Formation of Gold Branched Plates in Diluted Solutions of Poly(vinylpyrrolidone) and Their Use for the Fabrication of **Near-Infrared-Absorbing Films and Coatings**

Iván Pardiñas-Blanco,[†] Cristina E. Hoppe,^{*,†} Yolanda Piñeiro-Redondo,[‡] M. Arturo López-Quintela,[†] and José Rivas[‡]

Laboratory of Magnetism and Nanotechnology, Institute of Technological Investigations, Department of Physical Chemistry, and Department of Applied Physics, University of Santiago de Compostela, Santiago de Compostela, Spain

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Ribbon-like and branched gold nano- and microstructures were produced by simple heating of diluted aqueous solutions of poly(vinylpyrrolidone) (PVP) and HAuCl₄. The reaction was carried out in a one-pot, one-step process at mild temperatures. Modification of the synthesis variables allowed the obtaining of structures with different sizes and branching degrees which formed stable hydrosols with characteristic colors. A mechanism for the growth of the crystals was proposed, based on the aggregation of metal units followed by reorientation and attachment processes facilitated by the presence of low concentrations of the polymer. These anisotropic structures were used to obtain large-area porous coatings on metallic, plastic, and glass substrates and to synthesize homogeneous polymer composites. The resulting gold-modified materials showed an important increase of absorption in the near-infrared (NIR) region of the electromagnetic spectrum, which could find interesting applications in the development of NIR-absorbing filters and coatings.

Introduction

The dramatic effect that shape anisotropy has on the electronic, optical, and catalytic properties of noble metal nanostructures makes the development of morphology-controlled synthesis strategies a main step toward the design of future nanodevices.¹⁻⁵ In this regard, the last years have been very prolific in the design of new procedures dealing with the synthesis of noble metal anisotropic structures (Au, Ag, Pt, Pd) such as nanowires,6-8 nanoplates,9-12 nanocubes,13,14 and nanorods15 with wellcontrolled size and low polydispersity. Recently, some examples concerning the synthesis of branched nanostructures (monopod, bipod, tripod, tetrapod, multipod),¹⁶⁻²¹ star polyhedral crystals,²²

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nanoflowers,²³ and ringlike nanostructures²⁴ have also been reported. Nevertheless, reports on the formation of more intricate, interconnected shapes, such as hyperbranched and networked²⁵ structures, have remained more elusive, especially in the case of gold. These kinds of structures present unique properties with potential applications in the field of electronic,¹⁶ catalysis,²⁶ sensing,^{27,28} and SERS (surface-enhanced Raman spectroscopy) enhancement.²⁹ They also constitute promising building blocks for the design of new two- and three-dimensional metallic materials and composites. Thereby, the development of simple one-step techniques conducting to these morphologies is highly desirable. Only some examples corresponding to the synthesis of branched noble metal structures can be found in the recent literature. Kaniyankandy et al.30 reported on the synthesis of silver nanodendrites by electrodeposition using AgNO3 in ammoniacal solution. Dendritic flat gold nanostructures were obtained by Swami et al. by reduction of chloroaurate ions constrained to a monolayer at the air-water interface.³¹ Recently, hyperbranched silver nanocrystals were obtained in aqueous solution using trisodium citrate and L-ascorbic acid,32 and gold

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^{*} Corresponding author. Fax: +34 981 595012. Tel.: + 34 981 563100. E-mail: hoppe@fi.mdp.edu.ar.

Department of Physical Chemistry.

fractal structures could be obtained in sheared lamellar phases.33

In this work we present a novel and facile one-step method for the synthesis of very stable hyperbranched and ribbon-like gold nano- and microstructures in aqueous solutions at mild temperatures. The synthetic approach is based on simple modifications of a previously reported strategy for the synthesis of gold nanoparticles based on the use of poly(vinylpyrrolidone) (PVP) as a capping and reducing agent in aqueous solution.³⁴ PVP is a water soluble, nontoxic polymer extensively used as a protecting agent for the synthesis of metal nanoparticles by the polyol process.^{7,35} The ability of this polymer to act as a reducing agent in the synthesis of metal nano- and microstructures has been proved, giving place to the development of strategies for the synthesis of gold and silver nanoparticles and nanoplates.^{34,36,37} In this work, we show that by introducing simple variations in the synthesis conditions this simple and clean synthetic route can be directed to the formation of water dispersible gold nanoand microplates characterized by different degrees of branching. A possible growth mechanism is proposed based on aggregation of initial gold units followed by reorientation and attachment in conditions of low polymer protection. Finally, the ability of the highly branched products to act as building blocks in the formation of NIR-absorbing coatings and films is analyzed.

