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A new method to prepare colloids of size-controlled clusters from a matrix assembly cluster source

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A new method for the production of colloidal suspensions of physically deposited clusters is demonstrated. A cluster source has been used to deposit size-controlled clusters onto water-soluble polymer films, which are then dissolved to produce colloidal suspensions of clusters encapsulated with polymer molecules. This process has been demonstrated using different cluster materials (Au and Ag) and polymers (polyvinylpyrrolidone, polyvinyl alcohol, and polyethylene glycol). Scanning transmission electron microscopy of the clusters before and after colloidal dispersion confirms that the polymers act as stabilizing agents. We propose that this method is suitable for the production of biocompatible colloids of ultraprecise clusters.
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There is a burgeoning requirement for colloids of ultraprecise nanoparticles, particularly for life science applications where precise control of nanoparticle size, shape, and composition is critical to delivering safe, consistent, and efficient nanoparticle-based diagnostics and treatments. Colloids are typically produced by batch chemical processes, where it can be difficult to precisely control size and dispersion. Variations between batches of the same product can arise due to small differences in the mixing or heating of the reagents. Moreover, developing new nanomaterials through chemical synthesis routes can be time-consuming and difficult. The physical production of nanoparticles using cluster beam technology offers the possibility to produce nanoparticles in an environmentally benign way (i.e., not involving hazardous chemicals or waste), with unparalleled control over nanoparticle size and allows new nanomaterials to be quickly developed.

In order to provide a storage and delivery solution suitable for life science applications, a means of transferring the cluster beam-deposited nanoparticles into biocompatible colloidal suspensions is required. In this paper, we present a proof-of-principle study of the preparation of colloidal suspensions of cluster beam-deposited size-controlled clusters. This is realised by depositing clusters onto a water-soluble polymer film that is subsequently dissolved to produce a colloidal suspension where the polymer molecules encapsulate the clusters and stabilize them against aggregation. The key feature of this approach is that pre-formed clusters are deposited onto the polymer in solid form before dissolution to produce a liquid. There have been previous attempts to prepare colloids of physically deposited clusters, e.g., by direct deposition into ionic liquids[1] or organic liquids such as castor oil.[2] However, in some of these cases the size control is limited due to the aggregation inside the liquid, while in others the resulting colloids are not biocompatible.

One factor limiting the use of cluster beam technology for colloid production is that it can be difficult to produce nanoparticles in useful quantities. This problem has recently been addressed with the development of the matrix assembly cluster source (MACS), which allows the production of large quantities of size-controlled clusters. The principle of the MACS is illustrated in Figs. 1(a) and 1(b), and has been described in detail elsewhere.[3–5] Briefly, a target matrix comprising metal

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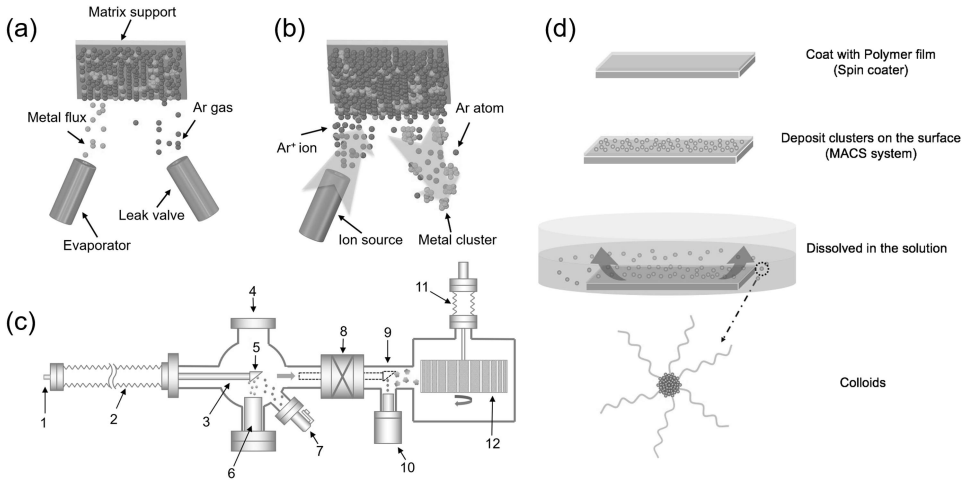

