## EXPERIMENTAL SECTION

Synthesis of Ag Nanocubes. Chemicals. Silver trifluoroacetate (CF<sub>3</sub>COOAg  $\geq$  99.9%), poly(vinylpyrrolidone) (PVP with MW  $\approx$ 55,000), sodium hydrosulfide hydrate (>66.7%), (3-aminopropyl)triethoxysilane (99.0%) (APTES), rhodamine 6G (99.0%) (R6G), and phosphate buffered saline (PBS) solution (pH = 7.4) were obtained from Sigma-Aldrich. Sodium chloride (99.0%) and sodium bromide (99.0%) were obtained from EMD Millipore. Methanol, acetone, ethylene glycol (>99.0% - Batch 0000132351), and isopropanol (IPA) (ACS grade) were obtained from Macron Fine Chemicals. Anhydrous ethanol was obtained from Pharmco-Aaper. All chemicals were used as received except for ethylene glycol. Prior to synthesis the ethylene glycol was heated over 3 h in an open flask and was cooled in an ice bath right before preparation of reagents. Silver precursors and sodium hydrosulfide were stored in an N2-filled glovebox that maintained oxygen and moisture concentrations below 0.5 ppm. Sodium chloride and sodium bromide were stored in a desiccator.

Synthesis. The synthetic procedure reported in this study is a modification of an approach described elsewhere.<sup>18</sup> Two separate solutions were prepared prior to reaction using the continuous flow reactor. In a typical synthesis, flask 1 contained either 282, 423, or 846 mM of silver trifluoroacetate in 20 mL of ethylene glycol. Flask 2 had reagents that were mixed in the following order: first, 6.25 mL of a solution containing 20 mg/mL of PVP dissolved in ethylene glycol was mixed with 2.5 mL of a 3 mM solution of NaCl in ethylene glycol; then, ethylene glycol was added to the solution until the volume was 19.7 mL; finally, a 0.3 mL solution containing 3.5 mM of NaHS in ethylene glycol was added to the solution just prior to the start of the reaction. Both flasks were pumped into two PEEK "Y" mixers that were in series. The first mixer was used to uniformly mix the two precursor solutions and the second mixer was used to inject argon gas to create a segmented flow regime just prior to entering the microwave reactor. The reaction setup had two main parts. The first part was a microwave reactor from Sairem (Model PCCMWR340PVMR1PE GMP 30 K; 2.45 GHz; 3 kW) where the microwave zone temperature  $(T_{\rm MW})$  was monitored using an infrared camera (FLIR model E40). The total irradiated length was 4.7 cm and the volumetric flow rate was set at  $\sim$ 3.8 mL.min<sup>-1</sup>, which resulted in a microwave zone residence time of ~1.5 s (Teflon tubing – I.D. = 1/16 in.). The second part of the reaction setup is the growth zone, which consisted of a coil of the same tubing submerged in an oil bath held at 135 °C. The tubing had different lengths, which gave different growth bath residence times  $(\tau_{GB})$ . Coils of tubing with lengths of 23, 15, and 8 m were used which gave average growth bath residence times of 12, 8, and 4 min, respectively. After the growth bath, the reaction liquor flowed through a 1-m-long coil that was placed inside an ice bath after which the products were collected. Each solution received approximately 12.5 mg of PVP per mL of liquor dispersion. For reactions followed by a sodium bromide bath, 5 mL reaction liquor was added to a 50 mL flask containing 20 mL of 0.375 mM NaBr in ethylene glycol at 135 °C. The NaBr solution was heated for 45 min before injection of the product liquor. After the desired batch reaction time the product was collected.

Purification. The reaction liquor was centrifuged twice at 4500 rpm for 15 min. After the first centrifuge step, the supernatant was collected and precipitated at 8000 rpm for 10 min after the addition of twice as much acetone. Acetone was used to precipitate particles and remove excess PVP. 18 M $\Omega$  water was used to disperse particles and remove any remaining salts, ethylene glycol, and PVP. Particles were precipitated at 14,500 rpm for 15 min. This last step was repeated

once before dispersing particles in ethanol for storage or IPA for film deposition.

