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# Arabinogalactan from the Western larch tree: A new, purified and highly water-soluble polysaccharide-based protecting agent for maintaining precious metal nanoparticles in colloidal suspension

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TEM and non-contact atomic force microscopy studies conducted on unprotected and protected platinum, palladium and silver nanoparticle suspensions provide evidence for the protective ability of a newly available polysaccharide known as arabinogalactan. The arabinogalactan offers advantages over conventionally used gum arabic in being highly water soluble, capable of being prepared in higher purity and not settling out insoluble material over time. Nanoparticle suspensions prepared in the presence of this protecting agent show a change in overall particle morphology and reduction in the necklace like aggregation typical of unprotected particles on the TEM grids. It is believed that the protective action exerted by the arabinogalactan on the metal nanoparticles arises out of its unique spheroidal structure adopted in aqueous solution which is thought to sequester individual metal particles by virtue of surface interactions between oxide functionalities on the colloid and hydroxyl groups on the arabinogalactan. *© 2002 Kluwer Academic Publishers*

## 1. Introduction

The preparation and properties of colloidal metallic and non-metallic elements (i.e. sols) and salts enjoyed a period of intense research interest in the late 19th and early 20th centuries with the better part of the efforts in this area excellently reviewed in the Colloid Science series by Weiser [1]. After a period of relative calm, research interest in this area is enjoying a comeback of unprecedented magnitude. The renewed interest is due [2] to recent developments in inorganic and organometallic chemistry, emergence of new or more sensitive characterisation techniques and developments in solid state physics. In particular, the theoretical impetus to study colloidal systems has been provided in most part by the predictions by physicists that particles straddling the size boundary between molecular and bulk matter (i.e. 1–10 nm) possess special chemical and physical properties which would make them of value in the electronics industry. In addition, there has always also been the traditional interest in the catalytic properties of the nanoparticle systems due to their large surface area.

In this study, we investigate a novel polysaccharide protecting group for keeping metal colloids in suspension. It is well known from the earliest systematic research in colloid science that colloids (and metals, in particular) maintain their characteristic colloidal state of homogeneous dispersal in a supporting medium by virtue of electrostatic repulsion between the electrical double layers present on each particle [3]. When the electrostatic stabilisation is insufficient to prevent the colloid particles from aggregating and dropping out of solution as a metallic precipitate, steric stabilisation is effective in preventing close interparticle contact. This results when macromolecules such as polymers or surfactants become adsorbed on the surface so providing a protective layer. Hence agents used to induce steric stabilisation in metal colloids are called "protecting agents". In the early days of colloid science, plant extracts and gums were used routinely for stabilising

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colloidal metal dispersions [1]. Gum arabic, a polysaccharide derived from acacia trees was and still is used widely as a general purpose protecting group for colloids. As a protecting agent, however, gum arabic has the following disadvantages: 1) It is difficult to dissolve in water. 2) Solutions of the dissolved substance destabilise and settle out insoluble matter with time.

In this study an alternative material known as arabinogalactan is used which has only recently become commercially available in pure form. Arabinogalactan, a polysaccharide, is commonly found in trees of the genus *Larix* and can be extracted in high yield from Western Larch, *Larix occidentalis* [4]. The arabinogalactan (AG) has the advantage of being readily water soluble in contrast to gum arabic and moreover has the property of forming solutions of low viscosity even at high concentrations [5]. This behaviour, which is remarkable for a polysaccharide, suggests a highly branched structure, which results in a molecular shape that more nearly approximates a spheroid rather than the fibre structure of a linear polysaccharide [6].

Structurally speaking, AG consists of a backbone of D-galactopyranose residues linked $\beta$-($1 \rightarrow 3$). The majority of these residues bear branches consisting of either one (23%) or two (46%) D-galactopyranosyl residues linked $\beta$-($1 \rightarrow 6$). Smaller percentages of main chain residues bear larger branches with terminal arabinose residues [7, 8]. Evidence suggests that individual AG molecules aggregate to form trimers and the putative spheroidal shape may also be attributable to this [9]. 0.2% of uronic acid residues have been detected in AG [4] which is very low compared with the 16% of such residues found in gum arabic [10].

The $^{13}$CNMR spectrum of AG is dominated by the spectrum of terminal galactopyranose (linked only through C-1) [11] even though the methylation analysis indicates that $\beta$-($1 \rightarrow 3$)-linked galactopyranosyl residues should be present in somewhat greater quantity, 30.5% versus 26.0% for the terminal residues [9]. This behaviour can be taken as an indication that the overall shape of the molecule results in residues that are "outside" and thus have very different relaxation behaviour than other residues that occupy an "inside" position.

Thus AG can be thought of as being comprised of spheroidal molecules or aggregates thereof, which are covered in terminal galactopyranosyl residues. This conclusion is supported by the development of an immunoassay for arabinogalactan [12] in which the antiserum is thought to bind multiple sets of branch terminal galactose residues, which are linked $\beta$-($1 \rightarrow 6$).

In this communication, we report the results of a study in which arabinogalactan has been trialled as a novel protecting agent for maintaining precious metal nanoparticles in colloidal suspension. This is outside its present commercial applications as an animal feed supplement, excipient in biomedical applications, a functional food and skin and hair care performance additive.

## 2. Materials and methods

Doubly distilled water prepared using glass distillation stills and giving conductivities consistently $<3\ \mu\mathrm{S\ cm^{-1}}$ was used in all colloid preparations. Glassware used in the preparations was usually cleaned beforehand with freshly prepared aqua regia made from a 3:1 mix of $HNO_3$ (AMCO brand) and HCI (A. R. BDH brand) followed by thorough rinsing with doubly distilled water. Colloids were prepared by chemical reduction of the corresponding precious metal salts. These were used in colloid preparations as received from the manufacturers or other sources without further purification. Platinum and palladium sols were prepared using Prolabo-brand chloroplatinic acid and anhydrous palladium dichloride (purchased from the University of Wollongong, Australia). Silver sols were prepared from 99.99% silver nitrate (Scientific Supplies Ltd). All precious metal salts were soluble in water apart from the palladium dichloride which required 2 mole equivalents of NaCl to aid its dissolution in aqueous solution as the tetrachloropalladate(II) ion. Chemical reducing agents used in the preparations were hydrazine hydrate (99–100% purity from Sigma Chemical Co), sodium borohydride (>98% purity BDH brand) and CO gas (>99.5% purity from BOC gases). Metal sols were ion-exchanged immediately after preparation to reduce the level of electrolyte impurities by stirring with a (20–50 mesh) Fluka brand DOWEX mixed bed 50W × *(H+)/ 1 × 8(OH-) (1:1) ion exchange with indicator. Conductivity was monitored using a conventional conductance cell with parallel platinised platinum electrodes and a Philips PWE 9505 conductivity meter. Whatman type 1 filter paper or tissue paper usually sufficed for filtering the sols after ion exchange. Arabinogalactan (both "high" and "low" purity grades) was extracted and purified from Western Larch trees by Larex International, Minnesota, USA. The high purity brand called "LAREX UF Arabinogalactan" is assayed to be >99% purity. The low purity sample (though possessing no detectable levels of chloride by SEM) was so named due to its perceived higher level of polyphenolic lignin impurities which imparted both a light yellow colour and distinctively strong odour to the material (the high purity material was, in contrast, odourless). Both arabinogalactan grades were practically identical in their capacity as protecting agents for metal colloids. This observation would be of significance from an industrial point of view given the crude larch extract is less expensive than the refined arabinogalactan by at least two orders of magnitude.