FIG. 1. ((a) and (b)) Principle of operation of the matrix assembly cluster source with (a) formation of matrix by co-condensation of metal and Ar gas onto a cryogenically cooled surface and (b) production of clusters by sputtering of the matrix with (1.5 keV) Ar ions. (c) Schematic diagram of the MACS system with (1) liquid He and electrical feedthrough for coldfinger, (2) linear translator for (3) coldfinger, (4) pumping port for the matrix chamber, (5) matrix support, (6) evaporator, (7) Ar leak valve, (8) gate valve, (9) position of the matrix during sputtering to produce nanoclusters, (10) ion source, (11) linear translator, and rotary drive for (12) the sample carousel. (d) Schematic diagram of the preparation method to prepare colloids from MACS-deposited clusters.

atoms embedded in a noble gas matrix is produced by physical vapour deposition of metal atoms onto a cryogenically cooled support while simultaneously co-condensing the noble gas. The matrix is subsequently sputtered with Ar ions to produce cascades of atomic collisions inside the matrix, causing clusters to nucleate and ripen before eventually being ejected from the matrix. The cluster size is controlled via the metal concentration inside the matrix, the matrix temperature, and the sputter parameters. Size-controlled clusters can be deposited without the need for a subsequent mass-filtering step, which would invariably lead to significant loss of material.

The MACS used for these experiments is shown schematically in Fig. 1(c). It comprises two vacuum chambers that are maintained at a base pressure in the mid 10^{-8} mbar range. In the first chamber the matrix is prepared on an oxygen-free Cu support mounted on a cold finger that is cooled to below 20 K by a continuous flow of liquid He. The matrix is produced by metal deposition onto the support from a thermal evaporator while simultaneously introducing argon gas into the chamber. Once the matrix is generated it is then sputtered by an ion source in the second chamber, which contains a sample carousel designed to hold up to 21 (2.5 cm × 7.5 cm) glass slides. The slides are coated with a polymer film by spin-coating a drop (0.3 ml) of 3.5 μM polymer solution on each slide at 4000 rpm for 10 s. The thickness of the resulting polymer film was determined by a profilometer to be typically between 10 nm and 50 nm. After cluster deposition the glass slides are immersed in deionised water for 5 min to dissolve the polymer film and release the clusters into the suspension. Cluster deposition times are typically selected to result in a cluster coverage between 10% and 20% on each polymer film. Dissolving all 21 polymer films in 10 ml of water results in a colloid with a metal concentration of ~10 μg/ml. The process is outlined schematically in Fig. 1(d).

Scanning transmission electron microscope (STEM) images of the as-deposited clusters were obtained by depositing clusters directly onto Cu TEM grids coated with an amorphous carbon film. Samples of the metal colloids were prepared for STEM by drop-casting a 20 μl drop of solution onto a TEM grid. The size distribution of colloids and as-deposited clusters was characterized by a JEOL JEM-2100F STEM equipped with a Cs corrector (CEOS) and a HAADF detector operating with an inner angle of 62 mrad and an outer angle of 164 mrad at 200 keV.

In order to demonstrate this method, both Au and Ag colloids have been prepared using polyvinylpyrrolidone (PVP, MW ~10 000, Sigma-Aldrich) dissolved in isopropanol (IPA, laboratory grade, Fisher Chemical). PVP was the first polymer tested due to its wide usage as a stabilizing agent in colloids.[6] Figure 2 compares the STEM images and size distributions of the as-deposited