Characterization of Particles and Films. To form films, a dispersion of Ag nanoparticles in IPA was drop-cast onto glass slides and the solvents were evaporated in a N2 environment prior to characterization. Raman spectra were obtained using a Horiba-Jobin Yvon HR-800 Raman spectrometer with incident laser source ( $\lambda = 532$ nm). Absorbance measurements were obtained using an UV-vis spectrophotometer (Thermo Scientific Evolution 220). Measurements were performed from solutions containing five droplets of the reaction liquor in deionized water without any purification steps. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were obtained using a FEI Titan FEG with acceleration voltage at 200 kV and a FEI Quanta 600 FEG SEM with 20-30 kV accelerating voltage, respectively. For TEM imaging, samples were prepared from an ethanol dispersion of Ag nanoparticles, which was sonicated at 130 W for 2 min prior to use (Branson model 2510). The solution was drop-cast onto a carbon coated copper grid, which was mounted in the microscope after drying for 5 min at 60 °C. We used the TEM images to measured particle width  $(d_{\text{TEM}})$ , which will represent diameters (for spherical particles) and edge lengths (for cubic particles). TEM images were also used to estimate the selectivity (%) to the cubic shape from the total amount that also included spherical and octahedral particles.

**Film Preparation and Sensing Experiments.** Glass substrates were pretreated using a Piranha solution at 110 °C for 15 min and then rinsed with acetone, methanol, and deionized water. Glass substrates were then immersed for 1 h into a solution of 50  $\mu$ L of APTES in 50.0 mL anhydrous ethanol which was held at 50 °C. The substrates were then rinsed with ethanol and DI water three times to remove excessive APTES. Substrates were blown dry with N<sub>2</sub> gas. For deposition of the Ag nanocubes, 3 mL of purified product liquor was dispersed in 3 mL of IPA and the glass substrates were placed in this solution for different contact times that varied from 1 to 24 h. The resulting films were then rinsed with ethanol and dried. A drop of R6G solution in PBS was placed on the Ag nanocube covered substrate and left to dry at ambient temperature overnight. Measurements were performed within 24 h.

## RESULTS AND DISCUSSION

Concentration Effects. To demonstrate the effect that different concentrations of silver trifuoroacetate has on the synthesis of Ag nanoparticles we have performed experiments with  $T_{\rm MW}$  set to 185 °C and  $\tau_{\rm GB}$  fixed at 12 min. As the TEM images in Figure 1A-C show, the size and shape of the Ag nanoparticles are strongly influenced by the initial concentration of silver trifluoroacetate. When 282 mM silver trifluoroacetate was used, spheres were formed with a  $d_{\rm TEM} \sim$  $7 \pm 1$  nm. Increasing the concentrations to 423 and 846 mM resulted in cubes with edge lengths  $\sim$ 43 ± 5 nm and  $\sim$ 60 ± 6 nm, respectively. As Figure 1D shows, an increase in particle size led to a shift in the absorbance peaks for each of the samples. These peaks were centered at 394, 440, and 469 nm for the 282, 423, and 846 mM silver trifluoroacetate concentrations, respectively. The increase in particle size resulted in the formation of cubes with sharp features, which has been previously associated with a characteristic UV-vis feature at  $\sim$ 360 nm.<sup>18</sup> The absorbance peaks were not only due to absorption but also to light scattering. For example, absorbance peaks located between 400 and 700 nm are related to light scattering effects which are strongly correlated to particle size.<sup>30</sup> However, peaks located between 320 to 420 nm are due to resonances that are associated with the cubic shape of the particles.<sup>30</sup> A shoulder located at higher wavelengths (500-550 nm) was also observed for samples synthesized at higher concentrations (423 mM and 846 mM), which was

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**Figure 1.** TEM images of particles synthesized at  $T_{MW}$  = 185 °C,  $\tau_{GB}$  = 12 min using different concentrations of silver trifluoroacetate: (A) 282 mM, (B) 423 mM, and (C) 846 mM. (D) UV–vis spectra for the solutions of the as-synthesized particles from each concentration used.

previously associated with the formation of larger or agglomerated particles.<sup>15,31</sup> For 423 mM and 846 mM concentrations, shoulder peaks were located at 386 and 390 nm, respectively, which are consistent with the formation of cubic nanoparticles.