The general procedure for preparing the unprotected colloids of platinum, palladium and silver followed the procedures employed by Mucalo *et al.* [13] with some modification: 1.4–2 mL of of the 0.03–0.04 mol $L^{-1}$ precious metal salt solution was placed in a beaker containing a magnetic stirrer. Depending on whether "high", "medium" or "low" density colloids were desired, 7, 12.5 and 84 mL of water was then added with the resultant solution being cooled to 0–5°C in an ice-water bath. 3.5 mL of the reducing agent (0.033 mol $L^{-1}$ hydrazine or sodium borohydride in water) was then slowly added dropwise to the stirred solution. This resulted in the almost immediate appearance of a black intense colour in the solution signifying formation of the colloid. Sols prepared in the presence of arabinogalactan were prepared in almost identical fashion except that 3 mL of the water volume added to each preparation was replaced with an equivalent volume of aqueous 5% (w/v) LAREX UF arabinogalactan solution. Unprotected palladium colloids prepared by CO gas reduction were generated by passing CO gas vigorously through solutions (for ca. 10 minutes) containing 2 mL 0.03 mol $L^{-1}$ $PdCl_2/NaCl$ solutions diluted with 10.5, 16.0 or 88 mL of water corresponding to the "high", "medium" and "low" density colloids respectively. The arabinogalactan-protected counterparts to the CO-gas-reduced palladium colloids were obtained by an identical procedure except that 3 mL of the aforementioned volumes of water added to the 2 mL 0.03 mol $L^{-1}$ $PdCl_2/NaCl$ solutions for generating "high", "medium" and "low" density colloids were replaced with 3 mL of 5% w/v LAREX UF arabinogalactan solution.

In addition, solutions of precious metal salt and arabinogalactan alone were also prepared to investigate the possibility of chemical reactions of arabinogalactan with the respective platinum, palladium, or silver salt solutions. The control systems (having no prior hydrazine, or borohydride added) were prepared by adding to a stirred beaker 2 mL 0.03 mol $L^{-1}$ $PdCl_4^{2-}$, $AgNO_3$ or $H_2PtCl_6$, 7.5 mL doubly distilled water and 3 mL 5% w/w LAREX UF arabinogalactan.

Ion exchanging as a means of partial purification of all prepared colloids (initial conductivities were in the range of 1500–8000 $\mu$S $cm^{-1}$) was then carried out until a conductivity of less than 10–20 $\mu$S $cm^{-1}$ was obtained. In contrast to the unprotected colloids, arabinogalactan-containing metal colloids could only be ion exchanged to conductivities in the region 30–50 $\mu$S $cm^{-1}$ suggesting interference by the arabinogalactan with the ion exchange resin.

All U.V./Vis. spectrophotometric characterisation of the colloids was carried out on a Cary 1E spectrophotometer using quartz cuvette cells of 1 cm pathlength. Colloid samples were usually diluted with water by a factor of 5 or more if necessary and examined over the 900–190 nm region using a scan rate of 60 nm/min. An indirect measure of sol density, viz., "U.V./Vis sol density index," was obtained by measuring the amount of light scattering in the U.V./Visible region (i.e. turbidity) at 450 nm as performed in the earlier studies by Mucalo *et al.* [13]. Samples for TEM were prepared by depositing undiluted samples (using either a Pasteur pipette or a $N_2$-gas-driven nebuliser device) of the colloids onto a 200-mesh or 400-mesh copper grid coated with a collodion film followed by vacuum desiccation overnight. These were then examined on either a Phillips 400 transmission electron microscope using an operating voltage of 80 keV or a Philips CM12 transmission electron microscope using an operating voltage of either 80 or 120 keV. Digital forms of the TEM micrographs were obtained by scanning as black and white 300 dpi images using a standard flatbed scanner. Particle size measurements were then carried out using SigmaScan Pro 4.0 image analysis software from Jandel Scientific. The particle size data collated was then entered into a Microsoft Excel 5.0 spreadsheet where it was statistically analysed and representative histograms representing particle size distributions produced.

Noncontact atomic force microscope (NC-AFM) images were obtained using a ThermoMicroscopes AutoProbe CP Research scanning probe microscope (ThermoMicroscopes, Sunnyvale, CA) operated in noncontact mode in air under ambient conditions as previously described [14–17]. Colloid samples were spray deposited or spin-coated onto freshly cleaved mica and allowed to air dry.

## 3. Results and discussion

Platinum, palladium and silver colloidal metal sols were investigated in this study. In general, the "high", "medium" and "low" density (see Experimental) borohydride-generated platinum colloids prepared without the addition of any protecting agent exhibited the typical intense black colour observed for these systems and showed good stability with only a small amount of sedimentation. Arabinogalactan-protected borohyride-generated platinum colloids, on the other hand, exhibited very good stability with no apparent sedimentation. The difference in stabilities between the unprotected hydrazine-reduced platinum colloids and the arabinogalactan-protected hydrazine-reduced platinum colloids was more dramatic with the unprotected colloid being extremely unstable and sedimenting into large black flocs minutes after preparation. Hydrazine reduced platinum colloids prepared in the presence of arabinogalactan gave, in stark contrast, very stable, pitch black sols.

Unprotected palladium colloids prepared by either borohyride, hydrazine or CO gas reduction of palladium chloride are characteristically very unstable and thus sediment minutes to days after preparation. When prepared in the presence of arabinogalactan, the difference in stability is dramatic with intense black sols being formed that exhibit indefinite periods of stability.

Silver nanoparticle systems which were only studied as "high" and "low" density colloids, exhibited less consistent results. Arabinogalactan-protected silver colloids prepared by borohydride reduction were more stable than the unprotected silver colloids. The arabinogalactan-protected hydrazine-reduced silver colloids were no more stable to sedimentation than their unprotected counterpart.

