Eur. Phys. J. B **16**, 11–17 (2000)

THE EUROPEAN
PHYSICAL JOURNAL B
EDP Sciences

Preparation and characterization of nano-sized Ag/PVP composites for optical applications

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Received 10 November 1999

Abstract. A modification of the polyol process has enabled the direct synthesis of nm-sized Ag particles with narrow size distribution and controlled average dimension embedded in a polymeric matrix. Dispersion of colloidal silver was obtained by reduction of silver nitrate in ethylene-glycol in the presence of a polymeric protective agent (*i.e.*, poly(N-vinylpyrrolidone)) and ultrasounds. The final particle size was controlled by removing the colloid from the reactive mixture by addition of acetone. The very strong plasmon resonance peak at 410 nm and a feature at 350 nm in the UV-visible spectra are a clear consequence of the nano-size of dilute Ag particles. The proposed process offers the possibility to effectively use these synthesised materials for the production of colour filters for advanced optical devices.

PACS. 81.05.Ys Nanophase materials – 78.40.Fy Semiconductors – 78.40.Ha Other nonmetallic inorganics

1 Introduction

Recently, research on composite materials made of polymer and nanometric metal particles has received considerable attention because of the unique properties that they exhibit as a result of the reduced filler dimension. Quantum size effects may arise and influence all physical properties of such materials [1–4]. The prospect of exploiting size-dependent properties opens in turn the way toward the development of new functional materials and advanced devices [5–8]. For example, the use of optical properties of nanoparticles could result in new types of optical colour filters, substrates for surface-enhanced spectroscopies, biosensors, bio-probes, chemical sensors, etc.

Nowadays, several methods for the nanocomposite synthesis are used. They can be divided in two main groups: the first refers to a "top-down" approach, since it uses advanced lithographic technologies for the reduction of particle dimensions down to the nanometric range. Among these techniques, the best one is undoubtedly represented by the well established photo-lithography, even if limited in ultimate performance by diffraction-effects.

The second group, *i.e.* the "bottom-up" approach, was primarily used in the condensation from vapour technique and in the colloid-phase synthesis. By means of this synthesis strategy, much has been learned about the metal particle cluster size, the number of surface *vs.* interior atoms and quantum confinement effects. Any bottom-up approach is eminently capable of producing a wide variety of nanostructures and may yet become the industrial-scale nanofabrication methodology of choice.

Dispersion of metal colloids can be produced in both aqueous and non-aqueous solvents. The latter media are potentially more useful in the preparation of polymer-based nanocomposites and a number of techniques based on organic solvents have been proposed (for example, liquid polyol). Several metallic powders, such as Ag, Au, Ni, Co, Cd, Pb, and Cu have been successfully synthesised in μm and sub-μm ranges by the polyol process. A recent patent extends its use to the synthesis of refractory metals and metal alloys [9].

In this paper, we propose a modified polyol process which has been demonstrated to be successful to produce a polymer filled by high monodispersed nanosized Ag particles. The resulting material shows interesting optical properties which are characteristic of the reduced dimensions of metallic inclusions. In particular, in Section 2 the preparation process of the polymer-colloidal Ag systems based on ethylene-glycol solutions of Ag nitrate and liquid polyol is discussed. The characterisation of synthesised Ag/PVP nanocomposites by Transmission Electron Microscopy (TEM), powder X-Ray Diffraction (XRD), thermogravimetric analysis (TGA) and UV-spectrometry is presented in Section 3. A discussion of the observed nano-size induced material properties is reported in Section 4.