Experimental Section

Materials. PVP with two different average molecular weights, PVP10 ($M_w \approx 10\ 000$) and PVP K90 ($M_n \approx 360\ 000$), was purchased from Aldrich and used as received. Aqueous solutions of this polymer were prepared by weighting of the solid and stirring at room temperature. The polymer concentrations, [PVP]_{r.u.}, were varied from 0.004 to 0.269 M, ([PVP]_{r.u.} states for concentrations calculated in terms of moles of the repeating unit of PVP, with a molecular weight of 111 g/mol, per liter of solution). The aqueous solution of the metallic precursor, HAuCl₄·3H₂O (Sigma-Aldrich, purity \geq 99.5 wt %), was prepared with a concentration of 0.02 M. The reaction was carried out by adding a calculated volume of the aqueous solution of HAuCl₄ to 10 mL of PVP solution. After shaking for homogenization, the samples were heated to 70 °C and left standing without stirring for the reaction to proceed. After 16 h, samples were cooled at room temperature.

For the synthesis of nanocomposites, a 5 wt % aqueous solution of poly(vinyl alcohol) (PVA) (40-49 cPs, 87-89% hydrolyzed) was prepared by dissolving the solid in hot distilled water (70-90 °C). After cooling, selected volumes of this solution were mixed with concentrated hydrosols to obtain the desired gold concentration in the final material. The solutions were cast on silicon molds and evaporated in an oven under the following heating cycle: 1 h 45 min at 70 °C, 1 h at 100 °C, 2 h at 120 °C.

Techniques. Transmission electron microscopy (TEM) was performed with a Philips CM-12 microscope operated at an accelerating voltage of 100 kV. Dark- and bright-field TEM images were obtained using a JEOL JEM 2010F field emission gun microscope operating at an acceleration voltage of 200 kV. Samples were prepared by dropping a water dispersion of the particles on a copper grid coated with Formvar and a carbon film.

Scanning electron microscopy (SEM) was performed using a Leica 440 scanning electron microscope. High-magnification SEM images were obtained using a JEOL JSM-6700F FEG-SEM microscope. Samples were prepared by evaporating a few drops of the obtained hydrosols onto metal substrates. In branched coatings obtained on



Figure 1. Representative TEM images of the reaction products obtained with $[HAuCl_4] = 0.1 \text{ mM}$ and different concentrations of PVP K90 repeating units: (a) 0.045, (b) 0.038, (c) 0.030, (d) 0.013, and (e and f) 0.004 M.

polymer substrates, a fine gold layer was sputtered onto the samples to improve imaging at high magnifications.

UV-vis-near-infrared (NIR) spectra were measured with a Cary 5000 UV-vis-NIR spectrophotometer. Spectra up to 800 nm were measured in a diode-array Hewlett-Packard HP8452 spectrophotometer. The samples were placed in a 1 cm \times 1 cm \times 3 cm quartz cell, and spectra were recorded at room temperature.

X-ray diffraction (XRD) analysis was carried out on a Philips 1710 X-ray diffractometer using Cu K α radiation. Samples were prepared by slow evaporation of the hydrosols directly onto the supports.

NIR transmittance measurements of coated films were carried out using a Nicolet 6700 FT-IR spectrophotometer. Samples were measured in transmission mode in the range of $4000-11\ 000\ cm^{-1}$.

Thermogravimetry (Perkin-Elmer, TGA 7) was used to determine the percentage of gold in the final composites. Dynamic scans were performed under oxygen flow at 10 °C/min between 50 and 800 °C.