An interesting observation obtained from "control" experiments in which the precious metal salts were mixed with arabinogalactan alone without any reducing agent and allowed to stand showed that arabinogalactan itself had some partial reducing activity. In the $H_2PtCl_6$/ arabinogalactan solution, the UV-VIS spectrum featured dominant absorption features due to chloroplatinate(IV) ion which showed no noticeable change over a period of 4 days standing in ambient conditions so indicating no reaction at all with the arabinogalactan under ambient conditions. A small amount of cloudiness (possibly AgCl) was observed to form in the $AgNO_3$/arabinogalactan solution. The arabinogalactan used is likely to contain some ionic impurities which are carried over from the

UF(ultrafiltration) process employed in its manufacture. A cursory EDX analysis conducted on the UF arabinogalactan used in this study actually showed the presence of potassium and chloride which supports this assumption and indicates that AgCl could well have formed in the $AgNO_3$/arabinogalactan solution. In contrast, the $PdCl_4^{2-}$/arabinogalactan solution, was observed to darken within a few minutes of arabinogalactan addition under ambient conditions. Reduction, however, was judged to be incomplete due to the observation from the U.V./Vis spectrum that unreduced $PdCl_4^{2-}$ was still present. Each molecule of arabinogalactan has a single reducing end group which is a galactose moiety that is predominantly in the pyranose form but which is also in equilibrium with the open chain form having an aldehydo functionality. This aldehydo functionality is responsible for the reducing power of the so-called "reducing" monosaccharide sugars. Indeed the reduction of metal ions is the basis of the Tollen's and Fehling's tests for these types of sugars [18]. Arabinogalactan has 0.25% reducing sugar equivalents (compared to free monosaccharide galactose at 100%), some of which is attributable to reducing end groups and some to contamination with monosaccharide sugars such as galactose, which, presumably, is the origin of its weak reducing power.

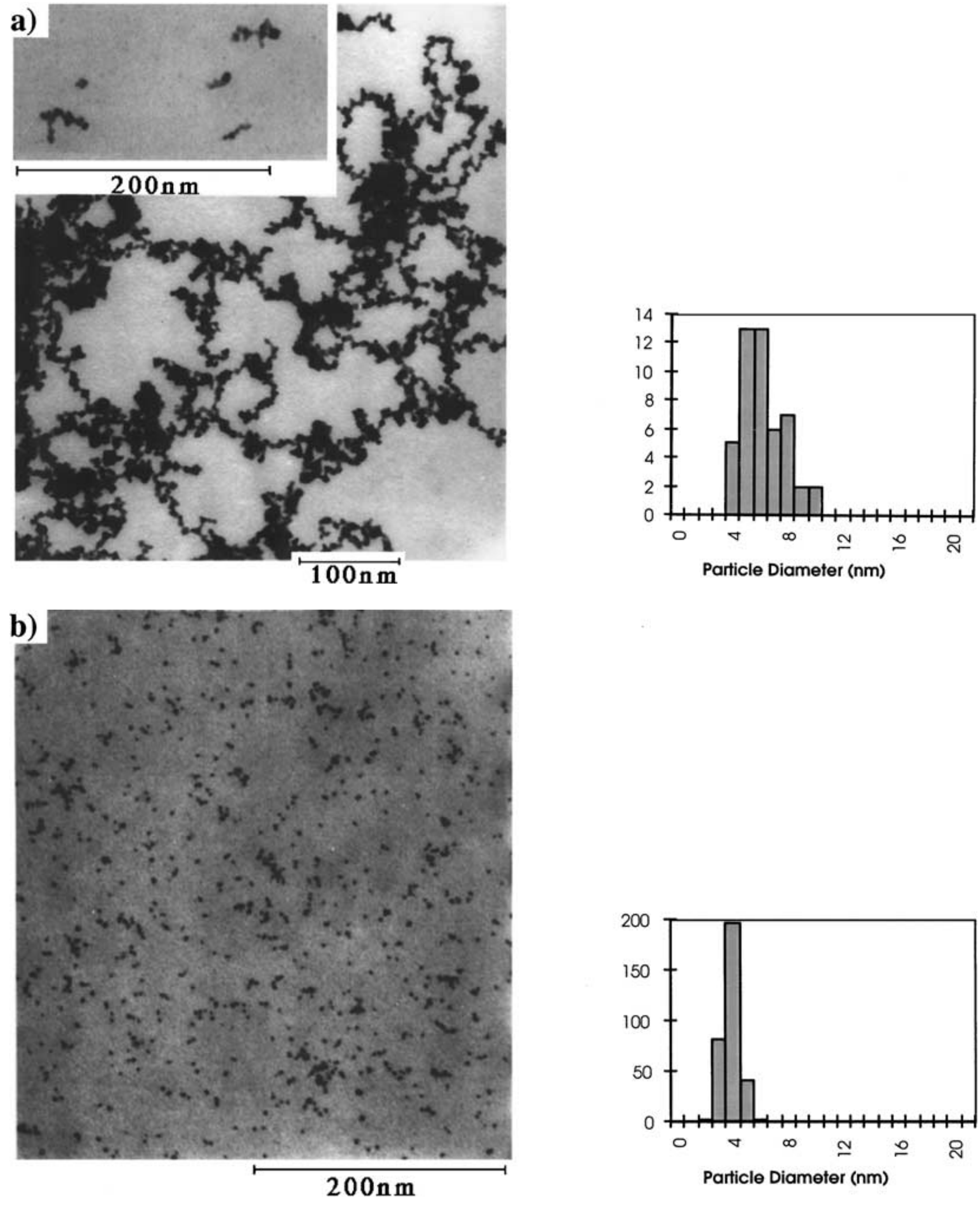
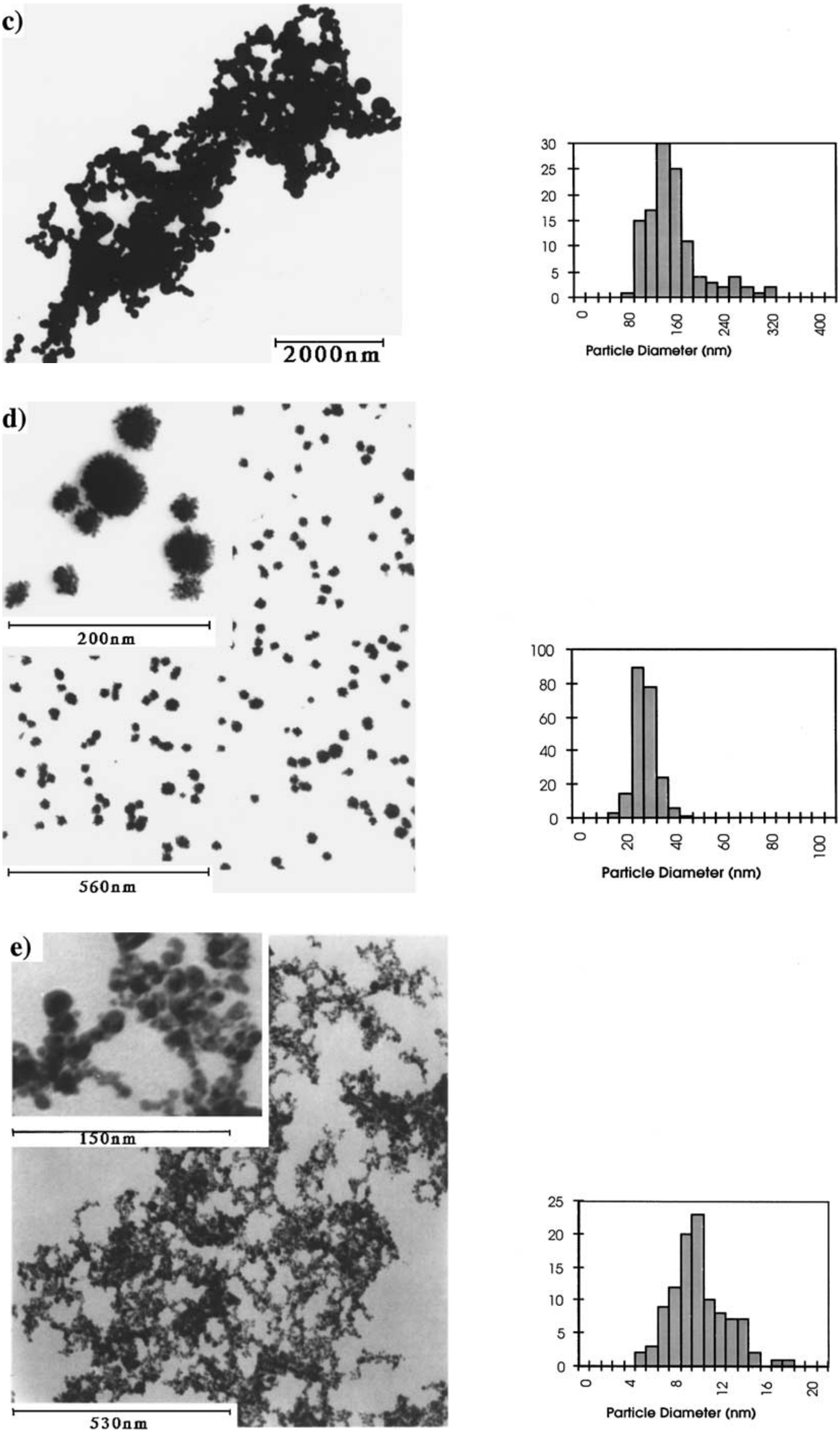