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2 The polyol process

The polyol process has been recently proposed as a method for the preparation of finely divided powders of easily reducible metals [10,11]. A suitable solid inorganic compound is dissolved or suspended into a liquid polyol (*e.g.*, ethylene-glycol, diethylene-glycol or a mixture of both). Afterward, the system is stirred and heated to a given temperature, which can reach the boiling point of the polyol for less easily reducible metals. The reduction of the starting compound yields the metal as a finely divided powder. The starting compound may be a hydroxide, an oxide or a convenient salt. The main feature of the reaction mechanism is that the reduction reaction proceeds *via* the solution rather than the solid phase. Therefore, the metal particles are formed by nucleation and growth from solution. According to this mechanism, the polyol acts as a solvent for the starting inorganic compound due to the rather high dielectric constant of these organic media. In particular, silver nitrate is soluble in ethylene-glycol to such an extent that a complete dissolution is observed as the first step of the reaction. Nucleation and growth must be completely separated in order to explain the fact that the obtained metal suspension is an almost homodisperse system. This condition, first expressed by La Mer [12,13] in his study about sulphur sols from acidified thiosulphate solution, appears as a general condition to obtain a homodisperse system. The metal is slowly provided in solution by the progressive reduction of the dissolved species. In particular, the reducing action of ethylene-glycol can be monitored by analysing the volatile compounds resulting from its oxidation. The formation of the main product, *i.e.* diacetyl, can be explained in terms of a double oxidation of acetaldehyde, previously produced by dehydration of ethylene-glycol [11], as follows:

$$\mathrm{CH_2OH - CH_2OH \xrightarrow{-H_2O} CH_3 - CHO} \qquad (1a)$$

$$\mathrm{2CH_3CHO \xrightarrow{2M(I)} 2M + 2H^+ + CH_3 - CO - CO - CH_3.} \qquad (1b)$$

During reaction (1b), the Ag concentration increases and rises to the saturation where the nucleation can occur. This condition results in the formation of many nuclei in a short burst. They grow rapidly and the metal concentration is lowered to a point below the nucleation concentration, but high enough to allow particle growth to occur at a rate that just consumes all generated metal. Therefore, μm-sized metal particles obtained in the standard experimental conditions are formed by nuclei which appeared spontaneously at about the same time and grow during the same time. These particles are then very homogeneous in size. The Ag powders obtained by reduction of silver nitrate in ethylene-glycol are poly-dispersed and show a wide range of shapes, arising from the sintering of quasi-spherical individual particles. In particular, because of the relatively high temperature used in the synthesis process, wide Brownian motions characterise the particles and the atoms on their surface have an elevated mobility. Consequently, the probability of particle collision, adhesion and subsequent coalescence by sintering is enhanced. By coalescence the system tries to attain the thermodynamic equilibrium by reducing its total surface area.

An envelopment of reduced metal atoms within a suitable layer could act as a protection for the nanometric particles during their growth [14–17]. A number of organic materials are known to work as protective agents for preventing colloid sintering [18]. Among them poly(N-vinylpirrolidone) (PVP) exhibits the best protecting properties. Prevention of particle sintering can be achieved by adding a critical dosage of an organic protective agent which covers the particles and inhibits any possibility of silver-silver particle bond formation. The presence of this agent at the solid/liquid interface does not interfere with the silver diffusion-surface deposition process since the particles grow to a definite size. Beside this steric stabilising activity, PVP allows the reaction to happen also at room temperature and decreases the particle size. PVP is a homopolymer whose individual unit contains an amide group. The N and O atoms of this polar group probably have a strong affinity for the silver ions and metallic silver. A PVP macromolecule in solution, which most likely adopts a pseudo-random coil conformation, may take part in some form of association with the metal atoms, thus increasing the probability of nucleus formation. It should be pointed out that ethylene-glycol can also act as a protective agent but in the polyol process it is not able to prevent particle sintering because of the high temperatures required for the reaction. Moreover, the presence of PVP also decreases the mean size of particles. This effect can be explained according to the above described reaction mechanism. Because of the PVP presence, the rate of spontaneous nucleation increases, and a higher number of nuclei are formed during the nucleation burst. Thus, the number of final particles increases as well, and for a given amount of precipitated metal, the mean particle size therefore decreases.

