Gold Nanoparticles

Controlled Light-Mediated Preparation of Gold Nanoparticles by a Norrish Type I Reaction of Photoactive Polymers

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Abstract: Gold nanoparticles (AuNPs) are subjects of broad interest in scientific community due to their promising physicochemical properties. Herein we report the facile and controlled light-mediated preparation of gold nanoparticles through a Norrish type I reaction of photoactive polymers. These carefully designed polymers act as reagents for the photochemical reduction of gold ions, as well as stabilizers for the in situ generated AuNPs. Manipulating the length and composition of the photoactive polymers allows for control of AuNP size. Nanoparticle diameter can be controlled from 1.5 nm to 9.6 nm.

Gold nanostructures with controlled size and shape have found countless applications in a wide range of areas such as nanoelectronics,^[1] optics,^[2] nanomedicine,^[3] and catalysis.^[4] Although various methods for their preparation have been reported,^[5,6] the development of processes which allow for the tuning and tailoring of nanoparticle size, shape, and composition is still challenging and of importance.^[7] AuNPs with defined size and shape have been prepared by using chemical reductants,^[8] electrochemical,^[9] and photochemical methods.[10]

AuNPs can be stabilized by low-molecular-weight ligands or by polymers. In systems where inorganic colloids are assembled into polymeric materials, the polymer serves as a matrix to prevent their agglomeration and precipitation, ensuring long-term stability of the AuNPs.^[11] Functionalized polymers can mediate nanoparticle growth by controlling entropic and enthalpic parameters.^[12] Various homo- and copolymers such as poly(vinylpyrrolidone),^[13] polyethyleneglycols,^[14] polystyrenes,^[15, 16] polyacrylamides,^[17] and dendritic polymers^[18] have been used for this purpose. Unfortunately, current protocols for the preparation of polymer/metal nanoparticle hybrids often require complex multistep procedures, and necessitate careful control of the addition of external, harsh reducing reagents. Long reaction times, high temper-

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atures, and complicated as well as expensive purification steps are other drawbacks.^[16,19]

In recent years, synthetic chemists have paid increasing attention to the use of light to drive organic reactions, due to both its infinite availability and ease of application in industrial processes.^[20] The preparation of AuNPs within a polymer matrix using a photochemical approach would therefore be a valuable strategy. Ideally, the reaction setup should be simple and the light-mediated process may facilitate control of the rate of nanoparticle formation. Spatial and temporal control should also be feasible offering additional synthetic flexibility in the design of nanoparticle/ polymer hybrids.^[21] In 2006, Scaiano and co-workers reported the synthesis of AuNPs by using the Norrish type I photochemical reactions for the in situ generation of reducing radicals (Scheme 1 a).^[22] Commercially available Irgacure-2959 (1) was employed to generate the ketyl radical 3a, which





able 1 for photochemical preparation of AuNPs.^[21,22] b) Photochemical polymer modification.^[23] c) Novel concept for the preparation of polymer-stabilized AuNPs.

is known to reduce metal ions.^[21,22] It was shown by mass spectrometry that the concomitantly generated benzoyl radical 2 is oxidized by O_2 to the corresponding benzoic acid, which then contributes to the stability of the formed AuNPs.^[21]

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We recently disclosed an efficient method for the photochemical postmodification of polymers bearing α -hydroxyalkyl ketone (HAK) substituents as photocleavable side chains. These polymers undergo a clean Norrish type I photoreaction to give the corresponding acyl and ketyl radical pairs which in the presence of nitroxides are efficiently trapped to provide alkoxyamines (Scheme 1 b).^[23]

Herein, we report the synthesis and application of homoand copolymers bearing α -hydroxyalkyl ketone (HAK) substituents for controlled photochemical generation of stable, spherical gold nanoparticles with adjustable diameter (Scheme 1c). The polymer plays a dual role: it first acts as an electron source for the photoreduction of Au salts to give AuNPs and the remainder of the photochemically modified polymer then serves as an organic matrix for AuNP stabilization.^[21,24] Importantly, we will show that the length and composition of the parent polymer allows for control of nanoparticle size leading to programmed nanoparticle preparation. The AuNP hybrids are analyzed by UV/Vis, ¹H NMR and solid-state ¹³C NMR spectroscopy, attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA).