*Figure 1* TEM micrographs (plus accompanying particle size distributions) of selected platinum, palladium and silver colloid systems with and without arabinogalactan added as a protecting agent: (a) Unprotected "medium" density borohydride-reduced platinum colloid, (b) arabinogalactan-protected "medium" density borohydride-reduced platinum colloid, (c) Unprotected hydrazine-reduced platinum colloids, (d) arabinogalactan-protected hydrazine-reduced platinum colloid, (e) Unprotected "high density" borohydride-reduced palladium colloid, (f) arabinogalactan-protected "high" density borohydride-reduced palladium colloid, (g) Unprotected borohydride-reduced silver colloid, and (h) arabinogalactan-protected borohydride-reduced silver colloid. (*Continued.*)



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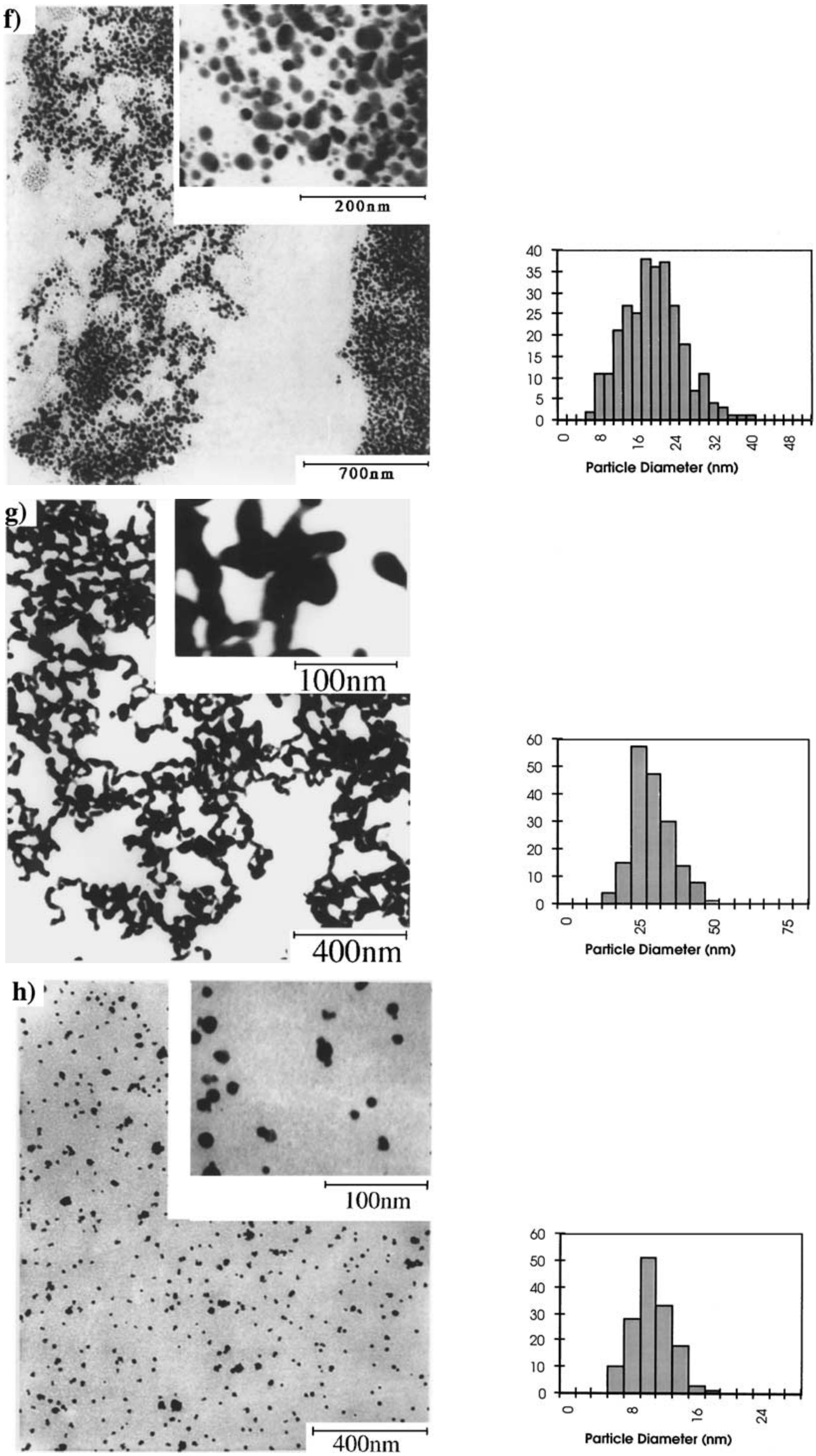


*Figure 1* (*Continued.*)

