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One-Pot Radiolytic Synthesis of Gold Nanorods and Their Optical Properties

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A novel one-pot synthesis method to prepare gold nanorods of different aspect ratios using radiolysis is presented. The gold nanorods are synthesized by radiolytic reduction of Au^{III} complexes in a micellar solution formed by a mixture of cationic surfactants (cetyltrimethylammonium bromide and tetraoctylammonium bromide) and in the presence of acetone and silver ions. The mechanisms of reduction of gold complexes and formation of the nanorods are discussed. The nanorods can be trapped in a poly(vinyl alcohol) gel formed under irradiation. The UV–visible absorption spectra of nanorod solutions are compared with calculations performed by using the discrete dipole approximation method, underlying the effect of the rod aspect ratio distribution.

1. Introduction

Gold nanorods (NRs) have recently attracted a lot of attention because of their exceptional optical properties. Indeed, they present two surface plasmon resonance (SPR) absorption bands corresponding to the electromagnetic wave-driven oscillation of the quasi-free electrons along (longitudinal SPR, LgSPR) and perpendicular (transverse SPR, TrSPR) to the rod long axis.^{1,2} The selective excitation of one or the other depends on the electric field polarization. Whereas the TrSPR is almost insensitive to the NR morphology, the spectral location of the longitudinal one (LgSPR) can be easily tuned from green to near-infrared by modifying the NR aspect ratio (the aspect ratio being the ratio of the largest axis to the shortest one): The longer the rod is, the smaller the LgSPR frequency. On the basis of these properties, noble metal NRs are thought to be good candidates for different applications,³ such as nanoparticle-mediated hyperthermal therapy against cancer⁴ and optical data storage.⁵

Esumi et al. were the first to use photochemical reduction in the presence of elongated micelles formed by the cationic surfactant hexadecyltrimethylammonium chloride (HTAC) to obtain anisotropic gold nanostructures.⁶ Wang et al. reported electrochemical synthesis of gold NRs in the presence of cationic surfactants, cosurfactant, and other additives, which were found

empirically to favor NRs formation.^{7,8} Various methods based on seed-mediated growth have also been reported for controlled synthesis of gold NRs.^{9–12} The reduction of a gold salt on premade small seeds is achieved by a weak reducing agent (ascorbic acid) in the presence of a cationic surfactant [frequently cetyltrimethylammonium bromide (CTAB)] leading to NRs of different aspect ratios and dimensions stabilized by a bilayer of CTAB. The seeds serve as nucleation sites for the anisotropic growth. This method was first developed by Murphy et al.^{9,10} El-Sayed et al. improved this synthesis method by using CTAB-capped seeds instead of citrate-capped ones, and they demonstrated that as observed in electrochemical growth technique, the control of NR anisotropy can be enhanced in the presence of Ag(I) during NR formation.¹¹ The factors affecting the nucleation and growth of gold NRs have been investigated by Mulvaney and Liz-Marzan groups.¹³ Nevertheless, this seed-mediated method suffers from poor reproducibility because it is very sensitive to numerous experimental parameters such as the nature and purity of the reactants (e.g., Au salt precursors, additives, reducing agents, and surfactants) and the size and surface coating of the seeds.^{14,15}

A dependence of the NR aspect ratio, R , on the size of the seeds has been observed. Increasing the seed size results in lowering R for a constant concentration of reagents.¹⁶ Gold NRs of well-controlled aspect ratios were also synthesized by photochemical reduction of gold salts in the presence of CTAB and silver ions.¹⁷ One-pot synthesis of gold NRs by ultrasonic irradiation was also reported.¹⁸ Recently, gold NRs of short aspect ratio were synthesized by radiolytic reduction of Au^{III} in the presence of chemically induced seeds, silver ions, and CTAB.¹⁹ All of these methods involve synthesis at temperatures close to room temperature. Zijlstra et al. reported seedless synthesis of gold NRs at high temperatures up to 97 °C.²⁰

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Radiolysis is a powerful method to synthesize nanoparticles of controlled size and shape.^{21–24} Solvent radiolysis induces the formation of solvated electrons and reducing radicals able to reduce metal ions. The advantage of the radiolytic process is that it induces a homogeneous reduction and nucleation in solutions and heterogeneous media. Herein, we report a one-pot radiolytic synthesis of gold NRs and the study of their stationary optical response. The mechanisms of reduction of gold complexes and the formation of rods are discussed. These NRs can also be trapped in poly(vinyl alcohol) (PVA) hydrogels induced by radiolysis.

2. Experimental Section

2.1. Materials. Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3), CTAB (98% purity), PVA (PW 86000, 98% hydrolyzed), acetone, propan-2-ol, and cyclohexane were obtained from Sigma-Aldrich and used as received. Ag_2SO_4 and tetraoctylammonium bromide (TOAB) were obtained, respectively, from Johnson Matthey and from Acros Organics. N_2 gas (purity >99.995%) and N_2O gas (purity >99.95%) were purchased from Air Liquide. All of the glassware and the cells were cleaned by aqua regia and rinsed with ultrapure water prior to the experiments.

2.2. Synthesis of Gold NRs. The Au NRs were synthesized by radiolysis. Briefly, HAuCl_4 and TOAB were added to a stirred aqueous CTAB solution [above the critical micelle concentration (CMC)]. The obtained solution was stirred at 50 °C for 1 h. Acetone, cyclohexane, and AgNO_3 were then successively added to the previous solution. The final solution contained 0.082 M CTAB, 7.5×10^{-4} M TOAB, 1.9×10^{-3} M HAuCl_4 , 0.139 M cyclohexane, 0.266 M acetone, and different concentrations of AgNO_3 (4×10^{-5} , 6×10^{-5} , 10^{-4} , 1.4×10^{-4} , and 1.8×10^{-4} M). The chosen concentrations refer to those used in the photoreduction synthesis of Au NRs.¹⁷ The prepared solutions were then flushed with nitrogen and irradiated by a ^{60}Co panoramic γ -source (dose rate = 2.3 kGy h^{-1}). The gold ions were reduced by the radicals induced by solvent radiolysis, and 14 h of exposure time (32.2 kGy) was necessary to reduce all of the gold ions. The deposited energy into the irradiated medium is expressed in Grays, 1 Gy = 1 J kg^{-1} (for aqueous solutions 1 Gy corresponds to 1 J L^{-1}). The NRs synthesized with increasing concentrations of silver were denoted NR1, NR2, NR3, NR4, and NR5. It has to be noted that the origin and the purity of CTAB are very important in the synthesis of Au NRs. Experiments done with CTAB of different purities or from different suppliers gave different results.^{25,26} The existence of impurities, mainly I^- , has been reported to affect the aspect ratio and the yield of the NRs by the seed-mediated method.^{26–28} We confirmed that the origin and the purity of CTAB are also important in the radiolytic synthesis of Au NRs as experiments done with different CTAB lead to different results. The results presented here were obtained with CTAB from Sigma Aldrich (98% purity).

2.3. Trapping Gold NRs in a PVA Gel. After the first radiolysis, 3 mL of a solution 0.5 M in PVA was added to 1 mL of the solution containing NRs. The obtained solution was deaerated and irradiated (dose rate = 2.3 kGy h^{-1}) under N_2 for 10 h to induce cross-linking and to form the PVA gel.

2.4. Characterization. UV–visible spectra of these samples were carried out on HP diode array HP8453 spectrophotometer. Transmission electron microscopy (TEM) observations were performed with a JEOL JEM 100CX II transmission electron microscope operating at 100 kV. High-resolution TEM (HR-TEM) images were taken on a JEOL JEM 2010 LaB₆ operating

at 200 kV, and image acquisition and analysis were performed using Gatan Digital Micrograph.

Ultrathin sections of NR-PVA hydrogels (about 60 nm thick) were cut using a Leica Ultracut microtome at a low temperature (−80 °C) and collected on copper grids. They were observed at ambient temperature.

3. Results

3.1. Initial Solutions. Solutions containing Au^{III} complexes, CTAB and TOAB as surfactants, cyclohexane, acetone, and various quantities of silver ions were prepared. In a 10^{-1} M CTAB solution, the micelles are spherical. The acetone concentration is too low to disturb the micellar structure.²⁹ Different factors contribute to the elongation of the spherical micelles. Cyclohexane swells the aliphatic part of the micelles and is known to promote elongation.³⁰ TOAB, with the same polar head as CTAB but a larger aliphatic part, acts as a cosurfactant and also promotes elongation. Because of its molecular shape, it is probably located on the cylindrical part of the micelles.