For the preparation of polymers of defined molecular weight we employed the nitroxide-mediated radical polymerization (NMP)^[25] and the reversible addition–fragmentation chain-transfer polymerization (RAFT).^[26] Poly[2-hydroxy-2methyl-1-(4-vinylphenyl)propan-1-one] (poly(HAK), **4**) and statistical poly[2-hydroxy-2-methyl-1-(4-vinylphenyl)propan-1-one-*co*-4-(*N*,*N*-dimethylamino)styrene] (poly(HAK-*co*-DMAS), **5**) were prepared by NMP. Statistical poly[2hydroxy-2-methyl-1-(4-vinylphenyl)propan-1-one-*co*-1-(methylsulfinyl)-4-vinylbenzene] (poly(HAK-*co*-MSVB), **6**), statistical poly[2-hydroxy-2-methyl-1-(4-vinylphenyl)propan-

1-one-*co*-methyl(4-vinylphenyl)sulfane] (poly(HAK-*co*-MVPS), **7**), and poly{[2-hydroxy-2-methyl-1-(4-vinylphenyl)propan-1-one-*co*-methyl(4-vinylphenyl)sulfane]-*block*-styrene} (poly((HAK-*co*-MVPS)-*b*-St), **8**) were obtained by RAFT. All polymers were characterized by NMR, GPC, and FTIR (see the Supporting Information). Besides the photoactive HAK moieties, copolymers **5–8** contain monomers that bear functionalized side chains able to interact with Au nanoparticles (Figure 1).

We first investigated photochemical AuNP preparation using homopolymer poly(HAK) **4** ($M_n = 14200 \text{ g mol}^{-1}$, PDI = 1.2). Initial studies were conducted in dimethylformamide (DMF) under argon atmosphere with poly(HAK) **4** and HAuCl₄ in an estimated ratio of 10:1 (ratio of photoactive HAK units (*m*)/HAuCl₄ 10:1). During irradiation ($\lambda =$ 254 nm), the solution of **4**/HAuCl₄ became pink/violet within 10 min indicating successful formation of AuNPs. These NPs showed a surface plasmon band (SPB) at $\lambda =$ 533 nm. Absorbance did not increase upon extended irradiation time indicating full conversion to AuNPs. TEM analysis revealed that the AuNPs formed are nonspherical with a rather broad size distribution ($16.5 \pm 4.8 \text{ nm}$; Figure 2a; Table 1, entry 1). However, these NPs showed ripening effects as observed by a shift of the SPB to $\lambda = 548 \text{ nm}$ after several



Figure 1. Homo- 4, statistical copolymers 5–7, and block copolymer 8 investigated.



Figure 2. TEM images of AuNPs prepared with polymer 4 $(M_n = 14200 \text{ gmol}^{-1})$ and polymer 7 $(M_n = 10600 \text{ gmol}^{-1})$: a) 4 without NaOH: $16.5 \pm 4.8 \text{ nm}$, b) 4 with 6.0 equiv NaOH: $5.1 \pm 1.0 \text{ nm}$, c) 7 with 6.0 equiv NaOH: $1.8 \pm 0.5 \text{ nm}$.

Table 1: Light-mediated preparation of polymer-protected AuNPs in DMF/H₂O with polymers **4–8** (ratio of photoactive HAK (*m*) unit to $HAuCl_4 = 10$ to 1).

Entry	Polymer	M _n [g mol ⁻¹] (PDI) ^[a]	<i>m/n/o</i> ^[b]	Equiv. NaOH ^[c]	Diameter ^[d] [nm]
] ^[e]	4	14200 (1.2)	_	0.0	16.5 ± 4.8
2	4	14200 (1.2)	-	1.0	9.6 ± 1.8
3	4	14200 (1.2)	_	3.0	7.0 ± 1.3
4	4	14200 (1.2)	_	6.0	5.1 ± 1.0
5	4	8000 (1.2)	_	6.0	$\approx 5^{[f]}$
6	4	12900 (1.2)	_	6.0	$\approx 5^{[f]}$
7	4	19500 (1.2)	-	6.0	$\approx 5^{[f]}$
8	4	26600 (1.2)	-	6.0	$\approx 5^{[f]}$
9	5	9400 (1.3)	1:1.0	6.0	5.0 ± 1.1
10	6	5800 (1.2)	1:1.6	6.0	3.5 ± 0.9
11	7	12500 (1.1)	1:1.3	6.0	2.5 ± 0.7
12	7	29300 (1.2)	1:1.4	6.0	2.8 ± 0.8
13	7	83 000 (1.5)	1:1.3	6.0	5.4 ± 1.1
14	7	12800 (1.1)	1:1.6	6.0	2.2 ± 0.5
15	7	10600 (1.1)	1:1.9	6.0	1.8 ± 0.5
16	7	10500 (1.1)	1:3.3	6.0	1.5 ± 0.3
17	8	19000 (1.2)	1:1.4:1.7	6.0	3.0 ± 0.9