TEM micrographs (plus accompanying particle size distributions) of some selected platinum, palladium and silver colloid systems with and without arabinogalactan added as a protecting agent are illustrated in Fig. 1. The unprotected "medium" density borohydride-reduced platinum colloid TEM (Fig. 1a) displayed the distinctive the necklacing of approximately spherical particles that has been commonly observed in previous studies [19]. Particle size distributions for the unprotected "medium" density platinum sol indicated a wide variety of particle sizes with an average size of 5–6 nm as found by earlier workers [19]. In contrast, TEM micrographs of the "medium" density arabinogalactan-protected borohydride-reduced platinum colloids displayed discrete (non-aggregated) approximately spherical particles (see Fig. 1b) with narrower particle size distributions centred at ca. 3.6 nm. This clearly shows the dispersion properties of arabinogalactan. Indeed when 0.5 mL of 50% w/v arabinogalactan was added to a "high" density *unprotected* borohydride-reduced platinum sol prior to spray nebulising the sample onto a grid for TEM analysis, the resultant image showed fragmentation and breaking up of the typical necklacing of particles in the unprotected colloids so giving at least physical indication that arabinogalactan interferes with how the particles are deposited when their dispersion medium is evaporated away and that it does not have to be added *pre*-reduction to exert its protective effect. The particle size distribution of this sample where arabinogalactan had been added *post*-reduction was found to be centred at 5.73 nm so showing that the arabinogalactan had not altered the morphology of the particles in the colloid samples. Fig. 1c illustrates the typical giant spherical fused agglomerate-type morphology of the unstable hydrazine-reduced platinum colloids without protecting agent added (this was observed for colloids of "high","medium" and "low" density). These gave an average particle size of 147 nm upon measurement with a wide particle size distribution. Arabinogalactan-protected hydrazine reduced platinum sols, on the other hand, showed a striking change in morphology (for all "high", "medium" and "low" density sols) in their TEM micrographs (Fig. 1d) which showed clearly separated spherical ca. 27 nm aggregates consisting of clusters of loosely held ca. 3.9 nm smaller spherical particles. The adoption of this rather unusual morphology and striking stability of these sols compared to the unprotected hydrazine-reduced platinum sol suggests that it is brought about by the sequestering of colloidal platinum particles within the spheroidal structure that arabinogalactan adopts in aqueous solution.

The TEM of a "high" density unprotected palladium colloid prepared by borohydride reduction is illustrated in Fig. 1e. Like the unprotected borohyride-reduced platinum colloids, it exhibited the typical necklacing effect of approximately spherical particles. The particle sizes occurred over a wide particle size distribution with an average particle size of 9.55 nm in agreement with earlier work [19]. The TEM of a "high" density arabinogalactan-protected borohydride-reduced palladium colloid is shown in Fig. 1f. In contrast to the colloid displayed in Fig. 1e, this colloid was much more stable and exhibited polydisperse, irregularly shaped particles with a larger average particle size of 18.4 nm. Like the unprotected/arabinogalactan-protected borohydride-reduced platinum colloids, there was an absence of necklacing in the protected colloids indicating the protecting action of arabinogalactan in the sol. The observation of a larger particle size relative to the unprotected sol is unusual and could represent particles that are aggregates of smaller particles as in the case of the arabinogalactan-protected hydrazine-reduced platinum sols. Unprotected and arabinogalactan-protected hydrazine-reduced palladium colloids exhibited the same trends. The unprotected sol was completely unstable and demonstrated necklacing of particles with an average particle size of 5.68 nm. In contrast, the arabinogalactan-protected colloid was very stable and gave spherical isolated particles in its TEM. The average particle size for a "high" density colloid was found to be 4.9 nm.

CO bubbling into $PdCl_2$/NaCl solutions without any arabinogalactan added led typically to the plating out of a palladium black mirror and the deposition of large black flocs in the reaction vessel. The TEM of the colloid (which had been ultrasonicated to re-attain colloidal dispersion prior to being nebuliser-sprayed onto the TEM grid) showed highly aggregated material in which individual particle boundaries were so ill-defined as to prevent any meaningful particle size measurements. Mucalo *et al.* [19] have determined from earlier studies that the average particle size of this colloid is 11.5 nm. In contrast, the use of arabinogalactan in the reaction vessel during CO gas treatment led to a colloid which apart from a small amount of sedimentation was largely stable. TEM micrographs featured approximately spherical well separated particles for the "high", "medium" and "low" density colloids produced. Average particle sizes for the colloids varied from 4–5.5 nm. This dramatic difference in sol stability relative to the unprotected palladium colloid for the arabinogalactan-protected colloid highlights its utility as a stabilising agent for precious metal nanoparticle systems.

The TEM of a "low" density unprotected borohydride-reduced silver colloid is illustrated in Fig. 1g. This revealed a distinctly interlaced network in which the particles appeared to have "necks". Indeed, the unprotected "high" density colloids were initially a chalky dark green colour which developed over time into a grey-black colour which was caused undoubtedly by aggregation processes within the colloid and as reflected in the interlaced appearance of particles in the TEM micrograph. TEM micrographs of the "high" density silver colloids revealed unsurprisingly large dense aggregates attributed to the agglomeration of many small particles on the TEM grid. Average particle sizes for the "high" and "low" density colloids were measured to be 38 nm (with a wide particle size distribution spanning 14 nm) and 27 nm (6.7 nm span of particle sizes) respectively. It is likely that the degree of aggregation in the TEM of the "high" density silver colloid would have influenced the discernment of particle boundaries during particle size measurement so leading to a larger overall particle size. The TEM of the arabinogalactan-protected borohydride-reduced silver colloid is shown in Fig. 1h. These colloids were very stable and exhibited a yellow-brown colour typical of colloidally stable silver sols. Sol stability was reflected by particle morphology in the TEM micrograph which was spherical and discrete with the absence of particle "necks". Average particle sizes for the "high" and "low" density silver colloids were similar at 9.4 and 9.7 nm respectively. However, the systems were far from being monodisperse given the wide particle size distributions obtained (see Fig. 1h). These results serve to affirm the utility of arabinogalactan as a good general purpose protecting agent for a wide variety of metal colloid systems.

The only system where arabinogalactan did not appear to demonstrate any dispersal properties was in the case of the hydrazine-reduced silver colloids where arabinogalactan could not offer any improvement in stability over the unstable highly aggregated unprotected hydrazine reduced silver colloid system. The reason for this difference is not clear but could suggest a strong tendency in this particular colloidal system for silver particles to aggregate (typically as observed with hydrazine reduced platinum colloid systems, the colloidal silver particles produced by hydrazine reduction were very large and fused) despite the presence of arabinogalactan. This system will likely form one of many bases for future investigation in this area.