Because of the high concentration of CTAB, Cl^- may be partly replaced by Br^- in Au^{III} halide complexes.^{31,32} Moreover, because of electrostatic interactions, such anionic complexes are also complexed by cationic surfactants as CTA^+ . Indeed, 1:1 AuCl_4^- :surfactant complexes with characteristic absorption and solubility constants lower than 10^{-12} M have already been reported.^{13,33} In our conditions, the complexes $\text{Au}^{\text{III}}\text{X}_4\text{CTA}$ are formed (X stands for Cl and Br), and $\text{Au}^{\text{III}}\text{Br}_4\text{CTA}$ (which is the major complex) absorbs at 240 and 400 nm ($\epsilon_{400} \sim 5250$ L mol^{-1} cm^{-1}).

In aqueous solutions, silver cations also form complexes with halide ions, $\text{AgX}_n^{(n-1)-}$ with $n = 1–4$, depending on the $[\text{Ag}^+]/[\text{X}^-]$ ratio.³⁴ In our experimental conditions, the $(\text{AgBr}_2^-, \text{CTA}^+)$ complex is probably the predominant complex.³⁵ Because of their steric hindrance, this complex and $(\text{Au}^{\text{III}}\text{Br}_4^-, \text{CTA}^+)$ are probably localized on the micelle caps. Silver halides are known to absorb in the UV spectral region^{36–38} as well as CTAB and acetone.

3.2. Effect of Silver Concentration on the Radiolytic Synthesis of Gold NRs. Deaerated solutions containing Au^{III} complexes, CTAB and TOAB as surfactants, cyclohexane, acetone, and various quantities of silver ions (from the AgNO_3 precursor) were submitted to irradiation. Figure 1 shows the UV–visible absorption spectra registered after an absorbed irradiation dose of 32.2 kGy. Typical absorption spectra of gold NRs with two SPR absorption bands (TrSPR at around 510–520 nm and LgSPR at $\lambda > 540$ nm) are obtained. By increasing the silver concentration, the LgSPR band red shifts, and its intensity increases. Consequently, increasing the Ag^+ amount leads to changing the size of the NRs and increasing their aspect ratio (R), which is confirmed by TEM studies (Figure 2). Additionally, the relative standard deviation of the R distribution in the solutions seems roughly independent of R (Figure 3 and Table 1). The increase in the aspect ratio is also accompanied by a decrease in the mean diameter (d) when the concentration of AgNO_3 is increased (Table 1). Whereas no NR was detected in the absence of silver ions, experiments conducted in the presence of another silver salt, Ag_2SO_4 , gave similar results (Figure S1 in the Supporting Information). We confirm here that silver ions mediate the formation of gold NRs, as already observed by chemical or photochemical synthetic methods.^{9,11,13,17}

Figure 4 shows HRTEM images of NRs. The analysis of HRTEM data reveals that the NRs are single crystals with no observable stacking faults or twins. The NRs grow in the $\langle 100 \rangle$ direction [i.e., by the stacking of (100) planes along the axis],

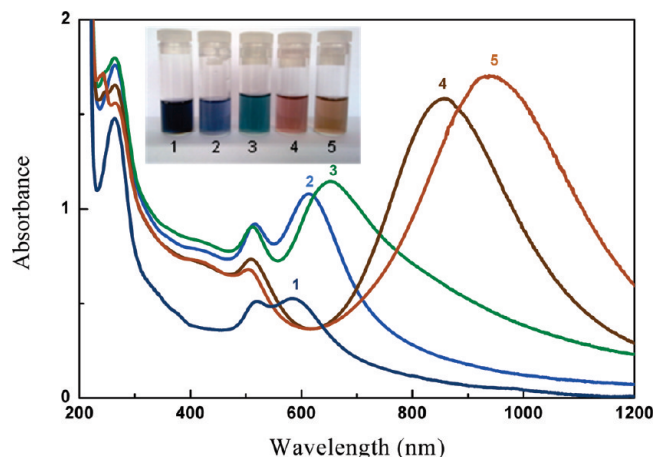


Figure 1. UV–visible absorption spectra of solutions containing Au^{III} and different amounts of Ag^+ (from the AgNO_3 precursor) (1, 4×10^{-5} M; 2, 6×10^{-5} M; 3, 10^{-4} M; 4, 1.4×10^{-4} M; and 5, 1.8×10^{-4} M) revealing the formation of gold NRs (NR1–NR5) with different mean aspect ratios after irradiation with a dose of 32.2 kGy. Optical path length = 2 mm. Inset: image of the vials containing the solutions with the synthesized gold NRs of different aspect ratios.

and their sides are mostly covered by the (100) and (110) crystallographic facets (Figure 4) and with (111) and (100) faces on the end (Figure S2 in the Supporting Information). Such a structure of the end faces has already been described for electrochemically synthesized Au NRs and for Au NRs studied by molecular dynamic simulations.^{39,40}

3.3. Calculations of the UV–Vis Spectra of the NRs by the Discrete Dipole Approximation (DDA) Method. UV–vis spectra have been compared with calculations performed by using the DDA method.⁴¹ This numerical technique amounts to replacing the nanoparticle by an object having the same shape and consisting of a large number of interacting dipoles, the polarizability of which is imposed by the electromagnetic properties of the nanoparticle. We have used the code DDSCAT developed by Draine and Flatau for calculating the optical absorption cross-section, with a random field polarization, of hemisphere-capped gold cylinders.^{42,43} This choice for the rod cap geometry, which has been shown to be an important parameter ruling the rod optical properties,⁴³ seems reasonable when observing the actual rod shape as shown on Figure 4.

The surrounding medium is water with the presence of CTAB at the rod surface, simulated by a relative dielectric permittivity of 2.025 as in ref 44. The rod diameter d is fixed at 10 nm. In our aspect ratio and diameter ranges (see Table 1), the variation of d is expected to have a negligible influence on the SPR maximum wavelength.⁴³ The aspect ratios of the different rods have been chosen as to make the spectral location of the LgSPR maximum roughly match the one measured on our samples. Let us note that the NRs are sufficiently diluted in the solutions as to neglect interactions between NRs, contrary to the case of Jain and co-workers.⁴⁵ The results are shown in Figure 5 for three different samples with increasing mean aspect ratios. The location of both the TrSPR and the LgSPR maxima are quite well reproduced by the calculation with R values (1.70, 2.05, and 2.50, respectively) very close to the ones derived from TEM images (see Table 1). However, it can be seen that the simulated spectra present a LgSPR absorption band much narrower than the experimental one. This reveals the dispersion of the rod aspect ratio in a given colloidal solution (see the TEM micrographs in Figure 2 as well as the aspect ratio distribution in Figure 3).^{1,2,43,46} Indeed, for our aspect ratio range, the width of the R distribution has been shown to significantly broaden the LgSPR band while having only a slight influence on its spectral location (see Figure 4 of ref 43). Using an analytical model, the simulation of the sample optical response taking into account the shape distribution has already been reported by Eustis and El-Sayed in ref 46. Note that a similar simulation has not been carried out here; because of the use of the DDA method, it would have been highly computing time-consuming for a weak added value only.

3.4. Dose Effect on NRs Formation. Figure 6 shows the UV–visible absorption spectra of solutions containing Au^{III} complexes and two different amounts of silver ions as a function of the absorbed irradiation dose. At the beginning of irradiation, for doses lower than 22 kGy, the absorption maxima of the Au^{III} complexes at 240 and 400 nm decrease with dose (Figure 6a,c), while no SPR band is observed in the visible domain.