3 Experimental results

Silver nitrate (Aldrich) was the starting material for the colloidal silver preparation. Reagent-grade ethylene-glycol (Aldrich) was used as solvent and reducing agent for $\mathrm{AgNO_3}$, and poly(N-vinylpyrrolidone) (PVP, Aldrich, $\overline{M}_\mathrm{w} = 10\,000$) was used as protective agent. All reagents were used without any further purification.

The polymer-colloidal silver nanocomposite samples were synthesised using two different methods. In the first method, PVP was dissolved in ethylene-glycol at room temperature and to this solution the required amount of $\mathrm{AgNO_3}$ was added. The solution was stirred at room temperature until complete dissolution of the silver nitrate was achieved. Then, the reaction was allowed to proceed at room temperature without further stirring. In the second approach, PVP was dissolved in ethylene-glycol at room temperature, and to this solution the required amount of an $\mathrm{AgNO_3}$/ethylene-glycol solution was quickly added under sonication (Ultrasonic Cleaner, J.P. Selecta, 40 kHz). Sonication was applied during the full reaction, which

Table 1. Compositions and reaction times of the nanocomposite synthesis.

Sample	PVP (g)	$AgNO_3$ (mg)	$C_2H_6O_2$ (ml)	Reaction time (h)	Color	Suspension type	Amount of added acetone (ml)
1	1.728	86.9	130	24	Dark yellow	Stable	400
2	1.728	44.5	65	24	Yellow	Stable	300
3	3.456	22.6	32	24	Red	Stable	260

proceeded at room temperature. The compositions and the reaction times were the same in both processes and they are reported in Table 1. When the colloidal dispersion had a yellow or red colour, the system was easily separated from the ethylene-glycol by addition of a large amount of acetone (1:5 by volume respectively), followed by sonication and centrifugation. The PVP/Ag nanocomposites were re-dispersed in ethyl-alcohol and precipitated again by acetone addition for purification. Finally, the material was dissolved in ethylene-glycol, then spun to prepare thin films and consequently dried in an oven (60 °C) at low pressures. Optical filter prototypes were obtained placing Ag/PVP/ethanol paste between two polycarbonate plates followed by the removal of the ethanol by heating at 60 °C. The plate edges were sealed by a silicon resin.

XRD data were collected by a Philips power diffractometer (PW1710) with Cu $K_{\alpha 1}$ radiation, in the range 10° and 80° in steps of 0.02° and by using a dwell time of 1 s. X-ray diffraction patterns of the various components, *i.e.* pure silver, silver nitrate and Ag-cluster/PVP nanocomposite, are presented in Figure 1. Referring to Figure 1a, the value of the Ag lattice constant has been estimated to be $a = 4.078$ Å, a value which is consistent with $a = 4.0862$ Å reported by the JCPDS file n° 4-0783. A mathematical approach based on a de-convolution of the peaks by a Lorentz function allowed a better determination of the peak parameters and hence of the crystallite sizes by means of the Scherrer formula:

$$d = \frac{k\lambda}{\beta_{1/2}\cos\theta} \tag{2}$$

where $\beta_{1/2}$ is the full-width at half maximum of the peak at 2θ, k is a constant ($k = 0.89$), and $\lambda = 1.54060$ Å is the $CuK_{\alpha 1}$ wavelength. Considering the $(111)^*$ direction in the XRD spectrum, a value of $d = 11 \pm 1$ nm was found. This estimation confirms the hypothesis of particle monocrystallinity.

