Adsorption of 2,2′-dithiodipyridine as a tool for the assembly of silver nanoparticles

Helena I. S. Nogueira, Paula C. R. Soares-Santos, Sandra M. G. Cruz and Tito Trindade*

Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
E-mail: ttrindade@dq.ua.pt; Fax: 351-234 370084; Tel: 351-234 370726

Silver nanostructured thin films stabilized by 2,2′-dithiodipyridine (2dtpy) were prepared. The Ag nanoparticles were obtained by treating the complex [Ag(2dtpy)]NO$_3$ with NaBH$_4$ in a methanol–toluene mixture. The films were transferred to borosilicate glass slips by a dip-coating method and were found to consist of Ag nanoparticles possibly linked *via* 2dtpy molecules. Surface-enhanced Raman scattering (SERS) studies have offered the possibility of investigating the adsorption modes of 2dtpy at the Ag nanoparticle surfaces in the films.

Introduction

The synthesis of nanostructured materials has been of much interest in the last decade.[1–5] A wide range of synthetic methods has now been established for nanoparticles of metals,[6–8] metal oxides[9] and semiconductors.[10] Although the synthesis and the physical characterization of metal nanocrystals have been thoroughly investigated, considerably less attention has been devoted to the fabrication of novel nanostructured materials containing metal nanocrystals as the building blocks.[11,12] Due to their unique physical properties, these materials will play a major role in future technological devices provided they can be assembled or positioned in a controlled manner. In this sense, nanostructured metal thin films would be of particular interest for molecular electronics and circuitry engineering.

The preparation in solution of noble metal nanoparticles, *e.g.* Ag, Au and Pt, generally involves the reduction of a simple metal salt and then a surface passivation step using Lewis bases to stabilize the sol formed. Here is reported a new solution method to obtain silver nanostructured thin films using a silver complex as the starting compound. The main idea underlying this synthetic method is to use the coordinated ligand (*e.g.* 2,2′-dithiodipyridine, 2dtpy) to cap the particles' surface, hence avoiding the agglomeration of the nanoparticles formed and, simultaneously, to link the Ag nanoparticles, hence promoting the formation of a three dimensional network. Compared to the thin film deposition of metal nanoparticles formed from conventional reductive techniques, this method offers the potential to design metal nanostructures using the coordinating organic ligand as an active template. In this sense, this preparative approach is strongly dependent on the modes of adsorption of the organic ligand at the metal nanoparticle surface. It will be shown here that a spectroscopic technique sensitive to the metal surface adsorption phenomena, such as surface-enhanced Raman scattering (SERS),[13–15] can be used as a valuable tool to investigate the adsorption of 2dtpy at the Ag nanoparticles which form the film.

Experimental

AgNO$_3$ and 2,2′-dithiodipyridine were supplied by Aldrich. Methanol and toluene were supplied by Panreac. All chemicals were used as received.

Instrumentation

Raman and SER spectra were recorded on a Brüker RFS100/S FT instrument (Nd : YAG laser, 1064 nm excitation). Infrared spectra were measured as KBr pellets on a Mattson 7000 FT instrument. UV–Visible spectra were measured on a JASCO V-560 instrument. ^{1}H NMR spectra were recorded using a Brüker Avance 300 NMR spectrometer. Scanning electron microscopy (SEM) was performed on an FEG-SEM Hitachi 54100 microscope operating at 25 kV. Transmission electron microscopy (TEM) was carried out on a Hitachi H-9000 microscope operating at 300 kV. An aliquot containing the nanodispersed sample was placed on a copper grid coated with an amorphous carbon film and then the solvent was evaporated. For TEM analysis of the Ag film the sample was prepared by displacing a small piece of the film to the top of the copper grid.