In a second step, at doses higher than 22 kGy, two absorption bands, located at 510–520 and 600–900 nm, appear and grow (Figure 6b,d). These bands are associated with the formation of Au NRs, and they correspond to the TrSPR and LgSPR, respectively. The position of the second band depends on the initial silver concentration and on the dose. For an initial

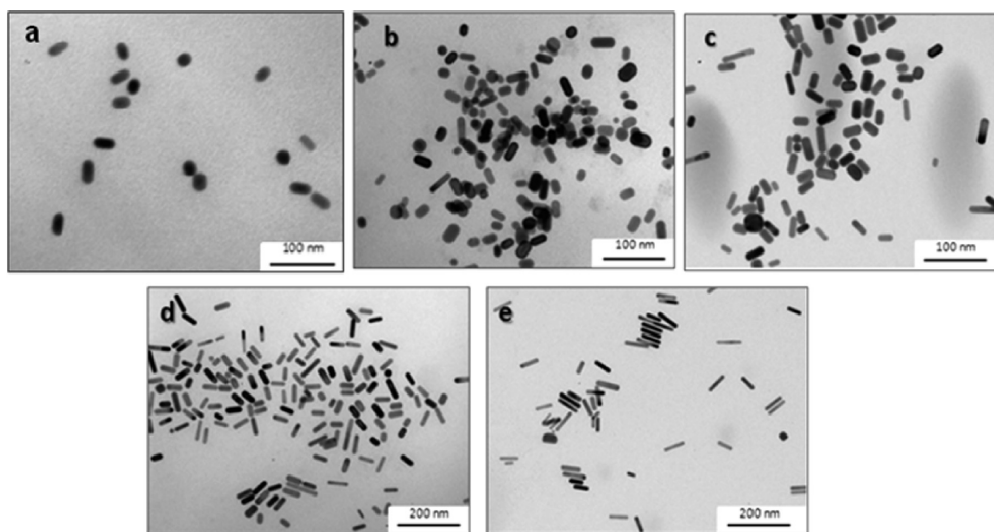


Figure 2. TEM images of the gold NRs of different aspect ratios synthesized with different amounts of silver ions (same conditions as in Figure 1): (a) NR1, (b) NR2, (c) NR3, (d) NR4, and (e) NR5.

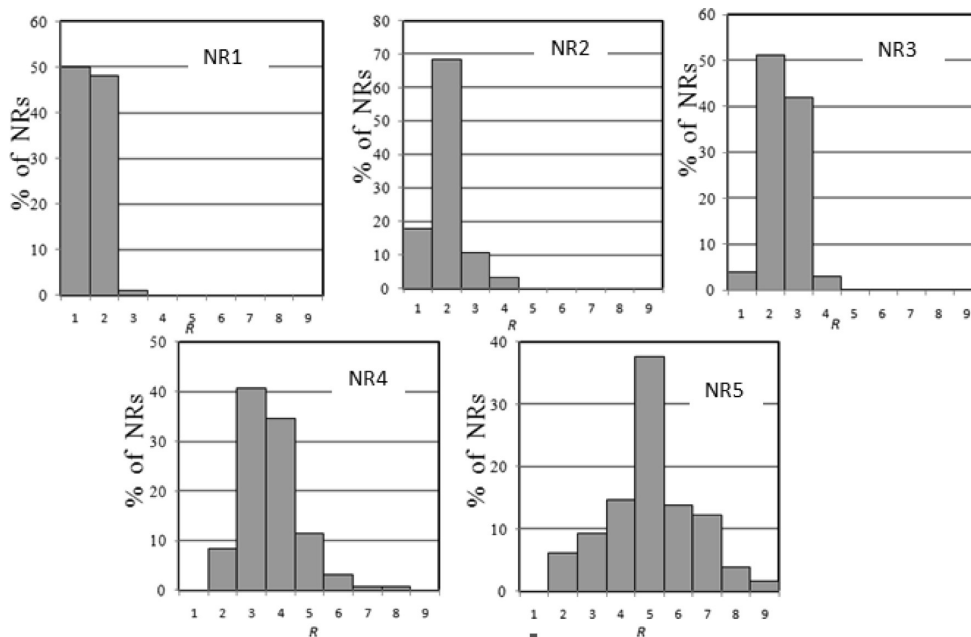


Figure 3. Histogram of the NR aspect ratio distribution for the different samples, as determined from TEM analysis.

TABLE 1: Parameters of the Gold NRs Synthesized after Total Reduction of the Gold Ions by Radiolysis as a Function of Silver Concentration (Figure 1)^a

	[Ag ⁺] (10 ⁻⁴ M)	λ (TrSPR) (nm)	λ (LgSPR) (nm)	R	d (nm)
NR1	0.4	520	590	1.7 ± 0.6	15
NR2	0.6	520	615	2.0 ± 1.0	13
NR3	1.0	510	650	2.5 ± 0.6	12
NR4	1.4	510	855	3.7 ± 1.0	10
NR5	1.8	505	935	5.2 ± 1.7	7

^a [Ag⁺] initial concentration of AgNO₃, λ (TrSPR) and λ (LgSPR) positions of the transversal and longitudinal SPR absorption bands, respectively; R , mean aspect ratio with standard deviation; and d , mean diameter of the formed NRs evaluated from TEM images.

concentration of silver equal to 1.4×10^{-4} M, after a dose of 23 kGy, two absorption bands are observed at 510 and 690 nm (Figure 6d). At higher irradiation doses, the intensity of both bands increases, but only the LgSPR band shifts toward longer wavelengths, and at 32.2 kGy, two maxima at 510 and 820 nm are obtained. A similar spectral evolution is observed at a lower silver concentration of 10^{-4} M (Figure 6a–b). First, the absorption band at 400 nm decreases; then, after a dose of 22 kGy, two SPR bands appear at 510 and 600 nm and evolve with the increasing dose. At 32.2 kGy (the dose necessary for total reduction), the TrSPR and LgSPR bands are located at 510 and 680 nm, respectively.

TEM and HRTEM images taken from solutions irradiated with a 5 kGy dose (before the total disappearance of the bands associated with the Au^{III}X₄CTA complex) show the formation of a few gold seeds homogeneous in size (Figure 7). These 2 nm seeds are single crystals and show the stacking of (100) planes (Figure 7 inset). No plasmon band is observed at this stage, because of the very small size of the seeds (very few seeds larger than 2 nm are observed; see Figure 7, inset). The seed structure is determinant for the growth mechanism.¹⁶ For example, it has been found that Au single seeds grow into crystalline NRs, while in the same growth solution, multiply twinned seeds grow into multiply twinned structures and, in particular, into the penta-twinned bipyramids.⁴⁷

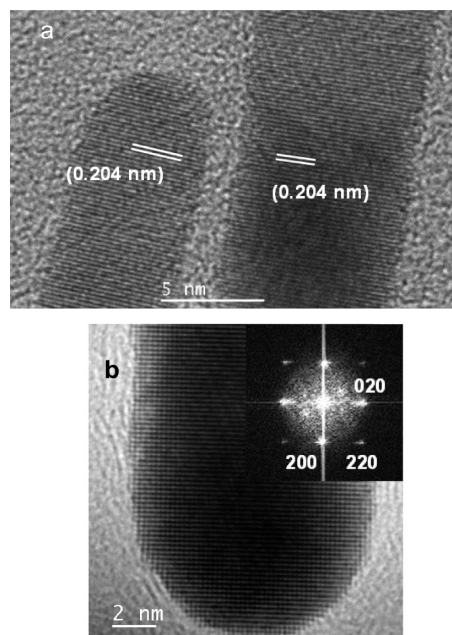


Figure 4. HRTEM images of the gold NRs synthesized by radiolysis (dose = 32.2 kGy) having side faces of Au(110) and (100) and confirming the growth of the NRs along the $\langle 100 \rangle$ direction. Inset: the corresponding FFT (fast Fourier transformation).

In short, the spectral evolution with increasing dose (Figure 6b,d) shows that two SPR absorption bands appear after a dose of around 20 kGy. With increasing dose, the longitudinal band shifts toward longer wavelengths, and its intensity increases.

3.5. Incorporation of Gold NRs in PVA Matrix. Supported metal nanoparticles highly dispersed in a host material are desired for practical applications, and in particular, polymers offer a suitable matrix for the synthesis of composites for optical applications. Thin films of gold NRs can be dispersed in PVA by drying a colloid in the presence of dissolved PVA.⁴⁸ Gold NRs with well-defined aspect ratios were homogeneously incorporated within PVA films and subsequently aligned by heating and stretching the nanocomposite films.⁴⁹ Silver nanoparticles were trapped in PVA hydrogels induced by irradiation.^{50,51}

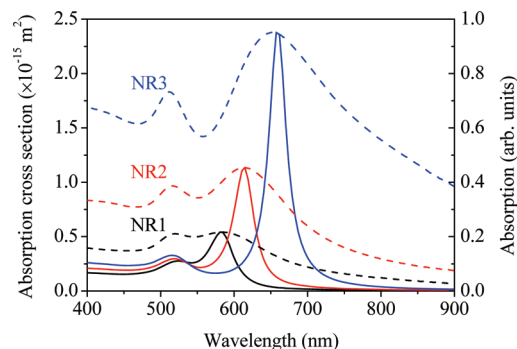


Figure 5. Experimental UV-vis absorption spectra of three solutions with increasing NR mean aspect ratio (dashed lines, right scale) and simulated absorption cross-section of hemisphere-capped NRs as calculated by the DDA method (full lines, left scale) with a mean aspect ratio (1.70, 2.05, and 2.50) chosen as to match the measured position of the LgSPR band maximum.