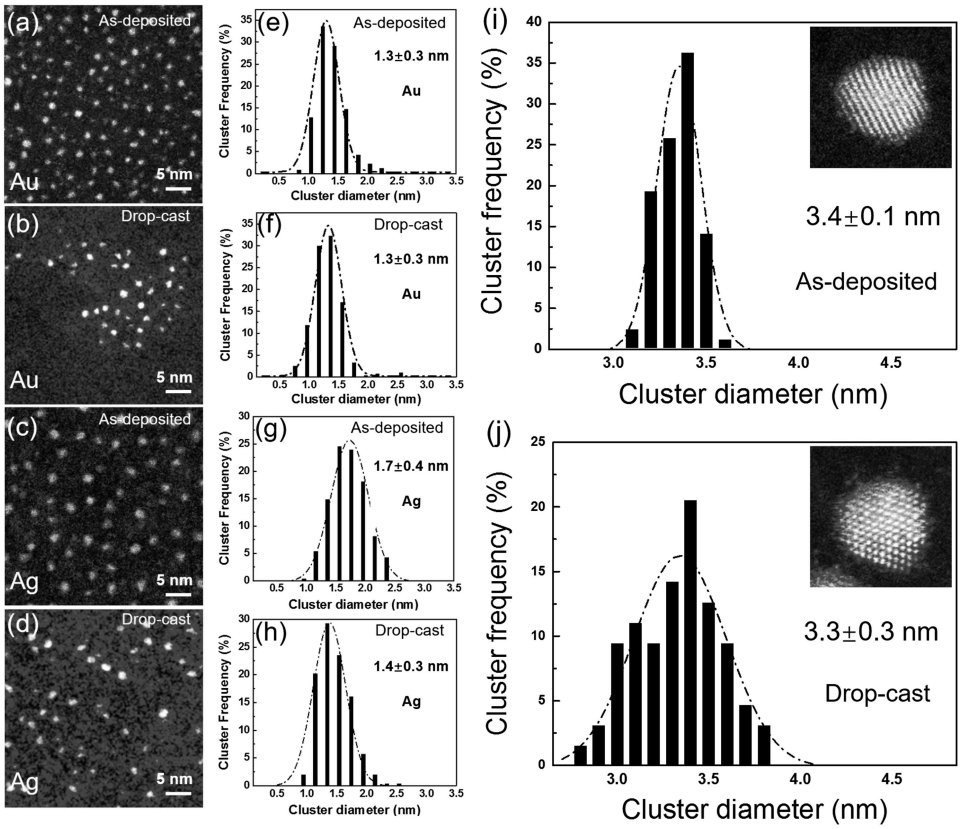

FIG. 2. PVP-stabilised Au and Ag colloidal clusters prepared by MACS deposition onto PVP films followed by dissolution of the cluster/polymer layer in isopropanol. STEM images and size distributions of as-deposited Au clusters ((a) and (e)), drop-cast Au colloidal clusters ((b) and (f)), as-deposited Ag clusters ((c) and (g)), and drop-cast Ag colloidal clusters ((d) and (h)). Panels (i) and (j) show size distributions of size-selected Au_{923} and its corresponding colloid produced with a mass-filtered magnetron sputtering gas condensation cluster source. The insets show the typical STEM images of the as-deposited and colloidal Au_{923} in the mean peak of the size distribution.

Au and Ag clusters with their colloidal counterparts. The as-deposited Au and Ag clusters have been deposited with a mean size of 1.3 nm (equivalent to ~70 Au atoms) and 1.7 nm (equivalent to ~150 Ag atoms), respectively. The deposited cluster coverage is low enough to ensure that the clusters are not aggregated prior to encapsulation by the polymer. After dissolving the cluster-coated polymer films in IPA, isolated Au and Ag clusters are still observed in the drop-cast colloid samples shown in Figs. 2(b) and 2(d), confirming that they do not aggregate while inside the polymer solution. This supports the notion that the polymer molecules encapsulate the clusters and keep them apart in the suspension. In the case of the colloidal Au clusters, the cluster diameter remains as 1.3 nm. It can be seen in Fig. 2(b) that the clusters have accumulated in only a part of the area imaged due to drying effect. In the case of the Ag clusters, the cluster size decreases slightly from 1.7 ± 0.4 nm to 1.4 ± 0.3 nm after dispersal into the colloidal suspension. A possible explanation for this is that PVP has a strong interaction with Ag atoms through multiple coordination of the >N-C=O groups[7] and that the O will bind with the metal atoms[8] and etch the Ag clusters to reduce their size. It has been reported that small Ag clusters can be synthesized via etching of large metal nanoparticles by adding excess ligands.[9]