In Figure 1D, we found significant differences in the full width at the half-maximum (fwhm) for the most intense peak in the UV–vis spectra for the three concentrations. The scattering of light is a function of particle volume and broadness of the peak located in the 400–700 nm range is related to particle size distributions in a given sample. We found that the Ag nanocubes synthesized at 423 mM had the narrowest peak, and we used this concentration to further optimize the Ag nanocube size uniformity.

 $T_{MW}$  Effects. To determine the role of nucleation effects we have used three different microwave zone temperatures (i.e., 135, 155, and 185 °C) for a fixed silver trifluoroacetate concentration (423 mM). For these studies, only the MW zone was used for the reactions. This resulted in the synthesis of only spherical particles as determined by TEM. However, the UVvis spectra in Figure 2 shows that  $T_{\rm MW}$  has a significant impact on the fwhm of the main absorbance peaks when only using the MW reactor. The increase in fwhm of the UV-vis spectra is related to an increase in particle size distributions, since the formation of larger or smaller particles results in shifts in the absorbance spectra. Increasing  $T_{\rm MW}$  resulted in a blue shift and narrowing of the UV-vis peak, which indicates formation of smaller particles with narrower size distributions. This may be due to the higher nucleation rates at higher  $T_{MW}$ , which results in faster reaction kinetics and the formation of more nuclei resulting in higher particle uniformity.

To further characterize the role of  $T_{MW}$ , several experiments were performed with a fixed concentration of silver trifluoroacetate (423 mM), a fixed growth bath temperature (135 °C), and residence time (12 min). Figure 3A–D shows



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**Figure 2.** UV–vis spectra of samples synthesized using the microwave zone only with different  $T_{MW}$ 's being set for a fixed concentration of silver trifluoroacetate at 423 mM.



**Figure 3.** (A) UV–vis spectra for the Ag nanoparticles synthesized at different  $T_{MW}$  and the addition of the growth bath with  $\tau_{GB} = 12$  min. The concentration of silver trifluoroacetate was fixed at 423 mM. TEM images show nanoparticles obtained under those conditions for the respective  $T_{MW}$ : (B)  $T_{MW} = 135$  °C, (C)  $T_{MW} = 155$  °C, and (D)  $T_{MW} = 185$  °C.

that for higher  $T_{\rm MW}$ , a slight decrease in particle size was observed along with a reduction in the fwhm of the UV-vis spectra. The values for  $d_{\rm TEM}$  were 44.4  $\pm$  7.6, 43.2  $\pm$  5.6, and 42.6  $\pm$  5.2 nm when using  $T_{\rm MW}$  = 135, 155, and 185 °C, respectively. The changes in sizes, after the addition of the growth bath, are not significantly different and are within the variation obtained for each  $T_{\rm MW}$ . However, much sharper cubic shapes were obtained for the two higher  $T_{\rm MW}$ . In Figure 3A, an increase in intensity for the shoulder at ~515 nm was observed, especially for  $T_{\rm MW}$  = 135 °C, and a slight reduction of the fwhm was observed in the UV-vis spectra for  $T_{\rm MW}$  = 185 °C. We found that the features in the UV-vis spectra at ~360 nm and ~400 nm only appear for higher  $T_{\rm MW}$ , suggesting sharper cubic shapes for these conditions. This analysis is consistent with TEM results shown in Figure 3B,C.