The optical properties of nanoparticles are strongly influenced by the interparticle separation. The ability to control interparticle distances of immobilized nanoparticles in a matrix is important for electrochemical and optical applications.⁵² Hydrogels have attracted much interest because of their high degree of shrinking and swelling, which may be controllable by stimuli such as solvent composition, solutes, pH, temperature, electric field, and light.^{52–55}

Here, the NRs synthesized in section 3.2 were trapped in a PVA hydrogels matrix induced by irradiation.^{56,57} The concen-

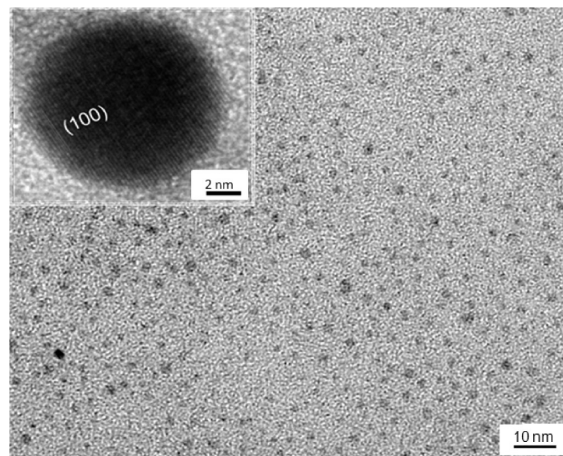


Figure 7. TEM image of gold seeds induced by irradiation in a solution containing Au^{III} precursors, CTAB, and 1.8×10^{-4} M Ag⁺ (dose 5 kGy). Inset: HRTEM image of one gold seed showing the (100) lattice planes.

trated PVA solution is added to the solution containing the NRs and irradiated.

Irradiation results in cross-linking of the polymer and in a three-dimensional network of the hydrogel where the NRs are homogeneously trapped (Figure 8). Previous studies have shown that the degree of swelling can be controlled by the irradiation dose.⁵⁸ The color of the gel obtained after 12 h of irradiation is

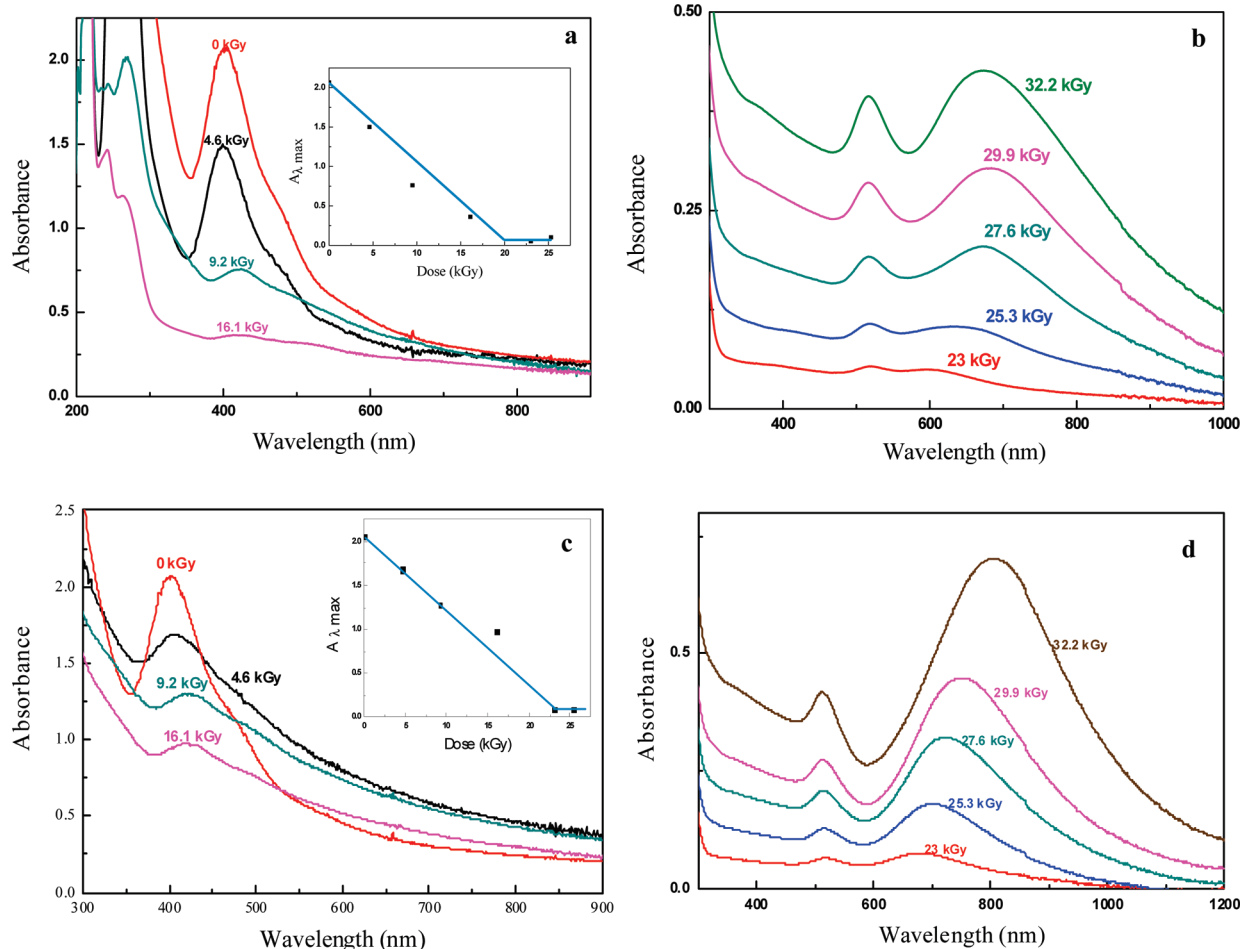


Figure 6. UV-visible spectra of a solution containing Au^{III}, CTAB, and (a and b) 10^{-4} M of Ag⁺ (NR3) or (c and d) 1.4×10^{-4} M of Ag⁺ (NR4) as a function of the received dose. Insets a and c: Absorbance at $\lambda_{\text{max}} \sim 400$ nm vs the absorbed dose. Optical path length = 2 mm.



Figure 8. Images of PVA hydrogels containing the gold NRs of different aspect ratios synthesized by radiolysis (NR1, NR2, NR3, NR4, and NR5 as in Figures 1 and 2).

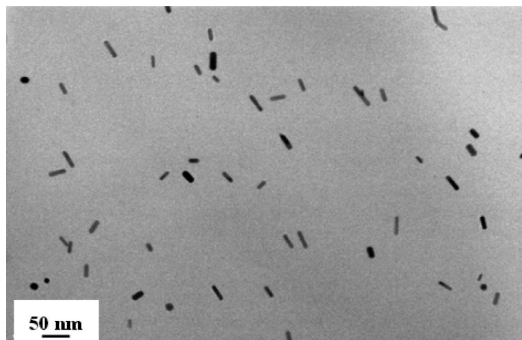


Figure 9. Microtome TEM pictures showing well-dispersed NRs (NR5) in the PVA hydrogel.

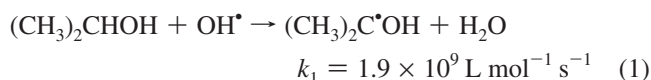
homogeneous and is similar to the color of the initial solution containing the NRs of controlled aspect ratios.

The hydrogel containing the gold NRs can be dried, which leads to shrinking of the gel. Microtome TEM pictures show that the NRs are homogeneously dispersed in the gel (Figure 9). At a high concentration of the NRs, the shrunken state can result in short interparticle distances and interparticle coupling effects. These considerations are presently under study.