Results and Discussion

Effect of the Synthesis Variables. Gold branched structures were obtained working at low metal concentrations (typically about 0.2 mM as HAuCl₄) and low PVP/metal ratios (in most cases not higher than 300 polymer repeating units per metal atom). Within these general conditions, a change in the PVP/ metal molar ratio produced a variation in size and branching level of the structures. In all the cases, final samples were characterized by a distribution of products with an average size that progressively increased with the decrease in the PVP/metal ratio. The number of branches was also enhanced by lowering the PVP concentration. Figure 1 shows representative structures obtained for a fixed gold concentration (0.1 mM) and variable concentrations of PVP K90 (from 0.045 to 0.004 M). At the highest concentration (Figure 1a), curly rods as well as a population of isolated spherical structures could be identified. The size of the spheres was in the order of tens of nanometers and similar to the width of the rods, which suggests that the last ones were formed by attachment of initially spherical or disklike

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Figure 2. TEM (a-c) and SEM (d) images of the reaction products obtained for different HAuCl₄ and PVP K90 concentrations at a fixed PVP/metal molar ratio equal to 290 (as moles of repeating units of PVP per mole of gold). HAuCl₄ concentrations for each sample: (a) 0.05, (b) 0.09, (c) 0.21, and (d) 0.53 mM.

units. When the concentration of repeating units of PVP was decreased to 0.038 M, irregular multipod structures could be seen (Figure 1b). A subsequent decrease in concentration up to 0.013 M led to the development of structures characterized by a higher branching level and larger size (Figure 1, parts c and d). Polygonal geometries at the end of the branches were also common features of this type of structure. For concentrations of polymer repeating units as low as 0.004 M, hyperbranched structures were no longer formed. Instead, curly ribbon-like morphologies (in several cases terminated by thin geometrical plates) were the main product of the reaction (Figure 1e). These nanowires reached several micrometers in length and average widths of about 40-50 nm and were similar to those obtained by Vasilev et al. by the reduction of HAuCl₄ with 2-mercaptosuccinic acid in aqueous solutions.⁶ Figure 1f shows a magnification of one of these wires, in which the ribbon-like tail can be clearly observed.

A low global concentration of reactants was crucial for the development of branched structures. Figure 2 shows the products obtained keeping constant the molar ratio between repeating units of PVP K90 and gold ions and changing the global concentration of both reactants. A change in gold concentration from 0.05 to 0.09 mM produced only slight changes in size. However, a subsequent increase in the metal concentration up to 0.21 mM changed completely the obtained morphologies. In this case the final products were mainly composed by large, irregular particles joined by thin ribbon-like structures. A further increase in the concentration led to the formation of micrometric particles of mixed morphologies (plates, polyhedral nanoparticles, and spiral-like structures).

Crystal Characterization of Highly Branched Structures. A complete crystal characterization was carried out on highly branched synthesis products. TEM images of representative structures can be observed in Figure 3a-e. The micrographs reveal complex structures composed of curly ribbon-like branches forming a network. Frequently, ends of the branches were found to be wider than the arms and in several cases characterized by a polygonal shape. A very low thickness could be inferred from the low contrast in TEM images and by the clear visualization of superposed zones of the same structure (see Supporting Information Figure S1). The mean average size of the crystals reached several nanometers or even micrometers depending on the reactants concentration.

An XRD powder diffraction pattern of the crystals obtained with $[PVP K90]_{r.u.} = 0.030 \text{ M}$ and $[HAuCl_4] = 0.1 \text{ mM}$ can be observed in Figure 3f. The expected diffraction peaks for the



Figure 3. Representative TEM images of highly branched products obtained under different experimental conditions: (a and b) [PVP $[K90]_{r.u.} = 0.030 \text{ M}, [HAuCl_4] = 0.1 \text{ mM}; (c \text{ and } d) [PVP K90]_{r.u.}$ = 0.013 M, [HAuCl₄] = 0.1 mM; (e) [PVP10]_{r.u.} = 0.030 M, $[HAuCl_4] = 0.2 \text{ mM}.$ (f) XRD pattern obtained for the sample shown in panels a and b. (g and h) Bright-field and dark-field TEM images of a selected zone of a crystal showing the presence of bending.

face-centered cubic structure of gold are present, although with an exceedingly high intensity ratio between (111) and (200) diffraction peaks with respect to the bulk. This feature is characteristic of thin structures primarily bound by {111} facets with high tendency to be oriented with the {111} face parallel to the substrate.38,39

TEM images also show the presence of lines and bands with different contrast in the structures. These fringes could result from bending of the {111} face of the thin plate, indicating slight deviations from the planar geometry.⁴⁰ These bending contours are clearly observed as changes in contrast in both bright- and dark-field TEM images (Figure 3, parts g and h, respectively).