[a] M_n and PDI were determined by gel permeation chromatography (GPC) in THF. [b] Ratio (m/n/o) of HAK to (functionalized) styrene CH₂= CHC₆H₄X was determined by ¹H NMR spectroscopy. [c] NaOH equivalents with respect to HAuCl₄. [d] Diameter and standard deviation of AuNPs were determined by TEM, see the Supporting Information. [e] Reaction performed in DMF. [f] Estimated by measurement of the SPB. hours. To overcome the observed ripening we repeated the experiment with a higher concentration of **4** (ratio of HAK units/HAuCl₄ 20:1). Disappointingly, AuNPs with a broad SPB at $\lambda = 564$ nm were obtained indicating the formation of polydisperse NPs with larger diameter.

We subsequently explored AuNP formation with polymer 4 in basic medium and found that NaOH has a distinct effect on the size, stability, and dispersity of the generated AuNPs. Irradiation of a mixture of 4/HAuCl₄/NaOH (ratio of 10 HAK units:1:1) in DMF for 5 min provided spherical gold NPs with narrow size distribution $(9.6 \pm 1.8 \text{ nm}; \text{Table 1, entry 2})$. Upon varying the amount of NaOH we found the average diameter of the AuNPs to decrease from 9.6 ± 1.8 nm to 7.0 ± 1.3 nm and 5.1 ± 1.0 nm (Figure 2b) as the concentration of NaOH increased from 1 then 3 and finally 6 equivalents with respect to HAuCl₄ (Table 1, entries 2-4). All experiments delivered spherical particles with narrow size distribution. TEM analysis agrees with the corresponding UV/Vis spectra where the SPB shifted from $\lambda = 524$ nm to $\lambda = 516$ nm as the amount of NaOH increased from 1 to 6 equivalents (see the Supporting Information). Comparison of AuNP diameters determined by TEM $(5.1 \pm 1.0 \text{ nm})$ and DLS $(8.2 \pm 2.4 \text{ nm})$ measurements indicates the presence of a thin roughly 1.5 nm thick polymer coating on the AuNP surface.

To study the effect of the polymer length on AuNP formation, different poly(HAK) polymers **4** ranging from $M_n = 8000 \text{ gmol}^{-1}$ to 26 600 gmol⁻¹ were tested (ratio of HAK units/HAuCl₄/NaOH 10:1:6; Table 1, entries 5–8). Photolysis in the presence of the Au salt and base gave AuNPs with a SPB at $\lambda = 516 \pm 1$ nm for all systems indicating no significant effects of polymer size on AuNP formation in the tested M_n range. Notably, NMP- and RAFT-derived poly-(HAK) provided the same result revealing that the end groups in these polymers do not influence NP formation. Importantly, no aggregation or precipitation of AuNPs was observed when the NPs were stored in DMF/H₂O for months (5°C).

We also studied the influence of the light source on AuNP formation (ratio of HAK units/HAuCl₄/NaOH 10:1:6) and chose a 365 nm UV light source. Under these conditions a significant decrease in the rate of AuNP formation was observed. After two hours of irradiation very polydisperse AuNPs with a range of diameters between 5 and 70 nm were obtained, indicating that the wavelength and intensity of the UV light source have a crucial influence on the AuNP formation process.

We then investigated whether functional groups within the polymer influence NP growth. It is known that compounds containing nitrogen (amines, amides)^[27] or sulfur (thiols, thioethers, sulfoxides) stabilize NPs.^[28] To this end, statistical copolymers **5–7** and block copolymer **8** were tested (see Figure 1 and the Supporting Information). Results obtained for the photochemical synthesis of AuNPs with **5– 8** are included in Table 1.