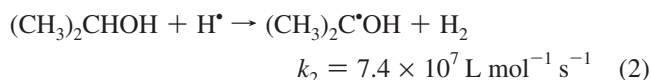
4. Discussion on the Radiolytic Synthesis of Au-NRs

The primary effects of the interaction of high-energy radiation such as particle beams, X-rays, or γ -photons with a solution of metal ions are the excitation and the ionization of the solvent leading to the formation of various species. In the case of aqueous solutions, the main reactive radicals generated by irradiation are solvated electrons (e_{aq}^-), hydroxyl radicals (OH^\bullet), and hydrogen atoms (H^\bullet). At pH 7, the radiolytic yields, G , of these radicals (quantity of radicals formed per Joule of energy deposited) are as follows: $G(e_{aq}^-) = 0.28$, $G(H^\bullet) = 0.06$, and $G(OH^\bullet) = 0.27 \mu\text{mol J}^{-1}$.⁵⁹

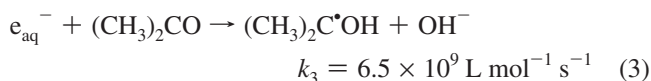
Solvated electrons e_{aq}^- [$E^0(H_2O/e_{aq}^-) = -2.87 \text{ V}_{NHE}$]⁵⁹ and H^\bullet atoms [$E^0(H^\bullet/H) = -1.88 \text{ V}_{NHE}$ at pH 7]⁵⁹ are strong reducing agents able to reduce metal ions to lower valences and finally to metal atoms. In contrast, OH^\bullet radicals have powerful oxidizing properties [$E^0(OH^\bullet/H_2O) = 2.34 \text{ V}_{NHE}$ at pH 7]⁵⁹ and can cause reverse oxidation of metal atoms. In general, alcohols are added in the media to scavenge OH^\bullet radicals. For instance, propan-2-ol reacts with OH^\bullet , but also H^\bullet , to form the alcohol radical according to reactions 1 and 2:



(see ref 60)

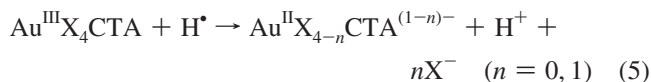
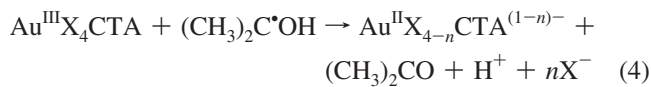


(see ref 60). In our experimental conditions, acetone reacts with solvated electron to yield the same alcohol radical as propan-2-ol:

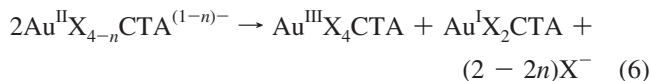


(see ref 60). The alcohol radicals are almost as powerful reducing agents as H^\bullet atoms [$E^0[(CH_3)_2CO/(CH_3)_2C^\bullet OH] = -1.8 \text{ V}_{NHE}$ at pH 7].

The radiolytic reduction of $Au^{III}Cl_4^-$ in aqueous solutions containing or not alcohols (propan-2-ol or PVA) and in the presence or absence of seeds has already been studied and well detailed.⁶² By analogy, the following reducing steps can be proposed here for the Au^{III} complexes. First, the Au^{III} complexes, $Au^{III}X_4CTA$ ($X = Cl$ or Br), are reduced by alcohol radicals and H^\bullet atoms into Au^{II} complexes:

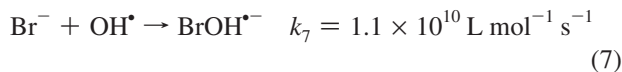


Reactions 4 and 5 are followed by a fast disproportionation of Au^{II} [$k_6 = (0.48 \pm 12) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ in case of $Au^{II}Cl_4^{2-}$]:

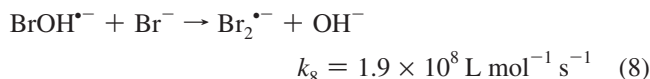


It has been shown that Au^I is strongly bonded by CTAB and that this binding is critical for gold rod formation.¹³ In our experiments, the absorbance at 400 nm associated with the $Au^{III}Br_4CTA$ complexes decreases continuously with the dose until 22 kGy, whereas no plasmon band indicating the formation of gold nanoparticles is detected (Figure 6). Consequently, this first step must mainly correspond to the reduction of Au^{III} into Au^I as already shown by kinetics studies conducted on radiolytic reduction of $Au^{III}Cl_4^-$ in aqueous solutions.⁶² This first step of reduction of Au^{III} —CTAB into Au^I —CTAB was also observed during the photosynthesis of gold NRs.³¹ The corresponding kinetics was very slow. Considering that in our conditions 20 kGy is the dose necessary to reduce all Au^{III} into Au^I , the reduction yield is found to be close to $0.2 \mu\text{mol J}^{-1}$. This value is lower than the maximum reduction yield possible in our conditions ($G_{red-max} = G(e_{aq}^-) + G(H^\bullet) = 0.34 \mu\text{mol J}^{-1}$). That may be explained by the fact that when Au^{III} ions are partly reduced after a certain dose by reactions 4 and 5, the accumulating Au^I ions may compete for the reaction with the reducing radicals. In fact, at this dose, a small part of the Au^I complexes

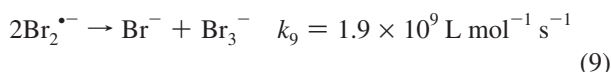
are already reduced into Au⁰ forming gold clusters and seeds as confirmed by TEM studies (Figure 7). So, the reduction yield of Au^{III} into Au^I should be slightly higher than 0.2 $\mu\text{mol J}^{-1}$. However, the low reduction yield is mainly due to the reactivity of OH[•] radicals. Indeed, in our experimental conditions, no alcohol is added to transform OH[•] into a reducing agent, but OH[•] radicals react with Br⁻, leading to the formation of Br₂^{•-} and Br₃⁻/Br₂ according to the following simplified mechanism:⁶³



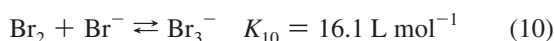
(see ref 64)



(see ref 64)

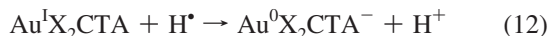
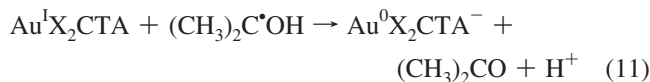


(see ref 65)



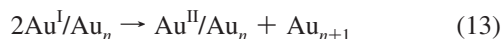
(see ref 66). Br₂^{•-} and Br₃⁻/Br₂ are oxidative species [$E^0(\text{Br}_2^{\bullet-}/2\text{Br}^-) = 1.7 \text{ V}_{\text{NHE}}$; $E^0(\text{Br}_2/\text{Br}_2^{\bullet-}) = 0.43 \text{ V}_{\text{NHE}}$],⁶⁷ which must cause a reverse oxidation of the gold low-valences ions or atoms, which decreases the reduction yield.

During the second part of irradiation (doses above 20 kGy), the complexed Au^I ions are reduced as follows:



Because of the quasi-uniform energy deposition into the irradiated medium, the metal atoms are formed with a homogeneous distribution throughout the solution. The radiolytic formation of gold atoms is probably followed by association of atoms with an excess of ions and finally by aggregation of these species into clusters of higher nuclearity surrounded by bromide and chloride ions and bounded to CTAB. At any stage of the coalescence, the ions adsorbed on the nanoparticles may be also reduced by the radiolytic species.

Au^IX₂CTA can also disproportionate very slowly to give Au^{II} and Au⁰ in the presence of catalyst or seeds:^{68,62}



where Au^I/Au_n and Au^{II}/Au_n denote gold ions adsorbed on the gold seeds.

This second reduction step leading to the formation of the gold NRs requires an additional dose of around 12 kGy to reach the total reduction of the gold ions. So, in our conditions, the

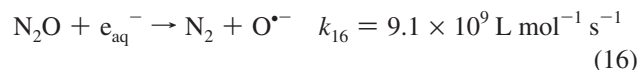
total dose to reduce all of the Au^{III} ions into Au⁰ atoms is 32 kGy, which corresponds to a reduction yield of around 0.2 $\mu\text{mol J}^{-1}$. This value is identical to that determined for the first step (reduction of Au^{III} into Au^I). As previously, the formation of Br₂^{•-} and Br₃⁻/Br₂ able to reoxidize gold atoms or clusters accounts for such a value, lower than $G_{\text{red-max}} = 0.34 \mu\text{mol}$.