Synthesis of [Ag(2dtpy)]NO$_3$

The silver complex was prepared by adding a methanolic solution (15 ml) containing 2dtpy (222 mg; 1 mmol) to 5 ml of an aqueous solution of AgNO$_3$ (171 mg; 1 mmol), with stirring. A colourless precipitate was formed, which was then filtered, washed thoroughly with distilled water and dried over silica gel. The molecular formula [Ag(2dtpy)]NO$_3$ for the compound is proposed on the basis of elemental analysis and the spectroscopic characterisation (infrared, Raman and ^{1}H NMR). Analysis: calculated for [Ag(2dtpy)]NO$_3$: C, 30.8; N, 10.8; H, 2.1; S 16.4. Found: C, 28.6; N, 10.1; H, 2.4; S 16.0%. Selected bands from infrared (solid, KBr pellet, v/cm^{-1})/Raman (solid, v/cm^{-1}; in italics) spectra and tentative assignments: 3043/*3068* [v(C–H)]; 1571/*1584* and 1559/*1560* [v(C–C) + v(C–N)]; 1287/*1287* and 1275 /*1238* [δ(C–H)]; 1147 /*1155*, 1114 /*1119*, 1083 /*1091* and 1043/*1053* [δ(C–H) + δ(CCC)]; 987/*1006* [δ(CCC)]; *542* [v(S–S)]; 428/*429* [δ(CSS) + δ(CCC)]; *221* [v(Ag–S)]. ^{1}H NMR (in (CD$_3$)$_2$SO solution): δ 8.485 (1H, m), δ 7.818 (1H, m), δ 7.630 (1H, m), δ 7.296 (1H, m).

Preparation of a Ag nanostructured thin film

The silver film was obtained by adding dropwise 75 ml of an aqueous solution of NaBH$_4$ (0.17%) to 75 ml of a previously sonicated toluene suspension containing the silver complex [Ag(2dtpy)]NO$_3$ (15.6 mg; 0.026 mmol). After complete reduction of Ag$^+$, the mixture was transferred to a separating

funnel and a purple silvery film was formed at the aqueous/organic interlayer. The film obtained adheres strongly to the glass walls and can be displaced to a glass substrate by a dip-coating process. SEM shows a non-uniform film of *ca.* 2.5 μm thick.

Preparation of samples for SERS

The aqueous silver colloid used in the SERS experiments was prepared by reduction of silver nitrate by sodium citrate, using the Lee–Meisel method.[16]

Solutions of 2dtpy were made up in methanol (0.1 mmol in 1 cm^3 of solvent) and transferred by means of a microsyringe into the silver colloid (10 μl in 1 cm^3 of colloid) such that the overall concentration of 2dtpy was 10^{-3} mol dm^{-3}. Colloid aggregation was induced by addition of an aqueous solution of MgCl$_2$ (1 drop of a 2 mol dm^{-3} solution). Polyvinylpyrrolidone was then used to stabilise the colloid (1 drop of 0.1 g per 10 cm^3 aqueous solution). The final colloid mixture was placed in a glass tube and the Raman spectrum registered.

Results and discussion

A silver nanostructured thin film was obtained by using the silver complex [Ag(2dtpy)]NO$_3$ as the starting compound and NaBH$_4$ as reducing agent. The infrared spectrum of the solid Ag/2dtpy film in a glass substrate shows the presence of the organic ligand in the film; it is distinct from the infrared spectrum of solid 2dtpy with some bands strongly shifted. The Ag film obtained dissolves in dimethyl sulfoxide (DMSO) yielding an optically clear solution with the visible spectrum shown in Fig. 1a (this sample will be named as Ag/2dtpy colloid). The broad band in the visible spectrum of the Ag/2dtpy colloid (Fig. 1a), at 480 nm, is the characteristic silver plasmon resonance band of the nanoparticles produced from reduction of the Ag(I) complex.[17] Another band at 360 nm is observed and we suggest that it might be the result of the absorption of an hybrid inorganic–organic structure containing very small Ag nanoparticles somehow interacting with each other as a result of surface passivation with the 2,2′-dithiodipyridine molecules, here originating a new type of Ag aggregates. A small distance between these Ag nanoparticles may be the origin of the band, as reported by Feldheim *et al.*[18] for a phenylacetylene-bridged silver nanoparticle array. DMSO solutions of both free 2dtpy ligand and its Ag(I) complex show absorption in the ultraviolet region, with a maximum at 281 nm, but in the case of the Ag/2dtpy colloid there is clearly a new band at 360 nm. Moreover, the band at 360 nm is not observed (Fig. 1b) in the UV–visible spectrum of a sonicated Ag/2dtpy colloid, even after standing over a period of hours. The latter observations suggest a process in which the hybrid inorganic–organic structure of interacting Ag/2dtpy clusters is irreversibly destroyed under ultrasound, generating small Ag clusters that may grow into larger Ag nanoparticles.