Whilst TEM micrographs and observations (by eye) may offer qualitative evidence for sol stability, U.V./Vis measurements of sol turbidity at 450 nm offer more quantitative assessments of the measure of arabinogalactan to *concentrate* metals in colloidally dispersed form. For this purpose, U.V./Vis spectra from 190–900 nm of the unprotected and protected platinum, palladium and silver salts were acquired before and after their reduction (after any subsequent ion exchanging) to the colloidal metal sols. For the platinum and palladium colloids, the U.V./Vis spectral profiles obtained were all monotonically increasing absorption profiles towards short wavelengths as is typically observed in U.V./Vis spectra of colloidal metal dispersions of these metals [13, 20, 21]. There was no trace of U.V./Vis absorptions from the original unreduced chloroplatinate(IV) and chloropalladate(II) salts indicating complete reduction of the metal salt to the metal. U.V./Vis spectra of aqueous solutions of arabinogalactan at similar concentrations to the background concentration present in the protected metal colloids were also recorded to ascertain whether the arabinogalactan gave any spectral interferences over the 900–190 nm region. Apart from weak features at 200 and 260 nm which were due possibly to the low level of aldehyde (-CHO) functionality in the arabinogalactan, the U.V./Vis spectra were essentially featureless. This confirmed little if any contribution to the U.V./Vis spectral profile of the colloids by the arabinogalactan itself. A U.V./Vis sol density index based on the measured turbidity of the colloidal sols at 450 nm [13] could thus be used as an indirect means of comparing the loading of metal particles between the sol preparations. Colloids which completely aggregated before any $A_{450}$ value could be measured were deemed "non-measurable" by ultraviolet/visible spectrophotometry due to the complete loss of the colloidal dispersion by aggregation. This was the case for unprotected metal colloids, most notably the unprotected hydrazine-reduced metal colloids which aggregated in a matter of minutes after their preparation. In general, the "low" density colloids (prepared using 81–84 mL of water *in addition to the* water added with the precious metal salt and the reducing agent) stable (arabinogalactan-protected) palladium colloids produced using hydrazine, sodium borohydride or CO gas gave U.V./Vis. sol density index values (i.e. $A_{450}$ values) of 1.5–2.0. In contrast, "medium" density arabinogalactan-protected palladium colloids prepared by reduction with CO gas gave an $A_{450}$ value of 11.5 compared to a value of 19.5 given by the "high" density arabinogalactan-protected palladium colloid prepared also by reduction with CO gas. The arabinogalactan-protected "low" density platinum colloids generated by borohydride and hydrazine reduction were found to have $A_{450}$ values of 1.5–2.5 whereas the "medium" density platinum colloids gave $A_{450}$ values in the 4.0–6.5 range. Thus the $A_{450}$ values were clearly able to distinguish between sols of "low", "medium" and "high" density. Table I summarises $A_{450}$ values for the "high" density unprotected and arabinogalactan-protected platinum and palladium sol samples prepared by the various reducing agents. In almost all cases, a higher sol density is observed for the sol preparations involving the use of arabinogalactan as a protecting agent. This shows that the polysaccharide is extremely useful in the synthesis of high density (and hence higher surface area) colloidal dispersions relative to the unprotected case. This makes such dispersions potentially more useful for catalytic purposes where surface area is an issue and moreover allows the preparation of colloids which are notoriously unstable in the unprotected state (e.g. the series of colloid preparations prepared by hydrazine reduction of precious metal salts).

TABLE I $A_{450}$ values for the "high" density platinum and palladium colloids prepared in this study

| Metal colloid | Reducing agent | Protecting agent | $A_{450}$[a] |
|---|---|---|---|
| Pt | Sodium borohydride | None | 10.05 |
| Pt | Sodium borohydride | Arabinogalactan[b] | 9.80 |
| Pt | Sodium borohydride | Arabinogalactan[c] | 12.20 |
| Pt | Hydrazine | None | No Value (agg) |
| Pt | Hydrazine | Arabinogalactan[c] | 11.00 |
| Pd | Sodium borohydride | None | 7.55 |
| Pd | Sodium borohydride | Arabinogalactan[c] | 11.35 |
| Pd | Hydrazine | None | No value (agg) |
| Pd | Hydrazine | Arabinogalactan[c] | 11.75 |
| Pd | CO gas | None | No value (agg) |
| Pd | CO gas | Arabinogalactan[c] | 20.00 |

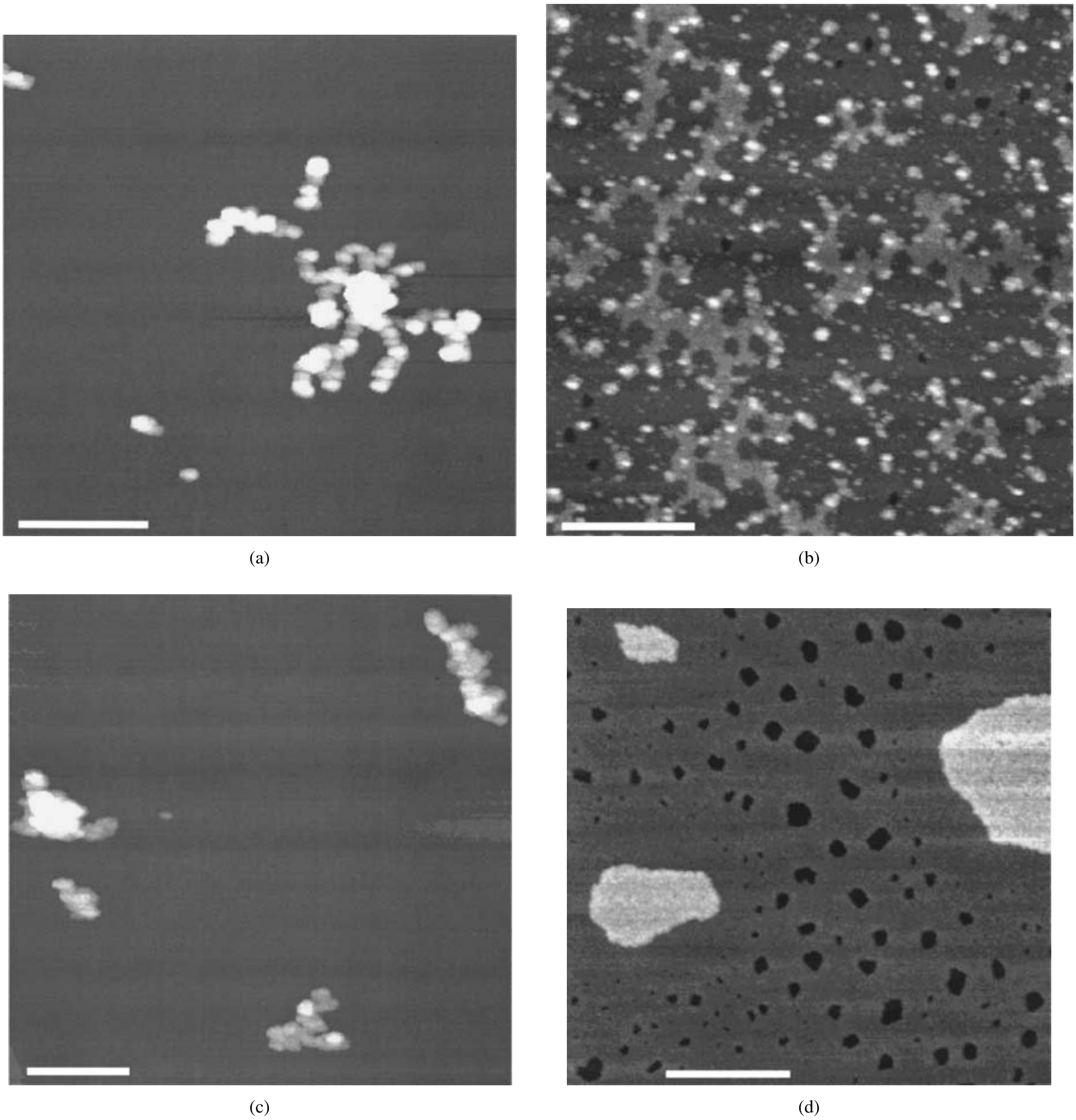
[a] Absorbance at 450 nm for 5-fold or greater dilutions of the colloid *multiplied by* the dilution factor.