We have shown that the radiolytic formation of NRs requires the presence of acetone since only spherical gold nanoparticles were obtained in the absence of acetone. The presence of acetone has also been found crucial in the NRs synthesis by photoreduction.^{31,32} To explain the role of acetone, different hypotheses were presented. Miranda and Ahmadi suggested that the excited acetone transfers its energy to gold complexes facilitating their reduction.³¹ It was also proposed that under UV irradiation, ketyl radicals are generated via excitation of acetone and subsequent hydrogen abstraction from CTA⁺.⁶⁹



where RH and R[•] denote CTA⁺ and its alkyl radical generated by hydrogen abstraction. Then, the radicals could be responsible for the reduction of Au^{III}.

In our experiment, the same alkyl radical, (CH₃)₂C[•]OH, is produced by the reaction between acetone and solvated electron (reaction 3). However, as already mentioned, such radicals can also be generated by radiolysis with the reaction of OH[•] and propan-2-ol (reaction 1). So, we performed experiments with solutions containing propan-2-ol instead of acetone. However, if we used for propan-2-ol the concentration of acetone (0.266 M) due to the rate constants of reactions 1 and 7 in competition, most of the OH[•] radicals would be scavenged by Br⁻ ($k_{\text{app}7} = k_7[\text{Br}^-] = 9.1 \times 10^8 \text{ s}^{-1}$), and few alcohol radicals would be formed ($k_{\text{app}1} = k_1[\text{propan-2-ol}] = 5.1 \times 10^8 \text{ s}^{-1}$). Consequently, we increased the concentration of propan-2-ol to 1 M to favor reaction 1 ($k_{\text{app}1} = k_1[\text{propan-2-ol}] = 1.9 \times 10^9 \text{ s}^{-1}$). In a first experiment, as previously, the solution was deaerated by bubbling with nitrogen. Irradiation of this solution leads to the formation of spherical gold nanoparticles and no NRs. In this experiment, the reducing species produced by radiolysis were alcohol radicals and solvated electrons (not scavenged by acetone). However, solvated electrons are stronger reducing agents than alcohol radicals. Consequently, we conducted a second experiment with a solution bubbled and saturated in N₂O (solubility in water at 25 °C and 1 atm = 25 mM).⁷⁰ Indeed, N₂O is known to scavenge the solvated electron:



(see ref 60)

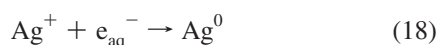


(see ref 60). In these conditions, the only reducing species generated in the solution were alcohol radicals, and irradiation induced the formation of gold NRs. The absorption spectra of the irradiated solutions are shown in Figure S3 in the Supporting Information. Note that the NRs obtained with propan-2-ol/N₂O

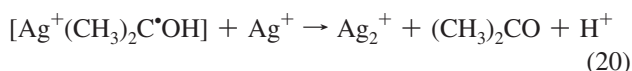
have a lower aspect ratio as those obtained with acetone (the LgSPR band is located at 680 nm) probably because of differences in the reduction kinetics. Third, we carried out experiments in the presence of both acetone and propan-2-ol. In this case, the alcohol radicals are also the unique reducing species. Figure S4 in the Supporting Information shows the spectral evolution of the solution versus the received dose. From the slope of the curve $\text{absorbance}_{400\text{nm}} = f(\text{dose})$, the reduction yield is found to be around $0.6 \mu\text{mol J}^{-1}$ (roughly three times the yield reported above). This value corresponds to the expected maximum radiolytic reduction yield, $G_{\text{red}}^{\text{max}} = G(\text{e}_{\text{aq}}^-) + G(\text{H}^\bullet) + G(\text{OH}^\bullet) = 0.61 \mu\text{mol J}^{-1}$. Indeed, under these conditions, the OH^\bullet radicals are scavenged by the alcohol (reaction 1) leading to the reducing alcohol radical and do not react with Br^- , eliminating the reactions (7–10). Therefore, the back oxidation reactions by $\text{Br}_2^{\bullet-}$ and Br_3^- are avoided. Because of the higher reduction yield, gold NRs are obtained after a shorter irradiation time as compared to those formed with acetone only, but their aspect ratio is lower: For example, for the experiments done with $1.8 \times 10^{-4} \text{ M}$ of Ag^+ , the aspect ratios of the Au NRs produced in the presence of acetone only and in the presence of both acetone and propan-2-ol are 5.2 and 1.9, respectively.

These experiments confirm the role of alcohol radicals in the reduction of gold complexes leading to the formation of gold NRs in radiolysis and photochemical methods. They also demonstrate that strong reducing agents, such as solvated electrons, have to be avoided for the synthesis of gold NRs.

Another factor that appears important in our experiments for the radiolytic synthesis of NRs is the presence of silver ions: Without silver ions, irradiation induces the reduction of gold ions into spherical nanoparticles. Radiolytic studies of aqueous solutions have shown that free hydrated cation Ag^{+71} and silver ions complexed by various ligands^{72,73,37} can be reduced by solvated electrons and alcohol radicals. Nevertheless, while reduction by the solvated electron corresponds to a direct electron transfer and the fast formation of silver atom (reaction 18),



reduction by the alcohol radical usually implies a slow two-step mechanism with a complexation by the radical and an electron-transfer reaction involving a second silver ion (reactions 19 and 20).



In our solutions, silver ions are probably associated with Br^- and CTA^+ , leading to a complex, Ag^+Br_2^- , CTA^+ . Under irradiation, this complex can be reduced only by the alcohol radical through a complexation step as the solvated electron is scavenged by acetone. Blank experiments were conducted on solutions without Au^{III} but containing AgNO_3 , CTAB, TOAB, acetone, and cyclohexane in the same concentrations as in the solutions leading to NRs synthesis. In this case, the irradiated solutions exhibited a SPR absorption band of silver nanoparticles at 400 nm. The TEM pictures showed small silver nanoparticles of 2–3 nm (Figure S5 in the Supporting Information). That indicates that silver complexes are reduced by alcohol

radicals in our conditions, but back oxidation by $\text{Br}_2^{\bullet-}$ and $\text{Br}_3^-/\text{Br}_2$ leads to a decrease in the radiolytic yield.

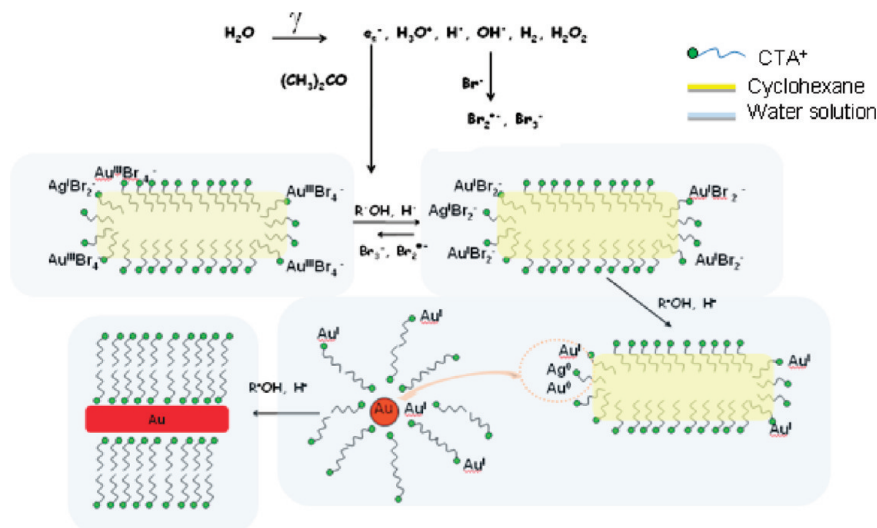
We have also noted that solvated electrons prevent the formation of gold NRs. However, solvated electrons reduce silver ions, even complexed, and such reduction takes place at the beginning of the irradiation. So, that suggests that if silver clusters are formed during the reduction step of Au^{I} , the NRs are not obtained.