The Raman spectra of the film Ag/2,2′-dithiodipyridine, the starting solid Ag(I) complex, [Ag(2dtpy)]NO$_3$, and the solid 2dtpy ligand are shown in Fig. 2, together with the
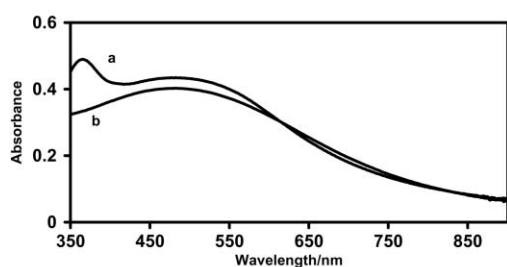
Fig. 1 Electronic spectra of a freshly prepared Ag film dispersed in DMSO (a) and after sonication during 10 minutes (b).
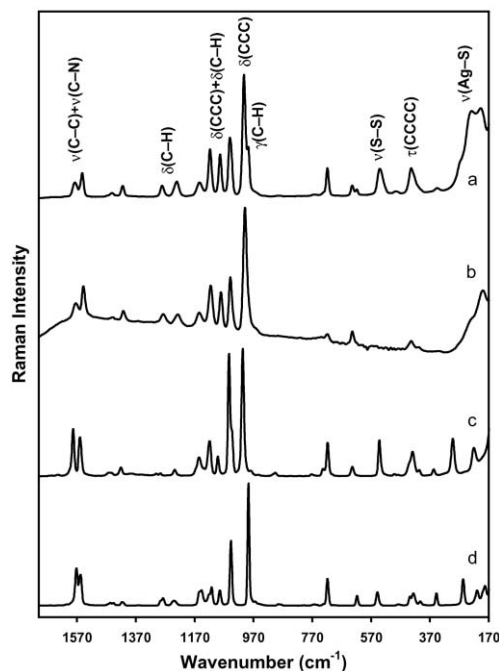
Fig. 2 SER spectrum of 2dtpy ligand in a silver aqueous colloid (a) and FT-Raman spectra of the solids: Ag/2dtpy film (b), [Ag(2dtpy)]NO$_3$ complex (c) and 2dtpy ligand (d).

surface-enhanced Raman (SER) spectrum of 2dtpy in a silver aqueous colloid. Tentative assignments are based on those found in the literature for 2,2′-bipyridine and related compounds.[19–21]

A FT-Raman spectrometer was used for recording all spectra shown in this paper, with an excitation wavelength of 1064 nm. This excitation has been largely used for recording good quality SERS spectra on silver;[22–28] work on the wavelength dependence of SERS has been reported and the need for further studies was pointed out.[29] The 2dtpy ligand shows a very strong SERS signal when adsorbed on silver colloids. The SER spectrum of 2dtpy in a silver colloid was recorded and is shown in Fig. 2a. According to the surface selection rules[30–33] for SERS, with regard to orientation of adsorbates on metallic surfaces, the normal modes of the adsorbed molecule involving changes in molecular polarizability with a component normal to the surface are subject to the greatest enhancement. The SER spectrum of 2dtpy shows a strong enhancement on the ring in-plane vibrational modes in the region 1040–1160 cm^{-1}, namely the in-plane δ(C–H) bending mode and δ(CCC) ring deformation, which could suggest the presence of an aromatic ring perpendicular to the surface. The very strong band assigned to the in-plane ring-deformation δ(CCC) at 1002 cm^{-1} is still the strongest band in the SER spectrum but it is relatively less enhanced than the latter vibrations, when compared with the Raman spectrum of the solid 2dtpy (Fig. 2d, δ(CCC) at 987 cm^{-1}). A strong enhancement is also observed in the band assigned to the γ(C–H) out-of-plane bending mode, seen as a shoulder of strong intensity, at 988 cm^{-1} in the SERS spectrum of 2dtpy; the corresponding band in the Raman spectrum of solid 2dtpy is seen as a weak shoulder at 965 cm^{-1}. The adsorption of 2dtpy to the silver surface should involve the two sulfur atoms, as shown by the broadening and the shift to 540 cm^{-1} in the band assigned to the S–S stretching, ν(S–S), seen in the SER spectrum (at 548 cm^{-1} in the Raman of solid 2dtpy).