[b] Arabinogalactan added *after* the reduction step of the metal salt.

[c] Arabinogalactan added *before* the reduction step of the metal salt. (agg) = aggregated

Silver sols in contrast do not exhibit the monotonically increasing absorption profiles in their ultraviolet/visible spectra as do the platinum and palladium colloids but instead feature the characteristic strong absorption maximum at ca. 400 nm which is called a plasmon resonance [22]. It was found in the present study that the bandwidth of the plasmon resonance appeared to be correlated to the state of aggregation of the silver colloid with bandwidth increasing for unprotected sols with a chalky or cloudy appearance whereas a narrower absorption maximum was observed for the stable yellow arabinogalactan-protected borohydride-reduced silver colloid.

Imaging of the colloids by scanning probe microscopy (SPM) operated in the noncontact mode (NC-AFM) was also carried out. In this technique, a vibrating cantilever is brought near the surface of a sample and the spacing between the tip and the sample is adjusted. In contrast to contact AFM, NC-AFM allows probing of the sample topography with little or no contact between the tip and the sample, which is advantageous for imaging soft or elastic samples which could be easily contaminated or distorted if allowed to come into contact with a cantilever tip. Gold colloids have been imaged using contact AFM [23] and the images compared with conventional high resolution transmission electron microscope (HRTEM) images of the same colloids. It was found that although metal particle *height* as estimated by the two techniques agreed remarkably well with each other, the image width of particles imaged by contact AFM grossly overestimated the true diameter compared to the estimate by HRTEM. Spatial resolution for identification of subtle differences in particle morphology between particles was also less well discerned or reproduced by contact AFM than with HRTEM (this is due to tip broadening). In the present study, NC-AFM


(a) (b)

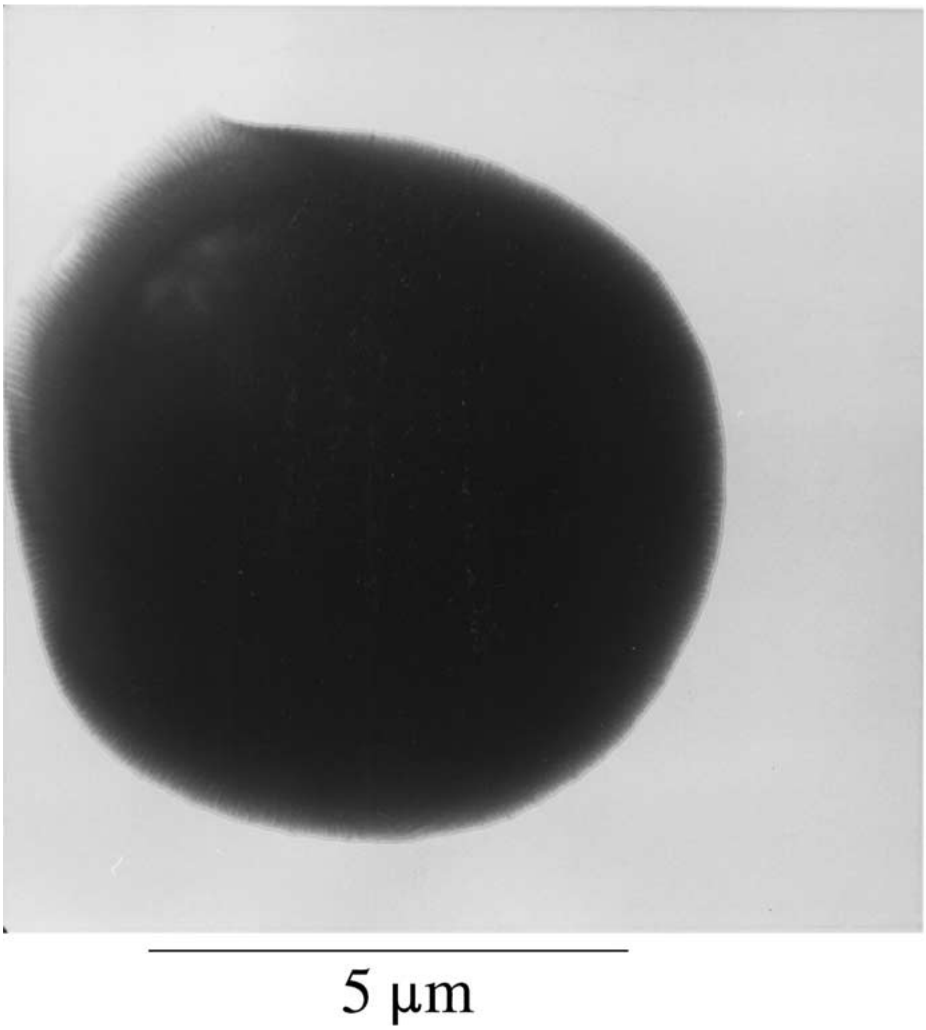
(c) (d)

*Figure 2* NC-AFM images of platinum colloids and arabinogalactan: (a) Unprotected borohydride-reduced platinum colloid, (b) arabinogalactan-protected borohydride-reduced platinum colloid, (c) borohydride-reduced platinum colloids prepared in the presence of simple galactose and (d) arabinogalactan alone as sprayed from a solution with a concentration equivalent to that in the arabinogalactan-protected metal colloidal suspensions.

was used to provide complementary information to the TEM on the unprotected and arabinogalactan-protected colloids and arabinogalactan-protected colloids.

