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Surface Spectroscopic Study of the Stabilization Mechanism for Shape-Selectively Synthesized Nanostructured Transition Metal Colloids

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Abstract: Nanoscale palladium and nickel colloids prepared in the presence of certain tetra-*n*-octylammonium carboxylates contain a high proportion of nonequilibrium trigonal cross section particles. Specifically, those carboxylates which bear a hydroxy function at the α-position, e.g., tetra-*n*-octylammonium glycolate, exert a strong influence on the shape of the metal colloids. It is shown by an in situ FTIR study of the preparation of colloidal nickel from bis(cyclooctadiene)nickel in the presence of tetra-*n*-octylammonium glycolate that the interaction of the α-hydroxy carboxylate with the surface of the colloidal metal particle is likely to be the morphology-determining factor in the shape-selective preparation of these metal particles.

Introduction

Nanoscale transition metal clusters are of current interest in the fields of catalysis, nanoelectronics, and materials science.[1] To attempt to take maximum advantage of those material or chemical properties which are affected by particle size and/or shape, synthetic methods are needed in which significant control can be exercised over those parameters. Colloidal metal preparation methods offer the possibility of developing such synthetic protocols, and the preparation of metals in this form, with control of particle size distribution and particle morphology, remains an important challenge in preparative metal colloid chemistry.

Among the various chemical approaches which have been developed for the preparation of colloidal metals, the reduction of metal salts is the most common, and reducing agents such as hydrogen, hydrazine, alcohols, carbon monoxide, $LiAlH_4$, $NaBH_4$, or $R_4N^+(Et_3BH^-)$ have been used to prepare metal colloids in the nanometer size range.[1,2] Chemical reduction offers a variety of parameters that can influence the physical and chemical properties of the resulting particles. Since the pioneering work of Turkevich et al. it has been accepted that particle size distribution in colloidal dispersions is strongly governed by the interplay between two processes which occur during preparation: nucleation and cluster growth.[3] This basic proposition and variations thereof have been discussed many times in more recent publications.[4] In principle the particle size can be determined by influencing the relative rates of nucleation and cluster growth. This can be achieved by varying such reaction conditions as temperature, type, and concentration of the metal precursor as well as the nature of the stabilizing or reducing agent.[2−4] Of course, the variation of two or more parameters of this kind in going from one system to the other makes direct comparisons difficult and therefore precludes straightforward interpretations.

Recently, we reported a new method for the redox-controlled size-selective preparation of palladium colloids by using a variety of tetra-*n*-octylammonium carboxylates $(n\text{-Oct})_4N^+(RCO_2)^-$ as reducing and stabilizing agents, all other parameters being constant.[5,6] The redox potential of the carboxylates was varied by introducing either electron-donating or -withdrawing substituents into the α-position of the carboxylate. No additional stabilizing agents were used. The use of these carboxylates as both reducing agent and stabilizer allowed the control of particle size in the resulting Pd-colloids in the range from 1.9 to 6.2 nm, depending upon the nature of R in the carboxylate RCO_2^-. Strongly reducing carboxylates lead to the formation of small particles in an overall fast process, whereas weakly reducing carboxylates induce slow reactions with the formation of larger colloids.[6]

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The control of particle morphology is more problematic. Shape-selectivity in the synthesis of nanostructured metal colloids has been observed in several cases with metals such as Au, Pd, Cu, Pt, and Ag.[7−11] For example, El Sayed and coworkers reported the shape-selective synthesis of cubic and tetrahedral platinum nanoparticles by using varying concentrations of sodium polyacrylate as a stabilizer.[12]

Whereas the theoretical basis of shape-selectivity in the growth of particles up to micrometer dimensions is presently uncertain, alternative synthetic approaches based on the ostensible physical constraints provided by nanoreaction chambers are more easily understood. Thus, the use of micelles in which the reduction of transition metal salts is carried out can lead to acicular particles,[13−16] and copper nanorods having various diameters and lengths have been prepared in this way.[15] The deposition of metals in the nanopores of solids such as Al_2O_3 also leads to rodlike geometries in the nanometer range.[17−19] However, in the present study such strategies were not used. Rather, the emphasis is on shape-selectivity during particle growth as influenced by the nature of the reducing and stabilizing agents.