The presence in the SER spectrum of enhanced out-of-plane and in-plane vibrational modes indicates two possibilities in respect of the adsorption position of the 2dtpy ligand on the surface of silver. Fig. 3 shows two possible adsorption modes of 2dtpy molecules on a silver surface: it can either adsorb *via* the two sulfur atoms with the two pyridine rings in a tilted position
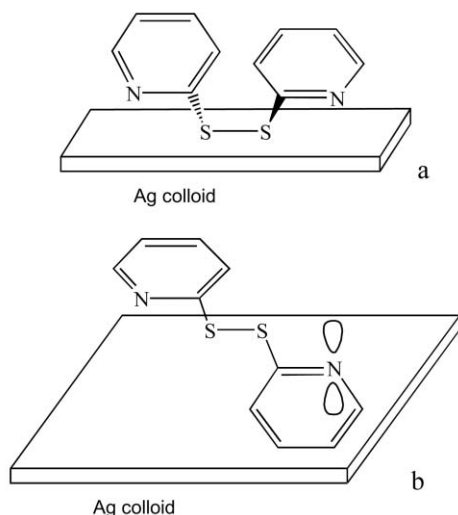
Fig. 3 Possible adsorption modes of 2dtpy molecules on a silver surface: (a) both pyridine rings are in a tilted position; (b) one pyridine ring is parallel to the surface and the other is in a perpendicular position.

(Fig. 3a), or *via* the two sulfur atoms and one nitrogen atom of one ring, having that ring in a parallel position to the surface and the other ring almost perpendicular to the surface (Fig. 3b). In the adsorption mode shown in Fig. 3a both out-of-plane and in-plane modes can be enhanced. In the adsorption mode shown in Fig. 3b, the out-of-plane modes can be strongly enhanced in the ring parallel to the surface and the in-plane modes can be strongly enhanced in the ring perpendicular to the surface. Other in-plane modes enhanced by the SERS effect are shown in the SER spectrum at: 1551 and 1577 cm^{-1}, assigned to the stretching modes ν(C–C) and ν(C–N); 1414 cm^{-1}, 1280 and 1230 cm^{-1}, assigned to δ(C—H). Another out-of-plane mode also enhanced is shown in the SER spectrum at 433 cm^{-1}, assigned to the ring torsion mode τ(CCCC).

It has been reported that there is a close relationship between complexation and adsorption involving organic ligands at silver centers.[25,26,34] There are similarities between the SER spectrum of 2dtpy and the Raman spectrum of its Ag complex, [Ag(2dtpy)]NO$_3$ (Fig. 2c). The bands shown in the SER spectrum of 2dtpy are generally seen in the spectrum of its Ag complex, with similar shifts in the position of the bands when compared with the Raman spectrum of solid 2dtpy. In aromatic systems, similarities between the SER in silver colloids and the Raman spectrum of the Ag complex have been associated with a perpendicular position of the aromatic ring in the silver surface.[25,26,34] The similarities shown in the corresponding spectra of 2dtpy could be related to a perpendicular position of an aromatic ring in the silver surface, according to the adsorption mode of 2dtpy shown in Fig. 3b. However, the difference in the relative intensity of the bands in the SER and in the Raman spectra of the Ag complex, indicates that the adsorption mode of 2dtpy should not consist of an exclusively perpendicular position of the aromatic rings, which is in agreement with both adsorption positions shown in Fig 3a and 3b. The Ag–S stretching mode, ν(Ag–S), is possibly assigned to the band at 221 cm^{-1}, in the Raman spectrum of the Ag complex of 2dtpy. In the SER spectrum of 2dtpy, the band at 228 cm^{-1} can also be assigned to ν(Ag–S); this type of spectroscopic feature corresponding to the sulfur–silver interaction in colloids has been reported previously for other aromatic ambidentate ligands.[26]