Electron diffraction analysis carried out by focusing the beam on a whole structure (Figure 4a) shows a pattern that was indexed based on the face-centered cubic (fcc) structure of gold. Although this pattern was not consistent with a perfect single crystal, it did not show the characteristic rings of a random distribution of individual grains either. The pattern could rather be interpreted as a structure formed by oriented individual fused grains sharing interfaces characterized by a slight crystallographic mismatching. As observed from the selected area electron diffraction (SAED) patterns taken from four different zones of the crystal (Figure 4b), the presence of additional spots indicating slight misorientation between planes is especially important in the inner zone of the crystal, where several branches joined forming a network (inset D in Figure 4b). Closer inspection of selected zones of the branched plate allowed the direct visualization of interface dislocations (Figure 4c-e). The origin of these defects is likely

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Figure 4. (a) Electron diffraction pattern of a whole crystal synthesized with $[HAuCl_4] = 0.1 \text{ mM}$ and $[PVP \text{ K90}]_{r.u.} = 0.030 \text{ M}$. (b) SAED patterns obtained from different zones of the same crystal. (c-e) TEM images showing the presence of interface dislocations in the crystal.

a consequence of the growing mechanism itself. When crystals are formed by coalescence of grains at crystallographically specific surfaces, a small misorientation at the interface can result in dislocations.⁴¹

SAED patterns of the outer zones of the structure (A, B, and C insets in Figure 4b) show patterns consistent with more perfect single-crystal structures. They show the presence of interfringe distances with values near to 0.25 nm, indexed to the $1/3{422}$ reflection, which is forbidden for a perfect fcc structure.⁴² These features have been frequently found in platelike metal fcc crystals^{38–40} and attributed to different structural characteristics. They are observable from atomically flat surfaces of gold and silver^{7,42} but can also be explained by the presence of parallel twin planes, surface reconstruction, or by the occurrence of (111)stacking faults parallel to the (111) surface.⁴³ In addition, both the presence of twin planes and (111) stacking faults have been suggested to be responsible for the anisotropic growth of noble metal crystals.42-44 However, the real nature of the mechanism conducting to the formation of platelike morphologies remains still under investigation.

Stability and Optical Characterization. Stable water-based colloids with characteristic colors were obtained by simple variation of the concentration of the reactants in the synthetic medium (see photographs in color in Supporting Information Figure S2). Even the largest structures remained well dispersed for several days, and after slow precipitation of the solid, homogeneous dispersions could be easily recovered by simple shaking of the sample. This high stability likely arises from the very efficient capping action of the polymer.

Figure 5 shows the UV-vis-NIR spectra obtained for samples prepared with a 0.1 mM fixed concentration of gold and variable

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concentrations of PVP with molecular weights of 360 000 (PVP K90) and 10 000 (PVP10). The optical behavior of the reaction products was very dependent on the size and degree of branching. For high PVP/molar ratios, the obtained spectra were characteristic of a mixture of spherical particles and different nanoplate shapes (see TEM images in Supporting Information Figure S3). The peak located at high energies (between 530 and 540 nm) was assigned to the dipole resonance of spheres, whereas the second absorption at longer wavelengths (near 800 nm) was associated to the in-plane dipole resonance band of platelike structures. Similar spectral features have been previously observed for mixtures of spherical particles and triangular nanoprisms with edge lengths in the order of hundreds of nanometers.⁴⁵

For lower polymer contents, as the degree of branching and size of the structures was enhanced, a clear increase in the absorption at longer wavelengths was observed. This was also easily observable by the change in color of samples prepared with decreasing amounts of polymer.

Samples prepared with the lowest PVP/metal molar ratios were characterized by wide absorption bands at long wavelengths. These results are consistent with the formation of highly branched, anisotropic structures with very high aspect ratios for which the in-plane dipole resonance band red shifts to the NIR region of the electromagnetic spectrum.^{46,47} Noble metal structures with absorptions in this region of the spectrum could find useful applications in biotechnology (by allowing local heating with low-energy irradiation)⁴⁷ and as filters and optical coatings for the attenuation of IR solar radiation.⁴⁶

In the case of products synthesized with PVP10, the development of the high-wavelength absorption band became evident at higher polymer concentrations than for PVPK90, indicating

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Figure 5. UV-vis-NIR spectra of gold hydrosols synthesized with $[HAuCl_4] = 0.1$ mM and different concentrations of PVP K90 (a) and PVP10 (b) repeating units, as indicated.

that shorter polymer chains favored the synthesis of branched structures. This was also confirmed from TEM images of products obtained in similar reaction conditions with PVP samples of different molecular weights (data not shown).