Silver colloids were characterised by TEM using a Philips-CM12 microscope. Samples were prepared by placing a drop of the colloidal silver dispersion onto a standard microscope grid coated with a carbon film. The mean particle size of the colloidal silver dispersions and the standard deviation of particle population were respectively determined by imaging analysis of the micrographs of these dispersions. TEM micrographs of thin nanocomposite films are shown in Figures 2 and 3. All particles

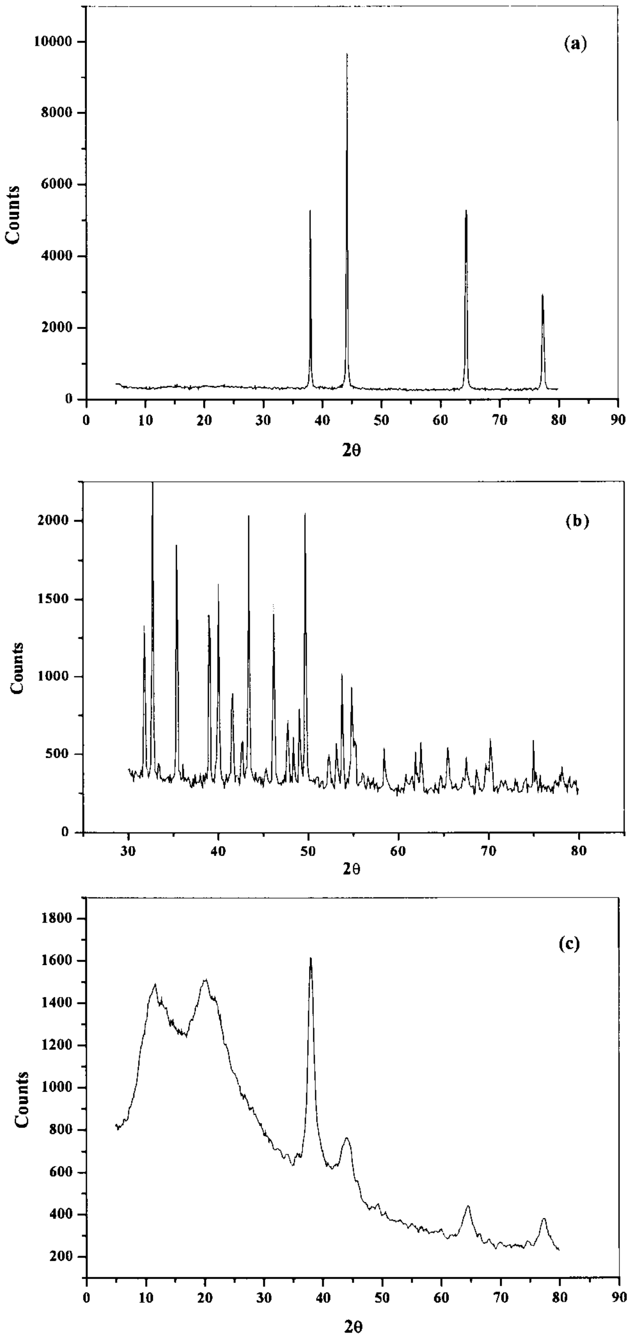

Fig. 1. XRD patterns of: (a) pure silver (sheet with oriented grains); (b) silver nitrate; (c) Ag- cluster/PVP nanocomposite.

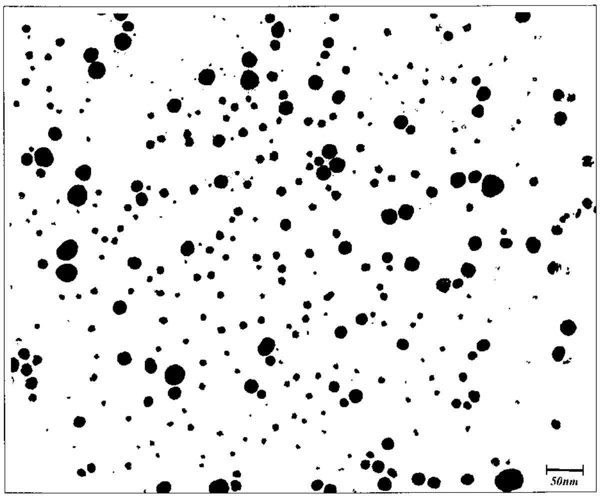

Fig. 2. TEM-micrograph of the silver nanoparticle microstructure. The sample has been obtained dissolving $AgNO_3$ in the PVP/glycol solution without the sonication treatment.