The Raman spectrum of the film Ag/2,2′-dithiodipyridine (Fig. 2b) is remarkably similar to the SER spectrum of 2dtpy (Fig. 2a). This similarity indicates that the interaction mode of 2dtpy with silver in both cases should be very close, with respect both to the atoms bound to silver and the adsorption

position of the 2dtpy molecules. There is only one noticeable difference between the two spectra, that is the absence of the band assigned to ν(S–S) in the Raman spectrum of the film, present in the SER spectrum at 540 cm^{-1}. This does not exclude the expected sulfur–silver interaction; the band was just not enhanced as for the 2dtpy/Ag colloid system.

All the Raman spectra presented in Fig. 2 also show bands in the region 3000–3150 cm^{-1} assigned to the C–H stretching modes, ν(C–H). These bands are very strong in the Raman spectra of solid 2dtpy and of its Ag complex, having a much lower intensity in both the SER spectrum and the Raman spectrum of the film Ag/2dtpy. The decrease in the intensity of ν(C–H) bands in the SER spectrum shows[24,35,36] that both aromatic rings should not be perpendicular to the silver surface, but the fact that these bands are seen also indicates that the rings are not flat on the surface; this is in agreement with the tilted position suggested in Fig. 3a. On this basis, the adsorption mode suggested by SERS is the one depicted in Fig. 3a, and this is possibly the position adopted by 2dtpy on the surface of the Ag nanoparticles in the Ag/2dtpy film, considering the similarities of the SERS and the Raman of the film.

The presence of the Ag phase in the Ag/2dtpy film was confirmed by transmission selected area electron diffraction. The diffraction pattern obtained appears as diffuse rings due to the small dimensions of the silver nanocrystals. Images of Ag nanocrystals dispersed within the organic matrix were obtained by TEM (Fig. 4a). The TEM images of the film showed Ag nanocrystals evenly distributed, in agreement with the formation of an hybrid inorganic–organic structure of interacting Ag/2dtpy clusters. Two main morphological patterns were observed for the nanostructured film, spheroidal Ag nanocrystals (typically less than 15 nm diameter) and larger plate shaped aggregates. These larger aggregates seem to result from a closer assembly of smaller Ag clusters, in a process that could be mediated by ligand–ligand interactions, from the 2dtpy ligand molecules that are passivating the Ag surface. In agreement with this hypothesis, no plate shaped aggregates were observed by TEM on samples deposited from a DMSO solution in which the film was dissolved and sonicated (Fig. 4b). The latter samples show larger Ag nanoparticles in agreement with the UV–visible observations (Fig. 1b). Research concerning the surface adsorption phenomena of the 2,2′-dithiodipyridine ligand at the Ag nanocrystals are in progress in our laboratories. It should be highlighted that the process reported here can be developed into a one step process to fabricate a nanostructured Ag/2dtpy hybrid film.
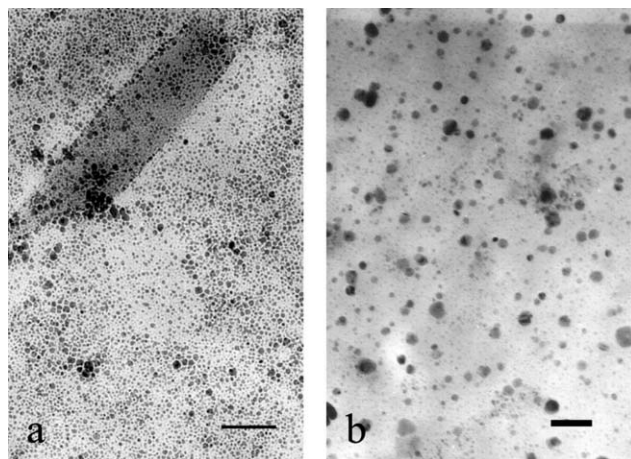

Fig. 4 (a) TEM image of Ag/2dtpy film (bar = 100 nm); (b) TEM image of Ag/2dtpy film nanodispersed in DMSO (bar = 85 nm).