When the amino-functionalized copolymer **5** was employed, spherical AuNPs with a diameter of 5.0 ± 1.1 nm were generated, indicating that the tertiary amines in **5** have no significant effect on NP growth, in comparison with results obtained with parent **4** (Table 1, entries 4 and 9). The sulfoxide-modified poly(HAK-co-MSVB) 6, however, provided AuNPs with a diameter of 3.5 ± 0.9 nm (Table 1, entry 10), indicating that the sulfoxide functionality has a measurable influence on AuNP growth. Thioethers are better ligands for Au and might be expected to show stronger effects. Indeed, a further decrease in the NP diameter was achieved in the presence of copolymer 7 (2.5 ± 0.7 nm; Table 1, entry 11). For 7 we noted that polymer length had a marked effect on the size of the formed AuNPs. The diameter increased from 2.5 to 5.4 nm when $M_{\rm p}$ was increased from 12500 to 83000 g mol⁻¹ (Table 1, entries 11–13). Similar polymer size effects were previously reported by Saito et al., who investigated the growth process of silver nanoparticles in organic media using poly(dihydroxystyrene-block-styrene) poly(DHSt-b-St) as reductant,^[29] and also by Wang et al. using dodecanethiol (DDT) terminated poly(methacrylic acid) for stabilization of AuNPs.^[30] We also investigated whether the relative ratio between stabilizing thioether entities and HAK moieties shows any effect on the AuNP formation and found that increasing the relative ratio of thioether entities with respect to HAK from 1.3 to 3.3 leads to a decrease of the AuNP diameter from 2.5 \pm 0.7 nm to 1.5 \pm 0.3 nm (Table 1, entries 11, 14-16). When the block copolymer 8 was used, AuNPs (Au@8*) with a diameter of $3.0 \pm$ 0.9 nm were obtained showing that the styrene block has little influence on NP growth (compared with Table 1, entry 11).

We also performed solubility and stability studies on our gold polymer hybrids. Au@4* (5.1 nm) was found to be soluble only in DMF. However, we expected good solubility for AuNPs prepared from copolymer 7 (Au@7*) in various organic solvents due to its hydrophobic solubilizing polymer coat. To this end, Au@7* (2.5 nm) was first isolated by the removal of DMF/H₂O (simple evaporation under vacuum). The Au/polymer hybrid was then washed several times with deionized water to remove NaCl, and these AuNPs (Au@7*) were found to be soluble in DMF, DMSO, THF, CH₂Cl₂, and CHCl₃. Importantly, these NPs do not show any ripening for weeks upon storage at 5 °C in these solvents. Block copolymer stabilized Au@8* show the same solubility properties.

To prove that the polymer is acting as a stabilizer for the AuNP, we performed TGA experiments with the isolated Au@7* (2.5 ± 0.7 nm). These experiments revealed a gold loading of 21 wt% in the hybrid material. Furthermore, we also deposited Au@7* by drop-casting on a carbon-coated TEM grid.^[31] After thermal annealing for 13 h under high vacuum at 150°C no significant size change for the AuNPs was observed (2.6 ± 0.7 nm) indicating that the polymer acts as a stabilizer for our nanoparticles (see the Supporting Information).^[32]

Organic solvents like DMF and some polymers are known to be reducing reagents for Au salts in the absence of light.^[33] In our case, AuNP formation in the presence of **4** without UV irradiation was not observed within 5 min. To exclude AuNP generation by reduction with the solvent upon irradiation, we ran an experiment in the absence of polymer **4** with light. Upon UV irradiation of a HAuCl₄/NaOH (ratio of 1:6) solution in DMF/H₂O, AuNP formation was observed to begin after > 2 min. Note that complete photocleavage of the HAK groups should occur in a few minutes, if one considers



Scheme 2. Suggested mechanism for generation of Au nanoparticles using (co)polymers **4**–**8**, NaOH, and light.

a triplet lifetime in the range of 0.37–13 ns and a quantum yield of 0.29–0.67 depending on the substituents at the *para* position of aryl group.^[34] In fact, AuNP formation upon UV irradiation in the presence of **4** (ratio of HAK units/HAuCl₄/ NaOH 10:1:6) was complete in ≤ 2 min showing that **4** rather than the solvent is the reducing reagent in our process.^[35]

Our suggested mechanism for AuNP formation is depicted in Scheme 2. As experimentally shown and discussed above, NaOH plays an important role. We assume that NaOH influences AuNP formation in three ways: Firstly, it is known that the presence of hydroxide ions changes the redox potential of Au³⁺ (HAuCl₄ is transformed into M⁺AuCl_n- $(OH)_{4-n}$) and influences NP growth.^[36] Secondly, after photocleavage the ketyl radical 3a is likely deprotonated by NaOH to provide ketyl radical anion 3b which has a lower oxidation potential than **3a**.^[37] Finally, hydroxide ions can probably trap polybenzoyl radicals 9 to generate the reduced poly(carboxylic acid) radical anions 10, which are in turn readily oxidized by the Au salts to the corresponding poly(carboxylic acid) salts **11**.^[38] We currently disregard formation of polyacids by air oxidation of the acyl radicals to the corresponding peracids followed by reduction as suggested by Scaiano et al.,^[21] since AuNP formation has to be conducted under argon atmosphere (O_2 is detrimental to this process).