To further investigate the effect of the colloid preparation process on cluster size and microstructure, size-selected clusters were also prepared using a magnetron sputtering gas condensation cluster source equipped with a time-of-flight mass filter.[10] Size-selected Au_{923} clusters[11] were deposited onto a PVP film and then dissolved in IPA. Au_{923} are relatively large in size (3.4 nm) making it easier to resolve their microstructure in the STEM. Figure 2(i) shows the size distribution of the as-deposited Au_{923} clusters. The as-deposited clusters have a narrow size distribution with an average size of

3.4 nm. After dissolving in IPA, the peak size of the clusters does not change, but the distribution becomes broader, which may be due to the influence of the dried polymer solution on the background intensity during analysis of the STEM images. No change in microstructure is observed when comparing the as-deposited clusters with their colloidal counterparts, confirming that the colloid preparation process does not affect the microstructure of the clusters.

In addition to PVP, both polyvinyl alcohol (PVA, MW 9000-10000, Sigma-Aldrich) and polyethylene glycol (PEG, MW ~1500, Sigma-Aldrich) have been tested as stabilizing agents. Figure 3 shows the typical STEM images and size distribution histograms of the as-deposited Au clusters, and the resulting Au colloids using PVA and PEG. The as-deposited clusters were deposited with an average size of 0.9 nm, which is equivalent to ~25 Au atoms. After dissolving the cluster-coated polymer films in de-ionized water the cluster size measured in both cases is larger, being 1.2 nm for Au/PVA clusters and 1.4 nm for Au/PEG clusters. This indicates that some limited aggregation occurs during the dissolving process. This might either be due to the weaker binding of PVA and PEG to the metal clusters compared to PVP, or, as PVA and PEG dissolve slowly in water, some cluster aggregation

