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Development of a New Generation of Stable, Tunable, and Catalytically Active Nanoparticles Produced by Helium Nanodroplet Deposition Method

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ABSTRACT: Nanoparticles (NPs) are revolutionizing many areas of science and technology, often delivering unprecedented improvements to properties of the conventional materials. However, despite important advances in NPs synthesis and applications, numerous challenges still remain. Development of alternative synthetic method capable of producing very uniform, extremely clean and very stable NPs is urgently needed. If successful, such method can potentially transform several areas of nanoscience, including environmental and energy related catalysis. Here we present the first experimental demonstration of catalytically active NPs synthesis achieved by the helium nanodroplet isolation method. This alternative method of NPs fabrication and deposition produces narrowly distributed, clean, and remarkably stable NPs. The fabrication is achieved inside ultra-low temperature, superfluid helium nanodroplets, which can be subsequently deposited onto any substrate. This technique is universal enough to be applied to nearly any element, while achieving high deposition rates for single element as well as composite core-shell NPs.

TOC GRAPHICS

KEYWORDS Nanoparticles, Helium Nanodroplet, Catalysis

Nanoparticles (NPs) are revolutionizing many devices and technologies which are shaping our lives, such as fuel cells¹, photocatalysis², and solar power³, to name a few. This utility is generally a result of four characteristics of NPs: their high surface area, their size-tunable properties, their morphology-dependent properties, and the dominant role that quantum mechanical effects play at this scale (*e.g.* quantum confinement)⁴. Despite many important advances in NP synthesis and applications, many challenges still remain. From a practical point of view, NPs produced by conventional methods often exhibit a fairly wide range of particle sizes, which results in substantial variability in their properties. Moreover, conventional methods of controlling NPs size and shape by utilizing capping agents⁵ result in surface contamination, which can undermine many of the NP benefits, particularly for catalysis. Subsequent attempts to remove capping agents often lead to agglomeration of the NPs, and, as a result, loss of their unique properties. Finally, NPs produced by conventional methods often suffer from poor stability under realistic application conditions, which also limit their practical use. The limitations mentioned above do not apply to all synthetic methods to the same extent, however. For example, mass selective method of NPs' synthesis can produce a narrow size distribution by applying quadrupole filters to select clusters of specific mass-to-charge ratios⁶. Given the complexity of this size-selection approach and low yield, however, exploring a wide range of sizes and producing more complex, composite structures (*e.g.* core-shell nanocatalysts)⁷ is impractical. Here we present the first experimental demonstration of catalytically active nanoparticles produced by a new alternative method: helium nanodroplet isolation. This NP fabrication and deposition methodology produces narrowly distributed, clean, and remarkably stable NPs formed inside ultra-low temperature, superfluid helium nanodroplets and deposits them onto any substrate. Furthermore, the technique is general enough to be applied to nearly

any element and is capable of producing complex core-shell particles at deposition rates as high as 10^{12} nanoparticles/second⁸.

Scheme 1. Helium nanodroplet deposition system. Nanodroplets are produced by expanding helium through a low temperature nozzle into a vacuum. The expansion is skimmed to form a beam which passed through a vapor cloud of a metal, in this case Au. When atoms collide with the nanodroplets, they condense inside to form nanoparticles which are then deposited onto a substrate down beam.

^4He , the most abundant isotope of helium, has a number of advantageous properties, which make it an attractive medium in which to produce NPs. Given the very weak He-He interactions, it remains liquid even at temperature near absolute zero and atmospheric pressure⁹. Moreover, at temperatures below the λ -point (2.2 K), ^4He transitions to a superfluid state, which exhibits unique physicochemical properties, such as near zero viscosity and a thermal conductivity approaching infinity¹⁰. These unusual properties can be exploited to fabricate NPs by first producing a beam of helium nanodroplets in a supersonic expansion from a temperature controlled nozzle into a vacuum and then capturing and condensing individual vaporized atoms of almost any element into NPs within the droplets.¹⁰⁻¹¹ Each droplet contains between 10^3 - 10^8 helium atoms (tunable by varying the nozzle temperature, T_n) and cools to ~ 0.4 K through the evaporation of helium atoms, thereby dissipating excess thermal energy of the captured atoms very efficiently.^{11a} Since this process occurs in vacuum with well controlled vapor clouds, these

“nanoscale cryostats” produce extremely clean NPs and, as a consequence, can offer unique advantages over other NP synthesis and deposition methods. Furthermore, the size distribution of the resulting NPs is remarkably narrow ($\Delta D < 0.3 D$), and is governed by favorable Poisson capture and nanodroplet formation statistics. Scheme 1 illustrates the helium nanodroplet deposition instrument used in this study. This method has been successfully demonstrated to produce a range of NP materials^{8b, 12}.

In this study, the capabilities of the helium nanodroplet method for the synthesis of tunable, stable and catalytically active NPs is demonstrated by depositing extremely small Au clusters on transmission electron microscope (TEM) grids, TiO₂ modified Environmental TEM (E-TEM) chips and TiO₂ single crystals. Subsequent TEM, E-TEM and catalytic ultra-high vacuum (UHV) studies of supported NPs have established several very unique properties of these samples. In the initial stage of the experiments, Au NPs were deposited on TEM grids in order to provide a general picture of the Au NPs produced by the helium nanodroplet method. Six samples were produced, utilizing two nozzle temperatures (T_N) of 6 K and 16 K, with three different deposition times (t_D) of 15, 45 and 135 minutes. The results are presented in Figure S1 in supplementary information (SI), which demonstrates the ability to tune the size of the clusters over a range of diameters (<0.75 nm to >3 nm). It is important to highlight that the sample produced using the highest nozzle temperature (T_N =16 K) and the shortest deposition time (t_D = 15 min), had the smallest average particle size that has been reported to date in the literature describing helium droplet method. These results confirm that this method has significant potential to produce tunable, small size NPs with a well-controlled size distribution.