Growth Mechanism. PVP-mediated reduction of HAuCl₄ has proven to be a clean and simple way to obtain spherical and platelike (triangular and hexagonal) gold nanoparticles.^{34,36} Hence, it seems surprising that the same general reaction could be used to obtain structures with a completely different morphology, in which branches and curly ribbon-like features are the main characteristics of the final products. To gain insight into the possible growth mechanism, the time evolution of the branched structures during the synthesis was investigated by TEM and UV–vis spectrophotometry.

Figure 6a shows the evolution of the spectra for different reaction times corresponding to a sample synthesized with [PVP10] = 0.030 M and $[HAuCl_4] = 0.1$ mM at 70 °C. After mixing, the first change in the spectra is evidenced as the decrease of the peak centered at 293 nm, assigned to the AuCl_4⁻ ions in the PVP solution. This change is likely associated to a first reaction step involving the reduction of Au(III) to Au(II) followed by fast formation of Au(I) by disproportionation. Au(I) would be further



Figure 6. (a) Evolution of the UV-vis spectra during reaction at 70 °C for a sample containing [HAuCl₄] = 0.1 mM and [PVP10]_{r.u.} = 0.030 M, from bottom to top: 0, 61, 95, 122, 144, 183, 214, 277, and 357 min after mixing. (b-e) TEM images corresponding to products at 61, 122, 144, and 277 min of reaction.

reduced to form Au(0) atoms and clusters.⁴⁸ A weak band covering a wide wavelength region appeared after 95 min. The intensity of the band increased with time, reaching its maximum value after about 6-7 h. During the synthetic process, the sample first turned from light yellow to colorless, reflecting the reduction of Au(III) to Au(I), and then to a green color typical of the final hyperbranched structures.

To follow the structural evolution of the structures by TEM, a few drops of the solution were withdrawn with a pipet at selected times, deposited onto TEM grids, and dried under a nitrogen flow. Figure 6b—e shows images taken at 61, 122, 144, and 277 min after mixing. The presence of aggregated structures is observed even for the shortest times analyzed. At 61 min, and although no significant signal in the UV—vis spectra was recorded (probably due to the low concentration of structures attained at this short reaction time), a low amount of metal particles along with some large aggregates could be observed. These structures seem to be formed by smaller particles joined together as inferred from the necks that give them a "curly" appearance. The same type of structure was observed for 122 min but in higher concentration. Samples corresponding to 144 min were characterized by the presence of a high amount of large, highly

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branched structures. In contrast to morphologies observed at shorter times, branches were shown to have lost some of their polycrystalline aspect (characterized by a strongly varying contrast along the structure) and exhibited a more monocrystalline appearance. Finally, at 277 min the structures showed the typical aspect of the final products, with ends of the branches showing polygonal shapes (triangular or hexagonal).

Both TEM and UV—vis analysis seem to indicate that formation of the branched structures starts with the aggregation of small gold units formed by reduction of the metal salt. The nature of these initial gold units would be determined by the synthesis conditions, especially by the reaction rate. Some groups have shown that at slow reaction rates (in conditions of kinetically controlled growth) formation of planar metal clusters (in general, clusters with less than approximately 10 atoms) would be favored, which would give place to seeds and nanoparticles with a planar configuration.^{49,50}

It seems that formation and aggregation of these seeds occur almost simultaneously during the first stages of the reaction producing a gradual increase in size and branching degree. The metastability of the initial polycrystalline structures is evidenced by the final change in the morphological aspect of the branches and by the growth of the polygonal ends.

During the early stages of the synthesis of gold plates obtained at higher PVP/metal molar ratios (Figure 7), intermediate corrugated, defective structures (apparently formed by initial smaller gold units) were observed previously to the formation of more perfect single-crystalline structures. This is in agreement with recent findings reported by other groups who found similar structures during the synthesis of platelike structures using nonpolymeric reducing agents.^{10,51} Hence, both kinds of structures (polygonal and branched) seem to be formed by a common mechanism involving aggregation and fusion of initial gold units.

The experimental results clearly showed that synthesis of branched structures was favored in conditions of high dilution, low PVP/metal molar ratios, and the presence of short polymer chains. This would indicate that very low reaction rates (associated to initial low polymer and metal concentrations)³⁴ and low protection efficiencies (favored by poor polymer coating and short chains) are key conditions for the synthesis of branched structures. A low supersaturation of gold atoms and a medium favoring aggregation could enhance the development of open, extended structures with a branched appearance. The only exception to this behavior was found for extremely low reactants concentrations (see the wires in Figure 1, parts e and f). The absence of branching in these conditions could be associated to a drastic decrease in the probability of encounters between metal subunits, which would favor a one-dimensional aggregation process.