To prove formation of the acid functionalities we etched the gold nanoparticles with KCN (Au@4*) and characterized the resulting polymer. NMR spectroscopy revealed formation of the suggested carboxylic acid groups. However, along with the acid functionality we also identified the N,N-dimethylamide entity (around 50%) as polymer side chain probably resulting from reaction of Au@4* with dimethylamine derived from DMF. The structure of this copolymer was further proved by independent synthesis (see the Supporting Information). Moreover, upon increased irradiation time the amide content in copolymer 12 also increased, indicating that the poly(carboxylic acid) salt 11 is formed first (as suggested in our mechanism) and is then likely further converted by DMF to copolymer 12 (see Scheme 2).

Solid-state ¹³C NMR investigations were also performed on poly(HAK) **4** ($M_n = 12900 \text{ gmol}^{-1}$, PDI = 1.2) and on the corresponding polymer-coated AuNPs prepared from this homopolymer (Au@**4***). Quantitative disappearance of characteristic signals of the HAK moiety ($\delta = 204 \text{ ppm}$, $\delta = 78 \text{ ppm}$, $\delta = 29 \text{ ppm}$) after irradiation indicated complete consumption of the photoactive entities (Figure 3). Importantly, a new signal at $\delta = 172 \text{ ppm}$ appeared which was assigned to the carboxylate carbon atom and amide function, supporting the formation of polymer **12** under the applied conditions (light, NaOH, DMF).^[39]

The oxidation state of gold nanoparticles in the hybrid was determined by XPS, unambiguously proving full photochemical reduction of gold ions to Au⁰. The XPS spectrum showed the two signals of the characteristic binding energies for Au⁰



Figure 3. Solid-state ${}^{13}C-{}^{1}H$ CP/MAS NMR spectra of a) poly(HAK) 4 ($M_n = 12\,900 \text{ gmol}^{-1}$, PDI = 1.2) and b) the corresponding polymer-coated Au@4*. Signal intensities normalized based on the polystyrene backbone (\approx 44 ppm).

(Au4 $f_{7/2}$, Au4 $f_{5/2}$; see the Supporting Information). Additional signals characteristic of gold ions were not detected.^[5,40] This was observed for both the larger (5.1±1.0 nm; Table 1, entry 4) and smaller (2.5±0.7 nm; Table 1, entry 11) AuNPs.

Finally, we tested the catalytic activity of the AuNPs prepared with the polymer **4** for the oxidation of 1-(4-methoxyphenyl)ethan-1-one using water as a solvent and H_2O_2 (2.5 equiv) as an oxidant at 90 °C for 6 h (see the Supporting Information).^[41] Pleasingly, with Au@4* (1 mol%) the ketone was quantitatively formed under these conditions. Notably, since the catalyst is dispersed in water, the product ketone can be readily and cleanly isolated by simple extraction with dichloromethane. The aqueous layer containing Au@4* was successfully reused three times without significant loss in



activity (cycles 1–3: 97%). However, in the fourth cycle a slight decrease in reaction yield was observed (91%).

In summary, we have presented efficient light-mediated formation of polymer-protected AuNPs by using readily prepared photoactive homo- and copolymers as reducing reagents. Upon photooxidation, polymers are converted to poly(carboxylate-co-amide)-copolymers which in turn stabilize the generated AuNPs. By simple variation of pH value and composition and length of the polymer, the diameter of the spherical AuNPs can be adjusted from 1.5 nm to 9.6 nm. The AuNPs are soluble in a wide range of organic solvents and show high stability over weeks. Moreover, they can be used as recyclable catalysts for the oxidation of benzylic alcohols. Our method for controlled and programmable AuNP preparation is experimentally very easy to conduct. It is an "instant" AuNP preparation process: just mix the photoactive polymer, the Au³⁺ salt, and NaOH in DMF/H₂O and irradiate for a few minutes: ready! Isolation is conducted by simple evaporation of the solvent. It is evident that this process should be general for the preparation of polymercoated metal nanoparticles. Experiments on the application of this methodology using other metal salts are currently underway.

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