 $\tau_{GB}$  Effects. To evaluate the role of the growth bath we have used three different  $\tau_{GB}$  (i.e., 4, 8, and 12 min) and three different  $T_{MW}$  (i.e., 135, 155, and 185 °C), with a constant silver

trifluoroacetate concentration (423 mM). Figure 4A–C shows UV–vis spectra for the different  $\tau_{\rm GB}$  and  $T_{\rm MW}$  values that were



Figure 4. UV–vis spectra of Ag nanoparticles synthesized using different  $\tau_{\rm GB}$  and different  $T_{\rm MW}$  for 423 mM silver trifluoroacetate. TEM average diameters/edge lengths ( $d_{\rm TEM}$ ) are summarized in (D) for different  $\tau_{\rm GB}$ .

used. There was a distinct red shift for the UV–vis peaks with longer  $\tau_{\rm GB}$ , as well as an increase in their fwhm. Figure 4D shows a summary of TEM results, which indicate an increase in  $d_{\rm TEM}$  for longer residence times. For the same  $\tau_{\rm GB}$ , a constant decrease in the  $d_{\rm TEM}$  was observed as  $T_{\rm MW}$  increased. However, the standard deviations shown in Figure 4D indicate that this difference is negligible. TEM results also indicated no change in nanoparticle shape until  $\tau_{\rm GB} = 12$  min, where only spherical particles were obtained for  $\tau_{\rm GB} \leq 8$  min.

Synthesis of Nanocubes with Edge Lengths <30 nm. To synthesize smaller Ag nanocubes we used lower silver trifluoroacetate concentrations (282 mM) and  $\tau_{\rm GB}$  = 12 min. We also added a sodium bromide bath at the end of the process to increase  $d_{\text{TEM}}$  while allowing formation of cubes with sharper edges.<sup>18</sup> Figure 5A shows that changing  $T_{MW}$  resulted in a small shift of the UV-vis spectra toward shorter wavelengths, which was also observed for the 423 mM silver trifluoroacetate precursor. Lower  $T_{\rm MW}$  resulted in larger nanoparticles and an increase in UV-vis fwhm as shown in Figure 5A. Figure 5B shows a TEM image of the synthesized nanoparticles after 20 min in the sodium bromide batch. Before the sodium bromide bath, the Ag nanoparticle size was  $7 \pm 1$  nm, as shown in Figure 1A. After 20 min in the sodium bromide batch, Ag nanocubes had  $d_{\text{TEM}} = 28 \pm 4$  nm. The increase in Ag nanoparticle size, and formation of Ag nanocubes with flat edges, resulted in a red shift in the absorbance peaks, as well as the appearance of two features at ~360 nm in the UV-vis spectra. A controlled concentration ratio of chlorides and bromides has been used to help formation of smaller and sharper metal nanocubes.<sup>32</sup> Chlorides and bromides act as capping agents for the  $(1 \ 0 \ 0)$ facet while also regulating reduction rates due to the formation of silver bromides and chlorides in the reaction medium.<sup>33</sup> As



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**Figure 5.** (A) UV–vis spectra of samples synthesized with 282 mM of silver trifluoroacetate with different  $T_{MW}$ 's being used and with a  $\tau_{GB}$  = 12 min. For the  $T_{MW}$  = 185 °C, samples had an additional batch growth containing NaBr which are also included in (A). (B) TEM image of nanocubes synthesized using  $T_{MW}$  = 185 °C and 20 min of NaBr batch. (C) HRTEM image of a single nanocube, and (D) SAED of single crystal cube shown in (C).

 $Ag^+$  is consumed, the respective halide salt slowly dissolves, inducing particle growth and preventing new nucleation by limiting the amount of  $Ag^+$  available for the reduction reaction.<sup>18</sup>

High-resolution TEM images are shown in Figure 5C, where a 0.20 nm *d*-spacing was obtained from the image, which corresponds to the (0 2 0) plane spacing for Ag. Figure 5D shows the selected-area electron diffraction (SAED) pattern obtained from the single particle shown in Figure 5C. An analysis for the SAED pattern gave *d*-spacings of 0.210, 0.143, 0.110, and 0.091 nm, which correspond to the atomic planes (2 0 0), (2 2 0), (0 -4 0), and (4 2 0), respectively. These results confirm formation of single crystalline Ag nanocubes.