We report here that the use of certain tetra-*n*-octylammonium carboxylates as reducing and stabilizing agents affects not only size but also the shape of nanostructured palladium and nickel colloids. Specifically, it is shown that those carboxylates which bear a hydroxy function at the α-position, e.g., tetra-*n*-octylammonium glycolate, exert a strong influence on the shape of the metal colloids. Characterization is achieved by transmission electron microscopy (TEM) and scanning tunneling microscopy (STM).[20] To shed some light on this phenomenon, an in situ FTIR study of the colloid preparation process has been performed. The interaction of the α-hydroxy carboxylate with the surface of the colloidal metal particle is proposed as the morphology-determining factor in the shape-selective preparation of these metal particles.

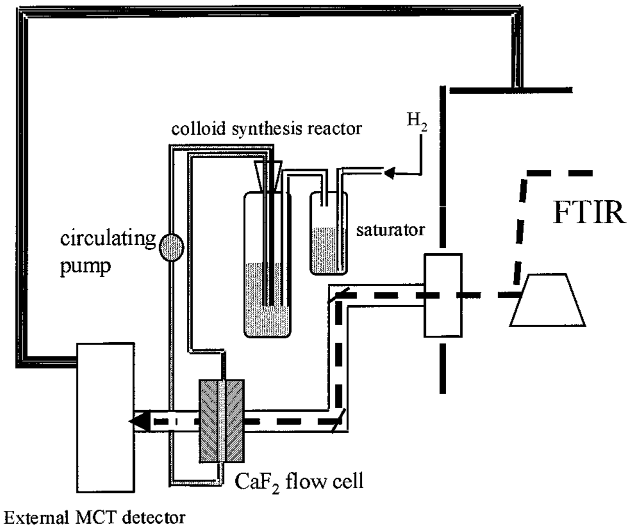

Figure 1. Schematic drawing of the FTIR flow experiment. For a full description see ref 21.

Experimental Section

Preparation of Glycolate-Stabilized Pd-Colloids. In a typical procedure 10 mL (0.03 mmol) of a 3 mM stock solution of $Pd(NO_3)_2$ in dry THF and 42 mg (0.08 mmol) of $(n\text{-}C_8H_{17})_4N^+(HOCH_2CO_2)^-$ were heated to reflux for 6 h. The resulting colloidal suspension was analyzed by transmission electron microscopy (TEM). A HITACHI HF 2000 microscope operating at 200 hV, equipped with a cold field emission system and an EDAX analyzer, was used for transmission electron microscopy. Samples for electron microscopy were prepared on carbon-coated copper grids in an argon-filled glovebox, mounted onto an evacuable stage and transferred under vacuum to the microscope.

Preparation of Glycolate-Stabilized Ni-Colloids. In a typical procedure 407 mg (1.48 mmol) of $Ni(COD)_2$ and 388 mg (0.720 mmol) of $(n\text{-}C_8H_{17})_4N^+(HOCH_2CO_2)^-$ were dissolved in 40 mL of dry THF under an argon atmosphere. A stream of hydrogen (saturated at room temperature with solvent) was bubbled through the reaction mixture while heating to 60 °C for 16 h under reflux. Analysis of the reaction mixture over a period of several hours showed the formation of cyclooctane. After filtration through Celite the solvent was removed under reduced pressure. The solid, waxy residue could be easily redispersed in such solvents as THF, DMF, or acetone.

Preparation of Other Carboxylate-Stabilized Ni-Colloids. The same procedure as above was applied, except that the glycolate was replaced by the tetra-*n*-octylammonium salts of lactic, tartaric, and gluconic acid.