Hence, our findings point toward a mechanism in which morphology might be controlled by gold atoms supersaturation and protection efficiency against aggregation. However, final structures cannot be explained based only in a random fusion of initial units, which more probably would give place to polycrystalline structures. As described above, progressive loss of the contrast variation within the branches and formation of more crystalline, polygonal ends were observed at the last stages of the reaction. Moreover, the presence of tiny holes and irregularities, as well as dimples and dislocations, was a very common



Figure 7. TEM images showing typical "corrugated" intermediate structures observed during the synthesis of polygonal platelike structures (time = 1 h after mixing). $[PVPK90]_{r.u.} = 0.064 \text{ M}$, $[AuCl_4^-] = 0.1 \text{ mM}$.

feature of these structures (see Figure 4c-e and more examples in Supporting Information Figure S4). Unraveling of the detailed mechanism will certainly require further investigation; however, a possible explanation for the presence of these structural characteristics is to consider that, in the initially aggregated system, individual units can rearrange to suffer an oriented attachment process (OA). OA involves spontaneous selforganization of adjacent particles so that they share a common crystallographic orientation, followed by joining of these particles at a planar interface.⁴¹ The occurrence of this process in colloidal aggregates of natural iron oxyhydroxy particles has been demonstrated by Banfield et al.52 In this process, formation of dislocations due to a small misorientation in the interface is common, as well as the presence of dimples and other defects.⁵³ On the other hand, in particles formed by Ostwald ripening or by recrystallization of randomly oriented primary particles, dimples and defects are expected to be absent.⁵³ It is also worth noting that triangular and hexagonal shapes formed at higher polymer concentrations also showed similar structural defects, which is in agreement with a common mechanism for the formation of both kinds of structures. OA could also explain the spiral growth observed in polygonal shapes obtained at high metal concentrations (see Figure 2d).⁴¹

Although the classical picture of OA involved small seeds (typically below 10 nm) and the use of high temperatures,^{41,54} recent results have shown that these are not true restrictions and

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Figure 8. SEM images of films obtained by evaporation of branched hydrosols onto metallic (a and b) and polypropylene (c and d) substrates. (Panels b and d are higher magnification images of panels a and c.) The inset in (a) shows a TEM image of aggregates formed on the grid. The inset in (d) is a TEM image showing a typical branched structure found in a sample scraped off the coating.

that OA can occur at moderate temperatures and with larger crystals.⁵⁵ Oriented attachment might be favored by the initial close contact between particles and their high mobility in the diluted polymer solution. The use of a neutral polymer acting as a loose capping on the particles and simultaneously avoiding fast precipitation of the products possibly plays an important role in this process. In branched systems, outer parts of the structures would be regions in which reorientation and attachment could be more favored, explaining the location of large fused structures at the end of the branches.

Coatings and Composites. Solid samples of branched plates could be recovered from the obtained hydrosols by evaporation or centrifugation. In the case of the largest sizes, solid fractions could also be obtained by slow deposition at the bottom of the vial after storage of the colloids for several days. TEM analysis of these aggregates showed that the individual hyperbranched crystals tend to form extended structures on the surface of the grid (see the inset in Figure 8a). Taking advantage of this ability, gold coatings were easily obtained by evaporation of the hydrosols onto metallic, plastic, or glass substrates (see photographs of representative samples in Supporting Information Figure S5). Figure 8, parts a and b, shows SEM images of the films obtained on metallic substrates. The structures tend to cover the surface, generating films with a high surface area and an intricate morphology. As observed in the magnification (Figure 8b), most of the plates were arranged with their largest surface parallel to the substrate, which is in agreement with the preferred ordering inferred from diffraction measurements. Nevertheless, some crystals appeared with a perpendicular orientation and allowed the observation of their extremely low thickness.