However, the role of silver is not clear. In seed-mediated synthesis, a CTAB growth solution containing Au^{I} complexes and silver ions is added to the seeds with ascorbic acid as a chemical reductant. Although in the CTAB solution, Ag^+ cannot be reduced to silver atoms by ascorbic acid in basic pH,^{11,74} Ag^+ can be reduced to Ag^0 onto a metal substrate. It has been suggested that silver complexes are adsorbed at the gold nanoparticles surface, restrict the growth, and stabilize the NR surface.⁹ The growth of (100) facets has been found to be somehow favored by the presence of Ag^+ ions.^{17,47} Recently, it has been demonstrated that the AgBr_2^- , CTA^+ complex adsorbs strongly on gold NRs.³⁵ In a *fcc* structure, unpassivated (110) facets are characterized by higher surface energy than that of (111) and (100) facets.⁷⁵ To explain anisotropic growth of seeded Au NRs, a mechanism of underpotential deposition (UPD) of Ag^+ ions has been proposed.^{47,76} The UPD of Ag^+ on Au surfaces shifts: (110) > (100) > (111). The Ag layer can be reoxidized by the Au^{I} species. Previous experiments on irradiation of mixed $\text{Au}^{\text{III}}/\text{Ag}^{\text{I}}$ solutions have shown that the nascent Ag^0 transfers its electron to Au^{I} .⁷⁷ This process of deposition/oxidation can favor one-dimensional (1D) growth. The (110) and (100) facets, which are partly covered by the Ag species, can grow faster resulting in elongation along the $\langle 100 \rangle$ direction. The role of Ag^+ ions in the ultraviolet-driven photochemical synthesis of Au NRs has been investigated, and preferential adsorption of zerovalent Ag species on (100) and (110) facets of the growing Au nanoparticles has been found.⁶⁹ Because of the strong face-dependent adsorption of the AgBr_2^- , CTA^+ complex and also its location at the caps of the elongated micelles, the 1D growth is promoted, and the aspect ratio increases with silver concentration.

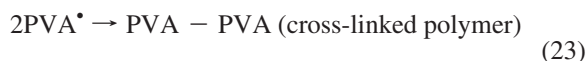
Mulvaney and co-workers have proposed the electric field-directed growth mechanism.¹³ The reduction of $\text{AuX}_4\text{-CTAB}$ leads to $\text{AuX}_2\text{-CTAB}$ micelles. The $\text{AuX}_2\text{-CTAB}$ complex binds to the CTAB-capped seeds through collisions that are controlled by the electric double layer between the positively charged seeds and the negatively charged $\text{AuX}_2\text{-CTAB}$ micelles. The collisions are faster at the tips than the sides of the seeds facilitating the rod-shaped growth. Silver could also play a role in the first elongation step. Because of the location of the silver-CTAB complex at the cap of some elongated micelles, silver could also promote the anisotropic growth of the gold seeds through an electron transfer from transient Ag^0 to Au^{I} adsorbed on the seeds. As observed for the AgBr_2^- , CTA^+ complex, Au^{I} adsorption could also be nonhomogeneous on the seeds. This can be also a possible explanation for the NRs growth. Scheme 1 summarizes the reduction and growth mechanism.

Besides, the spectral evolution with increasing dose (for doses higher than 22 kGy), observed whatever the amount of silver, indicates that the aspect ratio of the gold NRs increases with irradiation time. Experiments are in progress to understand the precise growth mechanism leading to the formation of gold NRs.

In section 3.5, we have shown that it is possible to trap the synthesized gold NRs in a PVA matrix. In this experiment, when the aqueous solutions containing PVA and the NRs are put under irradiation, PVA reacts with OH^\bullet and H^\bullet radicals induced by

SCHEME 1: Scheme Summarizing the Reduction and Growth Mechanism Leading to the Formation of Gold NRs by Radiolysis

radiolysis leading to PVA[•] radicals (due to the abstraction of one H atom), which recombine⁵⁰



Irradiation induces a reticulation of the polymer by the formation of bonds between chains via a radical mechanism. That leads to the formation of a gel. Contrary to the dried films, hydrogels (three- or two-dimensional) still contain water, and so, the trapped NRs keep some degrees of freedom and can be oriented by various stimuli for optical applications.

Nevertheless, to keep and control the aspect ratio of the gold NRs incorporated in the gels, it is necessary to take NRs in solution after total reduction of the gold ions. Otherwise, under the second irradiation to form the gel, further metal reduction takes place, slowing the gel formation and changing the aspect ratio of the NRs (see Figure S6 in the Supporting Information). Indeed, PVA[•] radical is an alcohol radical with reducing properties and contributes to the reduction of Au^{III}Cl₄⁻ and Au^I complexes adsorbed on seeds in aqueous solutions. PVA can also complex Au^I,⁶² and this can have a consequence on the final growth process leading to a decrease in the aspect ratio if gold is not completely reduced during the first irradiation. Note that PVA itself can also reduce slowly the Au^{III} complexes on preformed seeds.⁶²

5. Conclusion

Gold NRs of well-controlled aspect ratios were synthesized by a one-pot radiolytic reduction in CTAB-micellar solutions. The reduction mechanisms leading to the formation of gold NRs are discussed. The spectral evolution at increasing dose indicates that the reduction process to form NRs can be separated in two stages: The first step corresponds mainly to the slow radiolytic reduction of complexed Au^{III} to Au^I, and the second step is anisotropic crystalline growth induced by the radiolytic reduction

of Au^I complexes in CTAB-micellar solutions containing gold seeds induced by radiolysis. These monocrystalline seeds serve as nucleation sites for the formation of the NRs. We have shown that a slow reduction by alcohol radicals is needed for the rod formation as a fast reduction by solvated electrons leads to spherical NPs. The presence of Ag⁺ ions is also necessary. These NRs can be homogeneously trapped in a PVA hydrogel induced by irradiation. The UV–visible absorption spectra of the synthesized NRs have also been compared with calculations performed by the DDA method. This comparison has revealed the inhomogeneous broadening of the longitudinal SPR due to the rod aspect ratio distribution in the solutions. Further investigations are in progress to get a better insight into the accurate growth mechanism leading to the formation of gold NRs.

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Supporting Information Available: Figures of UV–visible absorption spectra of irradiated solutions, HRTEM images of a gold NR synthesized by radiolysis, UV–visible absorption spectra, TEM image of silver nanoparticles obtained by irradiation, and images of PVA hydrogels containing gold NRs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Link, S.; Mohamed, M. B.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 3073.
- (2) Noguez, C. *J. Phys. Chem. C* **2007**, *111*, 3806.
- (3) Huang, X.; Neretina, S.; El-Sayed, M. A. *Adv. Mater.* **2009**, *21*, 4880.
- (4) Jain, P. K.; El-Sayed, I. H.; El-Sayed, M. A. *Nanotoday* **2007**, *2*, 18.
- (5) Zijlstra, P.; Chon, J. W. M.; Gu, M. *Nature* **2009**, *459*, 410.
- (6) Esumi, K.; Matsuhisa, K.; Torigoe, K. *Langmuir* **1995**, *11*, 3285.
- (7) Yu, Y. Y.; Chang, S.-S.; Lee, C.-L.; Wang, C. R. C. *J. Phys. Chem. B* **1997**, *101*, 6661.
- (8) Chang, S.-S.; Shih, C.-W.; Chen, C.-D.; Lai, W.-C.; Wang, C. R. C. *Langmuir* **1999**, *15*, 701.
- (9) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Adv. Mater.* **2001**, *13*, 1389.