Selectivity Results for Each Synthetic Route That Resulted in Cubes. In these experiments, we developed three different routes for the synthesis of Ag nanocubes with  $d_{\text{TEM}}$ ranging from ~28 to 58 nm. An analysis of the selectivity for Ag nanocube size and shape was performed to evaluate each synthetic approach. Figure 6A shows the  $d_{\text{TEM}}$  and the selectivity to Ag nanocubes for each synthetic process. For this analysis, we compared different silver trifluoroacetate concentrations, and the addition of a 20 min sodium bromide batch process for Ag nanocubes synthesized with 282 mM silver trifluoroacetate. Higher silver trifluoroacetate concentrations resulted in an increase in the average size of the Ag nanoparticles, while the formation of larger particles resulted in a decrease in the selectivity to the formation of nanocubes. Selectivities for the formation of Ag nanocubes were 78%, 75%, and 40% as the silver trifluoroacetate concentrations were increased from 282 (including the bromide batch), 423, and 846 mM, respectively.

Although  $T_{MW}$  had a noticeable effect on the absorbance spectra for samples synthesized only using the microwave zone



**Figure 6.** Selectivity and TEM average diameter or edge length for spherical and cubic particles, respectively, were summarized. (A) Average edge lengths for the three routes ( $T_{\rm MW}$  = 185 °C,  $\tau_{\rm GB}$  = 12 min/Different silver trifluoroacetate concentrations) to synthesize ~28, 42, and 58 nm Ag nanocubes. (B) Average edge length/diameter ( $d_{\rm TEM}$ ) and selectivity for different  $T_{\rm MW}$ 's,  $\tau_{\rm GB}$  = 12 min, and silver trifluoroacetate concentration = 423 mM.

(Figure 2), Figure 6B shows that  $T_{\rm MW}$  had little influence on the final particle size after the growth bath. However, we found that selectivities were significantly improved (~73.3% and 75.0%) for the highest  $T_{\rm MW}$  (155 and 185 °C), respectively, compared to no formation of cubes for  $T_{\rm MW}$  = 135 °C.

A wide variety of synthetic procedures have been developed resulting in Ag nanocubes with high purity and sizes varying 15-60 nm. Synthetic approaches included the use of water as the only solvent,<sup>34</sup> different glycols as solvents,<sup>35</sup> the addition of sodium hydrosulfide,<sup>31</sup> and the use of bromide ions as capping agents.<sup>18</sup> The use of sodium hydrosulfide significantly reduced reaction times and the use of bromide ions have yielded nanocubes with higher selectivity.<sup>18</sup> These approaches were effective in the synthesis of Ag nanocubes; however, these methods produce small quantities and rely on batch reactors, which results in scalability issues.<sup>36–38</sup> The synthesis of silver nanocubes with edge lengths varying from 20 to 48 nm using a continuous flow has been demonstrated.<sup>8</sup> However, much lower shape selectivities were obtained for the synthesis of smaller Ag particles using this approach. In our studies, the segmented flow microwave-assisted reactor method resulted in Ag nanocubes with  $d_{\text{TEM}} \sim 28$  and  $\sim 44$  nm, a narrow particle size distribution, and high cube selectivities above 70%. These results suggest that this continuous flow methods could be effective for the scaleup of nanomaterials synthesis with excellent control of both size and shape, and that microwaveassisted approaches may provide further benefits.