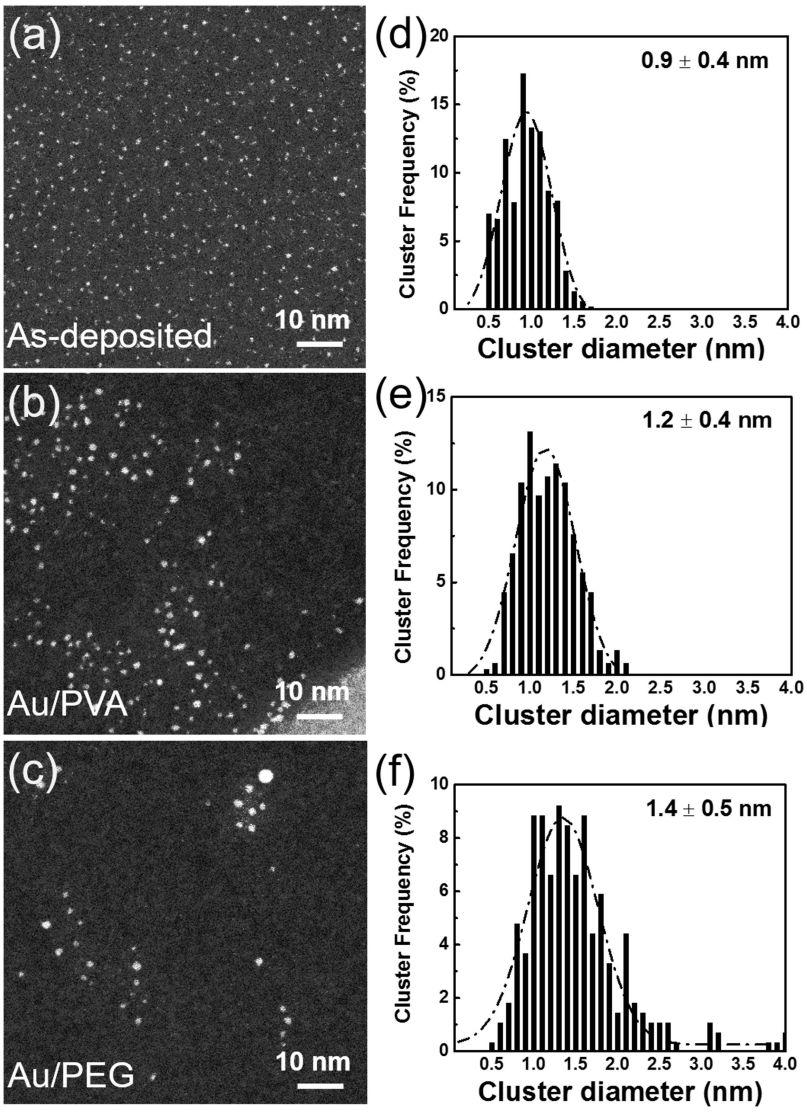

FIG. 3. Au colloids prepared with different polymer protecting layers dissolved in water. STEM images and size distribution histograms of the as-deposited Au clusters, ((a) and (d)), colloidal Au clusters in PVA solution, ((b) and (e)), and colloidal Au in PEG solution, ((c) and (f)).

might occur before the clusters are completely encapsulated. However, once the polymer films have been fully dissolved the clusters are stable against further aggregation.

In summary, we have demonstrated the proof-of-principle of a method for the preparation of colloids of physically deposited clusters. The colloids are prepared by depositing pre-formed size-controlled clusters from a cluster source onto soluble polymer films, followed by dissolution of the cluster-coated polymer films in a solvent. This has been demonstrated using different cluster materials (Au and Ag), polymers (PVP, PVA and PEG), and solvents (IPA and water). STEM measurements of the colloidal clusters revealed limited aggregation, confirming that the polymer molecules encapsulate the clusters and stabilize them against aggregation in suspension. Preliminary measurements indicate that no microstructure changes occur inside the clusters during the colloid preparation. We propose that this method can be used to prepare biocompatible colloids of ultraprecise clusters using cluster beam technology. Furthermore, we anticipate that it will be possible to functionalize the clusters by the addition of suitable agents to the polymer films.

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[1] D. C. Engemann, S. Roese, and H. Hövel, J. Phys. Chem. C **120**, 6239 (2016).
[2] H. Wender, L. F. de Oliveira, A. F. Feil, E. Lissner, P. Migowski, M. R. Meneghetti, S. R. Teixeira, and J. Dupont, Chem. Commun. **46**, 7019 (2010).
[3] R. E. Palmer, L. Cao, and F. Yin, Rev. Sci. Instrum. **87**, 046103 (2016).
[4] P. R. Ellis, C. M. Brown, P. T. Bishop, J. Yin, K. Cooke, W. D. Terry, J. Liu, and R. E. Palmer, Faraday Discuss. **188**, 39 (2016).
[5] V. T. A. Oiko, T. Mathieu, L. Cao, J. Liu, and R. E. Palmer, J. Chem. Phys. **145**, 166101 (2016).
[6] B. Santiago González, M. J. Rodríguez, C. Blanco, J. Rivas, M. A. López-Quintela, and J. M. Gaspar Martinho, Nano Lett. **10**, 4217 (2010).
[7] H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, and T. Tsukuda, Langmuir **20**, 11293 (2004).
[8] H. Zhang, N. Toshima, K. Takasaki, and M. Okumura, J. Alloys Compd. **586**, 462 (2014).
[9] X. Yuan, Z. Luo, Q. Zhang, X. Zhang, Y. Zheng, J. Y. Lee, and J. Xie, ACS Nano **5**, 8800 (2011).
[10] S. Pratontep, S. J. Carroll, C. Xirouchaki, M. Streun, and R. E. Palmer, Rev. Sci. Instrum. **76**, 045103 (2005).
[11] K. J. Hu, S. R. Plant, P. R. Ellis, C. M. Brown, P. T. Bishop, and R. E. Palmer, Phys. Chem. Chem. Phys. **16**, 26631 (2014).