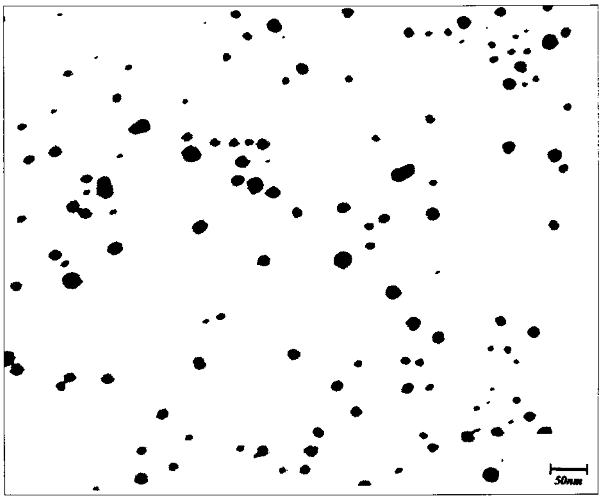

Fig. 3. TEM-micrograph of the silver nanoparticle microstructure. The sample has been obtained by "fast mixing" of the precursor solutions and the reaction was performed in presence of sonication.

obtained by direct mixing of $AgNO_3$ with PVP/ethylene-glycol solution in absence of sonication (Fig. 2) had a pseudo-spherical shape, even if deformations were more visible for particles with larger sizes. Anyway, the composite material did not contain aggregates or particles sintered together. The particle size was poly-dispersed with a diameter ranging from 3 nm to 45 nm. The mean value of the Ag particles diameter has been estimated to be 10 nm. Because of the diameter of a Ag atom is ~ 0.3 nm, particles contain about 30 000 atoms of silver. Such a low number allows any particle to give light scattering phenomena resulting in a behaviour different from that characteristic of the bulk metal. When the silver particles are obtained by a fast mixing of two precursor solutions, each including just one of the required reagents, and the reaction is performed in the presence of sonication (or strong stirring), a high homodispersed product is obtained (see Fig. 3). In this case a single nucleation stage takes place during the nanochemical process. All particles grow together at a rate which depends on the Ag^+ reduction speed.

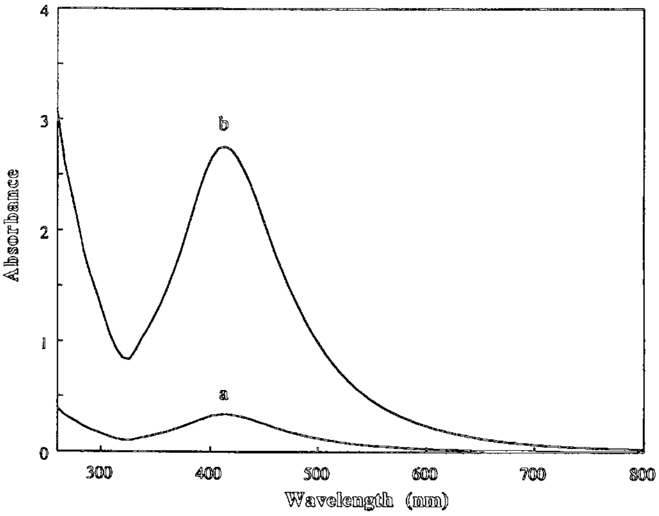

Fig. 4. (a) UV-visible spectrum of an alcoholic solution of Ag/PVP nanocomposite. The spectrum has been performed at two different silver particle concentrations: (curve a) 2 wt.% of silver; (curve b) 5 wt.% of silver.