In order to determine the stability of these supported Au clusters produced by the helium droplet method under realistic environmental conditions we utilized the E-TEM technique. By relying on

Figure 1. Typical STEM images and size distributions of gold nanoparticles deposited on TiO₂ coated DENS chips under different conditions in ETEM. (a) under vacuum at RT; (b) under 1 torr of mixture of CO and O₂ at RT; (c) under 1 torr of mixture of CO and O₂ at 373 K; (d) under 1 torr of mixture of CO and O₂ at 473 K.

a substantial body of literature concerning the catalytic activity of supported Au NP for CO oxidation, including studies of Au supported on TiO₂¹³, we modified a DENSsolutions' E-TEM chip with TiO₂ using physical vapor deposition (PVD). The sample was then transferred to helium nanodroplet deposition system for modification with Au NPs using $T_N = 6$ K and t_D min deposition conditions. Following the deposition, the sample was transferred to E-TEM for

Figure 2. Atomic resolution STEM image of focus ion beam milled interface of Au nanoparticles on a TiO₂ single crystal surface. The bright substance on top is the ZnO cap. The shape of Au nanoparticle is clearly shown.

characterization of the stability of the NPs under catalytically relevant conditions. Figure 1 shows medium angle annular dark field scanning TEM (STEM) images of Au NPs, together with their corresponding size distributions. These images were obtained during exposure of the sample to 1 Torr of CO and O₂ at different temperatures. Unexpectedly, the Au NPs remained stable up to 473 K, which was remarkably different from the published studies describing Au NP sintering during the CO oxidation reaction¹⁴ conducted in 300-410 K temperature range. This

Figure 3. TPR result and XPS spectra before and after TPR experiment. (a) Mass spectrometer (MS) signal of $^{13}\text{CO}_2$ indicates the catalytic activity of CO oxidation at around 300 K; (b) Au 4f XPS spectra (i) before dosing of gases and heating and (ii) after dosing of gases and heating to 373 K.

observation highlights the excellent stability of the Au NPs produced by this method under catalytically relevant conditions. In a recent paper, Haberfehlner *et al.* reported that NPs deposited by this method can undergo flattening due to a hard landing¹⁵ whereas other deposition studies have demonstrated soft landing^{8b, 12}. Calculations by deLara-Castells¹⁶ indicated that an Au atom in a small He droplet landing on TiO_2 is indeed a soft landing process. However, a unique feature of helium droplet method is that it offers a powerful means of controlling landing conditions by varying the excess helium in the droplet, which can serve to dissipate collision energy of the metal NPs residing inside, at the time of landing. By controlling the nozzle temperature, it is possible to tune the landing conditions for the nanoparticle. Also, since virtually any material can be deposited on any substrate, they can also be compared to isolated particle-substrate interactions. This can have important implications for the catalytic activity and stability of such particles, as both shape and interfacial geometry can have profound effect on both of these properties^{13d, 13f, 17}. To examine the particle-substrate interface more closely, Au

NPs samples deposited onto TiO₂ single crystal were coated with a layer of ZnO and then cross-sectioned with a Focused Ion Beam (FIB) prior to imaging in a TEM. Figure 2 shows such an image clearly indicating a ~ 2.5 nm and ~ 3.7 nm Au NPs that have been only slightly flattened upon deposition.

To examine the catalytic activity of the helium droplet fabricated NPs, temperature-programmed reaction (TPR) experiments were conducted under the UHV conditions. More specifically, the Au NPs were deposited onto a rutile (110) single crystal by utilizing the same conditions as those used in E-TEM experiments ($T_N = 6$ K and $t_D = 135$ min). The crystal was then transferred into UHV chamber to perform ¹³CO oxidation TPR experiments. The results presented in Figure 3a show an onset of CO oxidation at around 300 K consistent with published data¹⁸. Controlled experiment also ruled out the possibility that the catalytic activity may originate from TiO₂ single crystal (see Figure S2 in SI). The X-ray photoelectron spectroscopy (XPS) spectra of the sample before and after TPR experiment are shown in Figure 3b. As evident from Figure 3b, no significant changes were observed in Au 4f XPS spectra, indicating good stability of Au NPs during CO oxidation. Further heating the sample up to 475 K resulted in no notable changes in the XPS spectra, which is consistent with E-TEM results described earlier (see Figure S3 in SI). These results again confirmed the exceptional stability and the catalytic activity of the Au NPs produced and deposited by the helium nanodroplet method.

In conclusion, we experimentally demonstrated the promising capability of the helium nanodroplet method to produce well-defined, clean and stable NPs. We also showed that the particle sizes can be tuned down to average sizes below 1 nm by controlling the nozzle and oven temperatures. An unexpected stability of deposited NPs offers a unique pathway of controlling NP interactions with substrate by tuning landing conditions with He cushions. This pathway also

offers a potentially transformative opportunity to tune catalytic activity NPs by controlling the shape of nanoparticles and degree of their interactions with substrate. Although the particles' geometry and their stability on the surface can be also influenced by both particle size and substrate composition, as demonstrated in the published literature¹⁹ and our own work²⁰, the future experiments will systematically explore these factors. Finally, this research also presented the first ever demonstration of catalytic activity of NPs produced by the helium nanodroplet method.

ASSOCIATED CONTENT

Supporting Information.

The following file are available free of charge.

Experimental methods; Figure S1, figure S2, and figure S3.

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Notes

The authors declare no competing financial interests.

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