- (10) Jana, N. R.; Gearheart, L.; Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 4065.
- (11) El-Sayed, M. A.; Nikkobakht, B. *Chem. Mater.* **2003**, *15*, 1957.
- (12) Nikkobakht, B.; El-Sayed, M. A. *Langmuir* **2001**, *17*, 6368.
- (13) Perez-Juste, J.; Liz-Marzan, L. M.; Carnie, S.; Chan, D. Y. C.; Chan, D. Y. C.; Mulvaney, P. *Adv. Funct. Mater.* **2004**, *14*, 571.
- (14) Jiang, X. C.; Brioude, A.; Pileni, M. P. *Colloids Surf. A* **2006**, *277*, 201.
- (15) Jiang, X. C.; Pileni, M. P. *Colloids Surf. A* **2007**, *295*, 228.
- (16) Gole, A.; Murphy, C. *Chem. Mater.* **2004**, *16*, 3633.
- (17) Kim, F.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2002**, *124*, 14316.
- (18) Okitsu, K.; Sharyo, K.; Nishimura, R. *Langmuir* **2009**, *25*, 7786.
- (19) Biswal, J.; Ramnani, S. P.; Tewari, R.; Dey, G. K.; Sabharwal, S. *Radiat. Phys. Chem.* **2010**, *79*, 441.
- (20) Zijlstra, P.; Bullen, C.; Chon, J. W. M.; Gu, M. *J. Phys. Chem. B* **2006**, *110*, 19315.
- (21) Belloni, J.; Mostafavi, M.; Remita, H.; Marignier, J.-L.; Delcourt, M.-O. *New J. Chem.* **1998**, *22*, 1239.
- (22) Belloni, J.; Remita, H. In *Radiation Chemistry: From Basics to Applications in Material and Life Sciences*; Spothem-Maurizot, M., Mostafavi, M., Douki, T., Belloni, J., Ed.; EDP Sciences: Les Ulis, France, 2008; Vol. 97, p 116.
- (23) Krishnaswamy, R.; Remita, H.; Imperor-Clerc, M.; Even, C.; Davidson, P.; Pansu, B. *Chem. Phys. Chem.* **2006**, *7*, 1510.
- (24) Ksar, F.; Surendran, G.; Ramos, L.; Keita, B.; Nadjo, L.; Prouzet, E.; Beaunier, P.; Hagege, A.; Audonnet, F.; Remita, H. *Chem. Mater.* **2009**, *21*, 1612.
- (25) Smith, D. K.; Korgel, B. A. *Langmuir* **2008**, *24*, 644.
- (26) Smith, D. K.; Miller, N. R.; Korgel, B. A. *Langmuir* **2009**, *25*, 9518.
- (27) Millstone, J. E.; Wei, W.; Jones, M. R.; Yoo, H.; Mirkin, C. A. *Nano Lett.* **2008**, *8*, 2526.
- (28) Rayavarapu, R. G.; Ungureanu, C.; Krystek, P.; van Leeuwen, T. G.; Manohar, S. *Langmuir* **2010**, *26*, 5050.
- (29) Zhang, J.; Liu, M.; Zhang, A.; Lin, K.; Song, C.; Guo, X. *Solid State Sci.* **2010**, *12*, 267.
- (30) Tornblom, M.; Henriksson, U. *J. Phys. Chem. B* **1997**, *101*, 6028.
- (31) Miranda, O. R.; Ahmadi, T. S. *J. Phys. Chem. B* **2005**, *109*, 15724.
- (32) Nishioka, K.; Niidome, Y.; Yamada, S. *Langmuir* **2007**, *23*, 10353.
- (33) Torigoe, K.; Esumi, K. *Langmuir* **1992**, *8*, 59.
- (34) Lieser Von, K. H. Z. *Anorg. Allg. Chem.* **1957**, *292*, 97.
- (35) Hubert, F.; Testard, F.; Spalla, O. *Langmuir* **2008**, *24*, 9219.
- (36) Bobkov, I. S.; Ivanova, N. I. *Opt. Spectrosc. (USSR)* **1978**, *45*, 231.
- (37) Lampre, I.; Pernot, P.; Mostafavi, M. *J. Phys. Chem. B* **2000**, *104*, 6233.
- (38) Mirdamadi-Esfahani, M. Thesis, Université Paris-Sud 11, 2009.
- (39) Wang, Z. L.; Mohamed, M. B.; Link, S.; El-Sayed, M. A. *Surf. Sci.* **1999**, *440*, L809.
- (40) Wang, Y.; Teitel, S.; Dellago, C. *Nano Lett.* **2005**, *5*, 2174.
- (41) Draine, B. T.; Flatau, P. J. *J. Opt. Soc. Am. A* **1994**, *11*, 1491.
- (42) Draine, B. T.; Flatau, P. J. *User Guide to the Discrete Dipole Approximation Code DDSCAT 7.0*; 2008; <http://arxiv.org/abs/0809.0337v5>.
- (43) Prescott, S. W.; Mulvaney, P. *J. Appl. Phys.* **2006**, *99*, 123504.
- (44) Novo, C.; Funston, A. M.; Mulvaney, P. *Nature Nanotechnol.* **2008**, *3*, 598.
- (45) Jain, P. K.; Eustis, S.; El-Sayed, M. A. *J. Phys. Chem. B* **2006**, *110*, 18243.
- (46) Eustis, S.; El-Sayed, M. A. *J. Appl. Phys.* **2006**, *100*, 044324.
- (47) Liu, M.; Guyot-Sionnest, P. *J. Phys. Chem. B* **2005**, *109*, 22192.
- (48) Van der Zande, B. M. I.; Pages, L.; Hikmet, R. A. M.; Van Blaaderen, A. *J. Phys. Chem. B* **1999**, *103*, 5761.
- (49) Perez-Juste, J.; Rodriguez-Gonzalez, B.; Mulvaney, P.; Liz-Marzan, L. M. *Adv. Funct. Mater.* **2005**, *15*, 1065.
- (50) Kumar, M.; Varshney, L.; Francis, S. *Radiat. Phys. Chem.* **2005**, *73*, 21.
- (51) Krkljes, A.; Nedeljkovic, J. M.; Kacarevic-Popovic, Z. M. *Polym. Bull.* **2007**, *58*, 271.
- (52) Pardo-Yissar, V.; Gabai, R.; Shipway, A. N.; Bourenko, T.; Willner, I. *Adv. Mater.* **2001**, *13*, 1320.
- (53) Holtz, J. H.; Holtz, J. S. W.; Munro, C. H.; Asher, S. A. *Anal. Chem.* **1998**, *70*, 780.
- (54) Shiotani, A.; Mori, T.; Niidome, T.; Niidome, Y.; Katayama, Y. *Langmuir* **2007**, *23*, 4012.
- (55) Kozlovskaya, V.; Kharlampieva, E.; Khanal, B. P.; Manna, P.; Zubarev, E. R.; Tsukruk, V. V. *Chem. Mater.* **2008**, *20*, 7474.
- (56) Kerry, T. J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *265*, 1.
- (57) Ulanski, P.; Bothe, E.; Rosiak, J. M.; von Sonntag, C. *Macromol. Chem. Phys.* **1994**, *195*, 1443.
- (58) Nho, Y. C.; Park, K. R. *J. Appl. Polym. Sci.* **2002**, *85*, 1787.
- (59) Ferradini, C.; Pucheault, J. *Biologie de l'action des Rayonnements Ionisants*; Masson: Masson, Paris, 1983.
- (60) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- (61) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409.
- (62) Gachard, E.; Remita, H.; Khatouri, J.; Keita, B.; Nadjo, L.; Belloni, J. *New J. Chem.* **1998**, *22*, 1257.
- (63) Mirdamadi-Esfahani, M.; Lampre, I.; Marignier, J.-L.; De Waele, V.; Mostafavi, M. *Radiat. Phys. Chem.* **2009**, *78*, 106.
- (64) Zehavi, D.; Rabani, J. *J. Phys. Chem.* **1972**, *76*, 312.
- (65) D'Angelantonio, M.; Venturi, M.; Mulazzani, Q. C. *Radiat. Phys. Chem.* **1988**, *32*, 319.
- (66) Wang, T. X.; Kelley, M. D.; Cooper, J. N.; Beckwith, R. C.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 5872.
- (67) Henglein, A. *Radiat. Phys. Chem.* **1980**, *15*, 151.
- (68) Baxendale, J. H.; Koulkes-Pujo, A. M. *J. Chim. Phys.* **1970**, *67*, 1602.
- (69) Placido, T.; Comparelli, R.; Giannici, F.; Cozzoli, P. D.; Capitani, G.; Striccoli, M.; Agostiano, A.; Curri, M. L. *Chem. Mater.* **2009**, *21*, 4192.
- (70) *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Frederikse, H. P. R., Eds.; CRC Press, Inc: Boca Raton, FL, 1995.
- (71) Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 556.
- (72) Texier, I.; Remita, S.; Archirel, P.; Mostafavi, M. *J. Phys. Chem.* **1996**, *100*, 12472.
- (73) Texier, I.; Mostafavi, M. *Radiat. Phys. Chem.* **1997**, *49*, 459.
- (74) Orendorff, C. J.; Murphy, C. J. *J. Phys. Chem. B* **2006**, *110*, 3990.
- (75) Wang, Z. L.; Gao, R. P.; Nikoobakht, B.; El-Sayed, M. A. *J. Phys. Chem. B* **2000**, *104*, 5417.
- (76) Grzelczak, M.; Perez-Juste, J.; Rodriguez-Gonzalez, B.; Liz-Marzan, L. M. *J. Mater. Chem.* **2006**, *16*, 3946.
- (77) Tréguer, M.; de Cointet, C.; Remita, H.; Khatouri, J.; Mostafavi, M.; Amblard, J.; Belloni, J.; De Keyser, R. *J. Phys. Chem. B* **1998**, *102*, 4310.