The UV-visible absorption of each colloidal sample was characterized by an UVIKON 930 UV-spectrophotometer (Kontron Instruments) with a variable radiation wavelength between 300 and 800 nm. Figure 4 depicts the optical spectra of the metal particles at two different colloid concentrations. The presence of Ag(0) in solution has to be related to the broad absorbance peak, while any feature corresponding to Ag^+ species is masked by the peak due to organic species present in solution. In Figure 5a, the contribution of the PVP matrix has been subtracted in order to better evidence any size-induced quantum effect. The main peak occurs at $\lambda = 410$ nm, *i.e.* $\hbar\omega = 3.1$ eV. The half-width of this plasmon peak has been estimated to be $\Gamma = 0.6$ eV, which corresponds to a mean particle diameter of about 3 nm under the hypothesis of an almost spherical particle shape [20]. Beside this peak, a broad additional structure is visible at $\lambda = 340$ nm, *i.e.* $\hbar\omega = 3.75$ eV. Such a structure has been better evidenced in the UV absorption derivative curve shown in Figure 5b.

The reaction yield was obtained from the weight percent of silver particles incorporated into the polymer by thermogravimetric analysis (TGA) of nanocomposite samples in flowing N_2. As shown in Figure 6, a full polymer decomposition is visible at temperatures higher than 400 °C.

4 Discussion

The possibility of controlling the final size of metal particles in the nm range is undoubtedly one of the most

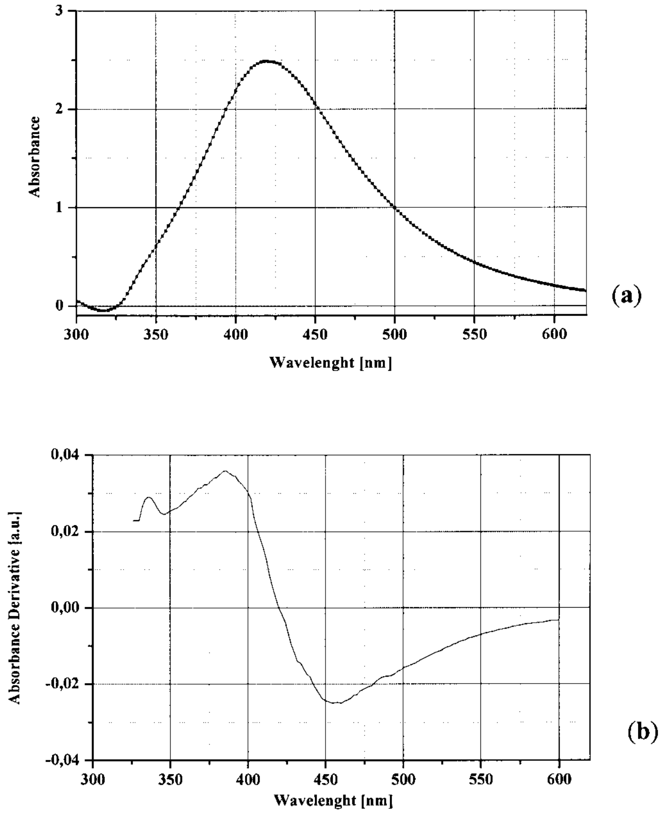

Fig. 5. (a) Particular of the plasmon induced structure in the UV spectrum after the subtraction of the background. (b) Derivative of the absorbance curve for a better definition of the structure wavelength position.

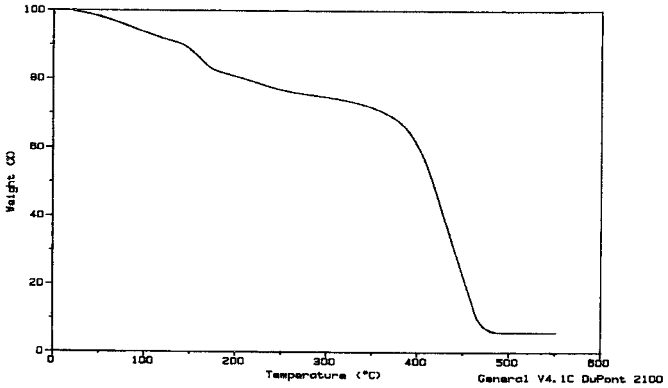

Fig. 6. TGA analysis of an Ag-cluster/PVP nanocomposite sample.