Acknowledgement

References

1 M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.*, 1990, **23**, 183.
2 H. Weller, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 41.
3 A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49.
4 J. H. Fendler and F. C. Meldrum, *Adv. Mater.*, 1995, **7**, 607.
5 A. P. Alivisatos, *J. Phys. Chem.*, 1996, **100**, 13226.
6 A. Henglein, *Chem. Rev.*, 1989, **89**, 1861.
7 K. Torigoe and K. Esumi, *Langmuir*, 1995, **11**, 4199.
8 D. V. Leff, L. Brandt and J. R. Heath, *Langmuir*, 1996, **12**, 4723.
9 R. A. Andrievskii, *Russ. Chem. Rev.*, 1994, **63**, 411.
10 T. Trindade, P. O'Brien and N. L. Pickett, *Chem. Mater.*, 2001, **13**, 3843.
11 K. V. Sarathy, G. U. Kulkarni and C. N. R. Rao, *Chem. Commun.*, 1997, 537.
12 R. Maoz, E. Frydman, R. C. Sidney and J. Sagiv, *Adv. Mater.*, 2000, **12**, 424.
13 *Surface Enhanced Raman Scattering*, eds. R. K. Chang and T. E. Furtak, Plenum, New York, 1982.
14 J. A. Creighton, *Anal. Proc.*, 1993, **30**, 28.
15 S. Nie and S. R. Emory, *Science*, 1997, **275**, 1102.
16 P. C. Lee and D. J. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391.
17 C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, New York, 1983.
18 J. P. Novak and D. L. Feldheim, *J. Am. Chem. Soc.*, 2000, **122**, 3979.
19 M. Kim and K. Itoh, *J. Phys. Chem.*, 1987, **91**, 126.
20 T. C. Strekas and P. S. Diamandopoulos, *J. Phys. Chem.*, 1990, **94**, 1986.
21 M. D. Couce, U. Russo and G. Valle, *Inorg. Chim. Acta*, 1995, **234**, 195.
22 E. Wentrup-Byrne, S. Sarinas and P. M. Fredericks, *Appl. Spectrosc.*, 1993, **47**, 1192.
23 T. Y. Koh, S. J. Greaves and W. P. Griffith, *Spectrochim. Acta Part A*, 1994, **50**, 857.
24 W. P. Griffith and T. Y. Koh, *Spectrochim. Acta Part A*, 1995, **51**, 253.
25 W. P. Griffith and T. Y. Koh, *J. Raman Spectrosc.*, 1995, **26**, 1067.
26 H. I. S. Nogueira, *Spectrochim. Acta Part A*, 1998, **54**, 1461.
27 H. I. S. Nogueira and S. M. O. Quintal, *Spectrochim. Acta Part A*, 2000, **56**, 959.
28 L. Rivas, S. Sanchez-Cortes and J. García-Ramos, *J. Raman Spectrosc.*, 2001, **33**, 6.
29 B. Chase and B. Parkinson, *J. Phys. Chem.*, 1991, **95**, 7810.
30 J. A. Creighton, *Surf. Sci.*, 1983, **124**, 209.
31 J. A. Creighton, *Surf. Sci.*, 1985, **158**, 211.
32 M. Moskovits, *J. Chem. Phys.*, 1982, **77**, 4408.
33 M. Moskovits and J. S. Suh, *J. Phys. Chem.*, 1984, **88**, 5526.
34 S. B. Lee, K. Kim and M. S. Kim, *J. Raman Spectrosc.*, 1991, **22**, 811.
35 M. Moskovits, D. P. DiLella and K. J. Manyard, *Langmuir*, 1988, **4**, 67.
36 Y. J. Kwon, D. H. Son, S. J. Ahn, M. S. Kim and K. Kim, *J. Phys. Chem.*, 1994, **98**, 8481.