Nanoparticles and nanostructures

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INTRODUCTION

The synthesis of core shell nanoparticles by simple chemical means has attracted considerable interest due to their great stability. These materials are of interest in providing a central metal core and a ligand shell with the possibility of controlling the core size, either a metal or a semiconductor, and the shell chemical functionality (1). Gold has been a preferred metal for the making the core due to its inertness. Also, silver presents interesting properties due to the sharpness of the plasmon band of nanoparticles prepared with this metal core (2,3). The aim of this work was to study the synthesis, purification and characterisation of metal core-shell alkane thiol nanoparticles.

EXPERIMENTAL

The synthesis of the core-shell materials followed essentially well rehearsed two-phase techniques (4). XPS spectra were obtained with a Scienta ESCA300 spectrometer at Daresbury, UK, (RUSTI facility).

RESULTS and DISCUSSION

The dependence of the gold 4*f* bands on nanoparticle size was investigated. The XPS spectra could be deconvoluted into two contributions, one due to the core and the other due to the surface atoms. The latter had a higher binding energy, as expected from the polar character of the sulphur-gold bond. The relative molar contributions corresponded to the calculated ratios of surface to bulk atoms calculated by Murray et al. (3) providing further evidence for the different nature of the atoms at the surface of the clusters, which are strongly affected by the capping ligand.

Silver nanoparticles capped with alkane thiols and with arene derivatives also displayed great stability. Purification of the material from the tetraoctyl ammonium bromide commonly used in the syntheses was achieved by solvent extraction and the degree of purification could be followed by XPS and mass spectroscopy. The presence of this quaternary ammonium slat greatly affects their solubility properties and methods have been developed for their rigorous purification.

Silver nanoparticles have been employed for the construction of multilayer structures and both ellipsometry and transmission spectroscopy has been used to characterise these films. As discussed in the literature, (5), effective medium models can be used in conjunction with a Drude model for describing the optical properties of the metal core to calculate the optical properties of nanostructures (6). These models have been used in the present work to calculate the spectroscopic properties of multilayer superlattices.

It is concluded that the properties of core shell nanostructures can be rationalised using simple models for the structure of these materials.

REFERENCES

1. A.C. Templeton, M.P. Wuelfing and R.W. Murray, Acc. Chem. Res. **33**, 27 (2000)
2. M. D. Malinsky, K. L. Kelly, G. C. Schatz and R. P. Van Duyne, J. Am. Chem. Soc, **123** 1471 (2001)
3. M. J. Hostetler et al., Langmuir, **14**. 17 (1998).
4. M. Brust, M. Walker, D. Bethell, D. Schiffrin and R. Wyman, J. Chem. Soc., Chem. Commun., 801 (1994).
5. T. Ung, L. M. Liz-Marzán and P. Mulvaney, J. Phys. Chem. B, **105**, 3441-3452 (2001)
6. P. Mulvaney, Langmuir, **12**, 788 (1996)