Coating of hydrophobic polymers such as polypropylene, polyethylene, or polystyrene could also be carried out using a simpler and more direct method. After mixing of the reactants, polymer substrates were introduced in the reaction vessel and kept immersed during the heating. During this process, spontaneous deposition of the branched structures onto the surface of the substrates was produced, conducting to the formation of gold coatings. SEM analysis of the as-formed coatings showed the presence of well-distributed gold branched plates on the polymer surface (Figure 8, parts c and d). A sample of this film was carefully scraped off the surface and examined by TEM (see the inset in Figure 8d). The morphology of the structures was very similar to that of the products obtained as colloidal hydrosols, indicating that the presence of the substrate did not alter the synthetic process. The ability of the structures to form coatings on different substrates is probably associated with their high aspect ratio and the amphiphilic character of PVP that enables compatibilization with both hydrophilic and hydrophobic surfaces.

PVA-branched gold composites could also be obtained using a simple casting procedure. Selected volumes of an aqueous solution of PVA and an aqueous dispersion of gold branched plates were mixed and evaporated on silicon molds. After drying, well-dispersed PVA-gold composites with a greenish hue were obtained. The aspect of the films was very uniform without visible scattering.

Coated materials and composites were analyzed by NIR spectrophotometry. Glass and polymer substrates coated with branched structures, as well as PVA–gold composites, showed a significant decrease in the transmittance in the 4000–11 000 cm⁻¹ range compared with the unmodified materials (Figure 9).

NIR-absorbing films based on gold have been recognized as an alternative to reflective coatings for blocking IR radiation, for example, in architectural applications.⁵⁶ Economic viability of gold-based approaches relies on efficiency, cheap application, and on a hue acceptable to consumers.⁵⁶ The composite films and coatings obtained by our procedure have a pretty greenish color without any evidence of scattering and an important absorption in the NIR spectral range. Both coatings and modified gold composites can be easily obtained at mild temperatures. Additional advantages of the approach include the use of water as the solvent and a physiologically compatible, nontoxic polymer as the reducing and capping agent.

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Figure 9. (a and b) NIR spectra of a coated and uncoated glass slide and polyethylene film. (c) Spectra of a PVA sheet and a PVA-gold composite with 0.7 wt % of Au.

It is important to underline the unique characteristics that make these hydrosols very interesting candidates as building blocks for coatings and composites development. As was stated before, the characteristic broad NIR absorption of these plates, similar to that found in continuous thin films of gold, arises from their high aspect ratio and interconnected morphology. Normally, this kind of morphology would be associated with a poor stability in the dispersion and a high probability of aggregation, precluding its use in the synthesis of homogeneous coatings and films. However, the presence of low amounts of PVP stabilizes the structures in such a way that enables storage in aqueous dispersions for long times. Moreover, the amphiphilic character of PVP facilitates the transfer of the crystal to both hydrophilic and hydrophobic substrates.

In summary, high surface gold coatings and PVA–gold composites could be obtained through simple techniques by using colloidal gold plates with high branching degrees. These systems showed an important NIR absorption, which make them attractive candidates for their use as optical filters and coatings for attenuation of solar radiation. Moreover, the large surface area and intricate morphology of the coatings could find additional applications in the development of porous electrodes²⁸ and solid substrates for SERS enhancement.

Conclusions

Ribbon-like and hyperbranched gold nano- and microplates were obtained in a one-pot, one-step process in aqueous solutions at mild temperatures, by reaction of a metal precursor with PVP. The size and degree of branching of these structures could be easily modified by changing the concentrations of both reactants. Stable hydrosols with characteristic different colors were obtained by simple variation of the concentration of PVP and metal in the reaction media. Growth evolution of the structures and crystallographic features might indicate that the growth mechanism is based on aggregation of initial metal units followed by reorientation and attachment of the crystals, facilitated by a low concentration of the polymer. Gold films formed by branched plates could be obtained on metallic, glass, and plastic substrates using simple techniques (evaporation or spontaneous deposition during synthesis). Gold-polymer composites could also be obtained by simple casting from aqueous solutions of PVA and gold branched plates. Composites and coated substrates showed an increased NIR absorption that could find potential applications in the design of optical filters and NIR-absorbing coatings for attenuation of solar radiation.

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Supporting Information Available: Figure S1, enlarged TEM images in which superposed branches of the crystal can be observed; Figure S2, photographs of hydrosols obtained under different synthetic conditions; Figure S3, TEM images obtained from a sample prepared with [HAuCl₄] = 0.1 mM and [PVP K90]_{r.u.} = 0.269 M; Figure S4, TEM images of branched structures showing common crystal defects; Figure S5, photographs of composites and branched coatings obtained on different substrates; also included is a brief discussion of the main variables affecting PVP protection efficiency. This material is available free of charge via the Internet at http://pubs.acs.org.

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