challenging issues of modern nano-chemistry. For the modified polyol process proposed in this paper, this possibility has been strictly related to some chromatic features of the produced films arising from optical absorption properties in nano-sized Ag particles. For this type of development, this approach seems to be very flexible for achieving in high-performance colour filters whose absorption band results located at a different wavelength in the optical range of interest, *i.e.* 200 nm–800 nm. At room temperature the rate of silver reduction by ethylene-glycol, which controls the particle growth process, is very low. So, it is possible to see a slow chromatic evolution in the reactive mixture produced by the colloidal silver polychromism, which can be effectively used for monitoring the particle growth and stopping the process at few nm-sized level. In particular, the silver colloid can be promptly separated from the ethylene-glycol-$AgNO_3$ solution by adding a large amount of acetone followed by centrifugation. The extraction of nanosized Ag particles follows the PVP precipitation by a mixture of two miscible solvents differing from their ability to dissolve the polymer. The polymer bonded to silver particles is highly soluble in ethylene-glycol and very poorly soluble in acetone. Consequently, a progressive addition of acetone to the Ag/PVP suspension causes the system to become cloudy at a given volume of added acetone ($\sim$ 5 times the volume of the ethylene-glycol solution) and hence to precipitate. This corresponds to the agglomeration of PVP and silver compounds as a result of the van der Waals interactions. Ethylene-glycol and unreacted $AgNO_3$ are soluble in acetone and therefore they can be completely separated from silver particles. In addition, the reduction reaction is completely stopped in the acetone medium because the reaction cannot happen at room temperature in the absence of PVP.

A key-role toward the achievement of nano-sized particles has been played by the sonication treatment which has been demonstrated to be particularly useful at this stage of the process, *i.e.* the separation between components in solution, since it allows a fast removal of the ethylene-glycol from the precipitate nanocomposite. Moreover, as far as the system is centrifugated and the agglomerated fraction containing the silver particles is collected, it leaves the ethylene-glycol and silver nitrate reagent in the supernatant. At the end of the process the polymeric matrix is partially plasticized by the ethylene-glycol presence. Nevertheless an accurate washing by acetone leaves a solid material. However, the polymer agglomeration is a reversible process and the precipitate can be redispersed in ethyl-alcohol giving a homogeneous clear solution and be precipitated again by acetone for purification.

Among the characterisation data presented in Section 3, the optical spectra offer the possibility to infer more about the achieved nano-sized regime of Ag particles and their properties. In fact, the presence of the absorption peak at 410 nm and the structure at $\sim$ 350 nm are clear signatures of quantum size effects occurring in the Ag particles absorption properties. The optical absorption and scattering of metal colloids are mainly due to excitation of surface plasmons of small metal particles by an external oscillating electric field [21–25]. When the particle size is small enough compared to the light wavelength, their optical response is mainly attributed to the light absorption by dipolar polarisation of the particles. For bulk metals these resonant wavelengths are generally located in the infra-red portion of the spectrum. However, when these materials are fabricated as small as nanoparticles, the gap between the excitation bands is widened. This means that only photons of a higher energy level will be absorbed and hence a response in the visible spectrum is obtained. According to Kubo theory [26], the presence of a particle distribution with a mean size less than a critical diameter d_c can produce additional electronic lifetime effects visible through a broadening of the first plasmon mode. This broadening may increase with increasing the particle size. Quantum-size effects vanish in particles where the energy level broadening δE exceeds the mean spacing ΔE between the levels. In particular two regions are defined as a function of the above introduced diameter d_c as follows

$$d < d_\mathrm{c} \quad \delta E < \Delta E \ \text{(quantum size region)}$$
$$d > d_\mathrm{c} \quad \delta E > \Delta E \ \text{(quasicontinuous energy bands).}$$