**SERS Sensing Using Ag Nanocubes.** To prepare samples for SERS experiments we have varied the substrate contact time with the Ag nanocube solution. This process controlled the quantity of Ag nanocubes adsorbed to the substrate surface. Figure 7 shows SEM images of Ag nanocube films after 5 and 24 h substrate contact times with the Ag nanocube solution. Figure 7A shows that after 5 h, isolated Ag nanocubes were observed on the substrate, while Figure 7B shows that after 24 h contact time, Ag nanocube islands were observed on the substrate. The increase in the number of silver nanoparticles for increased substrate contact times is due to the attraction of the particles to the amino functionalized surface.<sup>39</sup>

To illustrate that the synthesized Ag nanocubes can be used for SERS we have performed experiments on substrates prepared in different ways to determine the sensitivity for a probe molecule (R6G). Figure 8 shows Raman spectra



Figure 7. SEM images of Ag nanoparticles after different contact times with the Ag nanocube solution. (A) 5 h of contact time and (B) 24 h of contact time. Scale bar in insets corresponds to 50 nm.



Figure 8. Raman spectra of Rhodamine 6G when Ag nanocubes were present and when bare glass samples were prepared.

obtained using SERS with R6G for substrates prepared using different contact times with the Ag nanocube solution. The main vibrational modes of R6G were detected at 1652, 1576, 1512, and 1365 cm<sup>-1</sup>, which correspond to aromatic stretching modes of C-C bonds. Other vibrational modes for R6G were also observed at 1314 (C-O-C stretching mode), and 1184 and 1130 cm<sup>-1</sup>, which have been assigned to C–H in-plane bending modes.<sup>40,41</sup> As indicated in the lower portion of Figure 8, no R6G peaks could be detected when bare glass substrates were used for the range of concentrations explored in this study. For substrates prepared using 5 h contact times with the Ag nanocube solution the Raman signal was found to decrease when the R6G concentration decreased from  $10^{-4}$  to  $10^{-8}$  M. To increase the signal-to-noise for the Raman signal we also characterized substrates prepared using 24 h contact times with the Ag nanocube solution. This procedure resulted in an average increase in intensity of  $\sim$ 5× compared to films with 5 h of contact time. The enhancement of the Raman signal results from an increase in the electric field close to the sharp edges for the Ag nanocubes, and the narrow gap between the metallic nanoparticles.<sup>29,42</sup> The increase in electric field strength results in an enhancement of the Raman intensities which provides high sensitivity, even for R6G concentrations as low as 10 nM.

# CONCLUSIONS

In summary, we have developed a scalable approach for the synthesis of Ag nanocubes with high cube selectivities. Three different processes were developed which resulted in Ag nanocubes with  $d_{\text{TEM}} = 28$ , 45, and 58 nm. The optimization of the reaction parameters ( $T_{\text{MW}}$ ,  $\tau_{\text{GB}}$ , and silver precursor concentrations) indicated that the process has excellent control with narrow particle size distributions and high selectivity to

cubic shapes (>70%) for  $d_{\text{TEM}} = 28$  and 45 nm. Smaller particles were formed when higher  $T_{\text{MW}}$  were used, which demonstrates that uniform, rapid nucleation rates in the microwave zone are important for controlling size and shape of the Ag nanocubes. These results were confirmed by a reduction in the fwhm and a blue-shift in the UV–vis absorption spectra. Residence time dependence in the growth bath indicated an increase in Ag particle sizes as longer reactions were performed; however, Ag nanocubes only formed after  $\tau_{\text{GB}} = 12$  min. Silver trifluoroacetate concentrations had the largest impact on particle sizes for the synthesis of Ag nanocubes. Larger concentrations yield a larger number of nuclei, but can also result in higher growth rates resulting in the formation of larger particles over the course of the reaction.

SERS sensing experiments performed with Ag nanocubes  $(d_{\text{TEM}} = 28 \text{ nm})$  were used to detect R6G at very low concentrations (~10 nM). The Ag nanocubes resulted in an enhancement of the Raman signal and allowed the detection of RG6. A significant increase of the Raman signal was observed when the nanocubes formed clusters on the surface as opposed to isolated particles. The Ag nanocube clusters result in an increase of the local electric fields at the narrow insulating gap between conductive particles. Films with clusters of Ag nanocubes had a 5× more intense Raman signal for R6G compared to isolated Ag nanocubes.

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## Notes

The authors declare no competing financial interest.

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