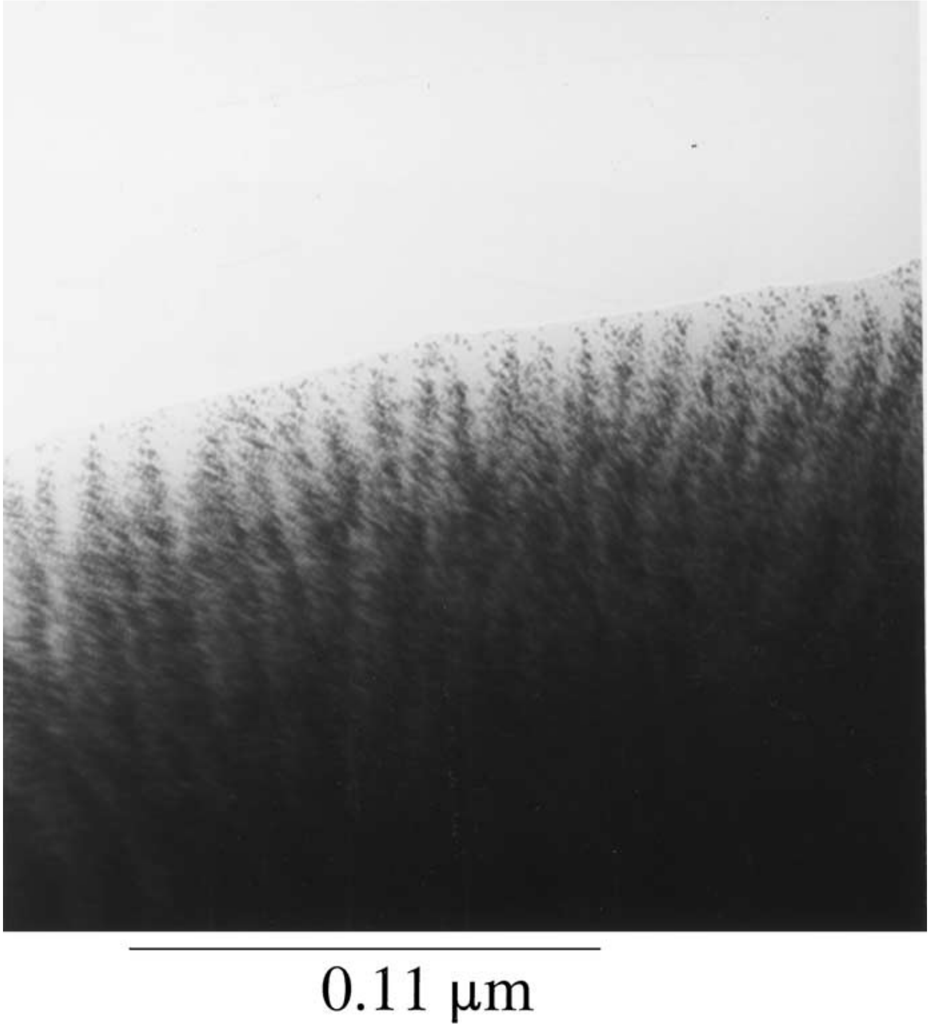
Fig. 2a is an NC-AFM image of an unprotected borohydride-reduced platinum colloid. These showed almost invariably large bright spots of irregular shape which represented large metal aggregates or clusters made up of smaller particles. These images were regarded as being representative of aggregation in the unprotected colloids as reflected in the TEM image (see Fig. 1a). In general, particularly bright spots observed in NC-AFM images are indicative of "piling up" of specimen on the mica surfaces that particles were examined on. Fig. 2b is an NC-AFM image of a borohydride-reduced platinum colloid protected with arabinogalactan. The image was very different from that displayed in Fig. 2a and showed many bright spots associated with less bright blobs. This characteristic pattern which was reproducibly observed for colloids prepared in the presence of arabinogalactan indicated the dispersal effect of the protecting agent on the metal colloid particles. The grey shaded areas represented deposited arabinogalactan within which the metal particles (bright spots) were encapsulated. This mirrors excellently the typical images obtained for arabinogalactan-protected colloids using TEM (see Fig. 1).

An obvious question that arises when studying the protective action of arabinogalactan is what structural feature of the macromolecule is responsible for its ability to disperse colloidal metal particles. It was reasoned that as the arabinogalactan structure possesses [9], the outside character of galactose, this molecule could be imparting a special affinity for the metal particles. A simple experiment involving preparation and comparison by TEM and NC-AFM methods of platinum colloids prepared in the presence of galactose alone was carried out. However this indicated that galactose alone imparted no special protecting action on colloidal metal dispersions. In fact the TEM micrographs and NC-AFM micrographs (Fig. 2c) displayed images typical of unprotected aggregated platinum colloids. Fainter spots observed in the background of the NC-AFM images of the galactose-protected platinum colloids were merely due to deposited galactose from solution (after comparison of Fig. 2c with NC-AFM images of galactose solutions which contained no colloidal metal). Hence it can be concluded that pure galactose imparts little if any of the protective action so characteristic of



(a)

*Figure 3* Images of the large black spots observed in the TEM micrographs of arabinogalactan-protected borohydride-reduced platinum colloid systems: (a) Low magnification image showing dense black spot on grid., (b) high magnification image of edge of dense black spot showing the distribution of platinum particles within spot. (*Continued.*)



(b)

*Figure 3* (*Continued*).

arabinogalactan. In addition, it may also be said that the comparable performance of arabinogalactan in colloid stabilisation with that of gum arabic indicates that this effect cannot originate from the uronic acid residues as these are few in number in arabinogalactan compared to gum arabic [4, 10].

It is thus reasonable to hypothesise that some unique peculiarity of the arabinogalactan molecule when dispersed in aqueous solution is responsible for the good protective action of the polysaccharide. The characteristic spheroidal morphology of the arabinogalactan aggregates in aqueous solution is thought to play a role in sequestering or organising the individual colloidal particles such that separation is imposed and aggregation of particles is avoided. NC-AFMs have been obtained before of evaporated solutions of arabinogalactan alone in water [11]. These showed spherical shapes in the image which were reasoned to arise due to the tendency of the arabinogalactan to adopt a spherical morphology in aqueous solution. This was reproduced in the present study by acquiring NC-AFM images of evaporated solutions of arabinogalactan in water at the same concentration as that in the arabinogalactan-protected platinum colloids (Fig. 2d). As expected, a distribution of large white spots of roughly circular or polygonal character was observed. In contrast, NC-AFM images of scleroglucan [15] show no such spots but instead distinct rod shapes which suggests that arabinogalactan molecules adopt a spheroidal shape in solution.

In TEM micrographs of arabinogalactan-protected platinum colloids, these "arabinogalactan spots" sometimes appear as large black circular areas (Fig. 3a). When using an 80 keV beam, the black spots were not sufficiently transparent and appeared as dense black areas but when a higher energy electron beam (120 keV) was used, transmissivity was increased and showed that the black spots consisted of a collection of many small spherical metal particles distributed in branch like or dendritic fashion throughout the spot. It was felt that this provided an illustration of how the arabinogalactan exerted its protective effect on the colloidal susupension by encapsulation of the metal particles (Fig. 3b). Certainly, none of the characteristic "necklacing" morphology as seen for unprotected colloids was observed in any TEMs of arabinogalactan-protected borhydride-generated platinum colloids. However, the influence of drying and consequent concentrative effects wrought upon the colloids as they are deposited on the grids should also not be discounted.

How the arabinogalactan actually forces colloidal metal particles to stay apart in colloidal metal suspensions could be via a hydrogen bonding interaction of the many –OH groups contained in the polysaccharide structure with some surface oxide functionality known to exist on metal colloids in aqueous dispersions [19, 24, 25]. Uronic acid groups would play a much minor role given the paucity of these groups in the AG relative to gum arabic. Given the advantages of handling (arabinogalactan has extremely high solubility and unusually low viscosity in aqueous solutions) this newly available polysaccharide compared to the more conventionally used gum arabic, arabinogalactan presents itself as a scientifically interesting and potentially valuable colloid dispersal agent which could find wide applicability in industries where synthesis of nanoscaled materials with control of size and dispersion properties is required.

## 4. Conclusions

Transmission electron microscopy coupled with NC-AFM has shown conclusively the effectiveness of arabinogalactan as a new dispersal agent for nanosized metal particles. The mode of protection arises from association of the individual colloidal metal particles with the branched spheroidal type structure which arabinogalactan adopts in aqueous solution. The nature of the interaction is presumably via surface interactions between oxide functionalities on the colloid and hydroxyl groups on the arabinogalactan.

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