In the preparation of metal nanoparticles used as pigments in colour filters or UV-absorbers, it is very important to be able to control the particle size and hence to produce particles with a diameter less than the critical value d_c. It depends on temperature and the preparation method because both ΔE and δE may be influenced by the form and crystalline structure of the particles and by the nature of the embedding matrix. In particular, PVP modifies the colloid reactivity and causes changes in the UV-visible absorption spectra [26]. A decrease of the extinction coefficient of the plasmon band can be explained in terms of the strong affinity of the polar amide groups, present in the individual unit of PVP, with the produced metallic silver. This effect would imply a change in the free electron density which in turn induces changes in the surface plasmon band of silver particles and yields a variation of the width and height of the plasmon band absorption. Actually, such an effect can be observed with all ligands able to complex the Ag^+ ions because they can be also strongly adsorbed on the surface of silver nanoparticles. For example, n-alkanethiols, n-alkylamines, and carboxylic acids, in addition to the amide compounds can be bonded to colloidal silver particles. The chemisorption of a nucleophilic molecule on the silver surface is also accompanied by a charge donation to the metal. The cumulative effect of the adsorption of many molecules produces a shift of the Fermi level energy [26]. This mechanism can be invoked to account for the changes in the absorption spectra and the modified reactivity of silver colloids (for example, the increased reactivity of the silver colloids toward dissolved O_2, despite the presence of a physical barrier to ion transport with dissolved species in solution).

Beside the main plasmon peak, the additional feature observed at $\hbar\omega = 3.75$ eV represents a further interesting quantum-size induced effect. A detailed inspection (see Ref. [20]) of the positions of the one-electron transitions of Ag quasi-spherical particles within a square-well potential model shows that a group of transitions could move from higher energies toward the plasmon region which might cause absorption structures similar to those reported in Figure 4a. It seems necessary to make anyway further investigations to clarify these important physical aspects. As far as concerns this paper, such structured optical spectra have to be considered as a proof of the success achieved by the proposed modified polyol process in the synthesis of a nano-composite material. The possibility to apply this process in the development of *ad hoc* Ag-based colour filters whose absorption band results in the optical UV range is undoubtedly interesting from the application point of view since it allows the modulation of filters performances to particular requests. The flexibility of the proposed process is further demonstrated by the ease of the choice of different protective agents for different optical performances. Moreover, thin films of Ag nanocomposite containing polymers of different nature can also be overlapped, producing a multi-layer with enhanced radiation absorption properties in a wide range of wavelengths.

5 Conclusions

Chemical routes for the polymer-based nanocomposites preparation offer the advantages of: (a) a cluster or atomic level control, and (ii) an efficient scale-up for processing and production. Here, the polyol process for the preparation of metal/polymer nanocomposite materials with a high homodispersed and size-controlled filler has been successfully enhanced. The method uses ethylene-glycol as reducing agent for the $\mathrm{AgNO_3}$ salt and PVP as protective agent to prevent the silver particle sintering. The reaction has been carried out at room temperature to decrease the reaction rate and in presence of sonication to allow the production of very thin colloidal particles. To end the particle growth process, acetone has been added when the reactive mixture colour was that corresponding to the desired particle size. The microstructural characterisation of the nanocomposite obtained both in absence and in presence of sonication shows that this step facilitates smaller size Ag particles and a more uniform size distribution. Optical absorption spectra show interesting features which are characteristic of the small size of synthesised Ag particles. In particular, the presence of the absorption peak at 410 nm and the observed structure at ~ 350 nm are clear signatures of quantum size effects occurring in the Ag particles' absorption properties. The high degree of particle size control in the nm range suggests a successful application of this method to the realisation of colour filters and/or UV absorbers with particularly interesting performances. The flexibility offered by the choice of the protective polymeric agent is a further element of interest toward future advanced optical applications.

The authors gratefully acknowledge Prof. A. Barone for helpful discussions during the development of this work.

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