FTIR Spectroscopic Investigation of the Interaction of Glycolate with Ni-Colloids during their Preparation. In a typical in situ FTIR experiment, 407 mg (1.48 mmol) of $Ni(COD)_2$ and 388 mg (0.720 mmol) of $(n\text{-}C_8H_{17})_4N^+(HOCH_2CO_2)^-$ were dissolved in 40 mL of dry THF in an argon atmosphere. After the reaction mixture was heated to 60 °C, hydrogen (saturated with solvent) was bubbled through the solution to initiate the colloid synthesis. The reaction mixture was circulated (200 mL min^{-1}) through an external CaF_2 window flow cell, and IR spectra were obtained using a remote MCT detector coupled to the external optical port of a Nicolet Magna 550 FTIR spectrometer, as shown schematically in Figure 1 and described in detail elsewhere.[21] IR spectra of the glycolate were measured in the region of 1550 and 1680 cm^{-1} (ν_{as} CO_2^-) while the reaction mixture was circulating through the flow cell during colloidal nickel formation.

Results and Discussion

In our initial study concerning the size-selective preparation of Pd-colloids stabilized by tetra-*n*-octylammonium carboxylates (Scheme 1), we generally observed no unusual effects with

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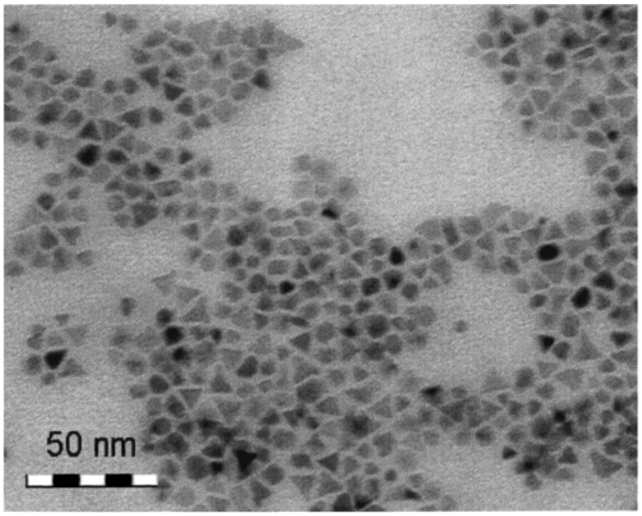


Figure 2. Electron micrograph of glycolate-stabilized colloidal palladium consisting of predominantly trigonal particles.

Scheme 1. Size-Selective Preparation of $R_4N^+(RCO_2)^-$-Stabilized Pd-Colloids

$$Pd(NO_3)_2 + (n\text{-}C_8H_{17})_4N^+(RCO_2)^- \xrightarrow[THF]{66\ °C} \text{Pd-colloid}$$

respect to shape selectivity.[6] Using acetate, dichloroacetate, pivalate, pyruvate, or formate, TEM analyses showed the presence of the usual spherical particles. In some cases a small percentage ($<5\%$) of trigonal particles was observed. In complete contrast, the use of tetra-*n*-octylammonium glycolate as reductant and stabilizer led to a marked increase in the abundance of trigonal particles. For example, upon treating $Pd(NO_3)_2$ with an excess of $(n\text{-}C_8H_{17})_4N^+(HOCH_2CO_2)^-$ at 66 °C in THF a colloid was obtained composed of 3.6 nm mean diameter particles, about 40–50% of which show trigonal geometry (Figure 2).

$$Pd(NO_3)_2 + (n\text{-}C_8H_{17})_4N^+(HOCH_2CO_2)^- \xrightarrow[THF]{66\ °C} \text{Pd-colloid}$$

Since a common factor in both the polyacrylate stabilized Pt-colloids[12a] and the $(n\text{-}C_8H_{17})_4N^+(HOCH_2CO_2)^-$ stabilized Pd-colloids described herein is the presence of carboxylate, it may appear that this functional group is responsible for morphology control. However, as already mentioned, when other carboxylates such as acetate, pivalate, dichloroacetate, pyruvate, or formate were used under identical conditions, the percentage of trigonal particles turned out to be very low, indicating that the α-hydroxy group plays an essential role.

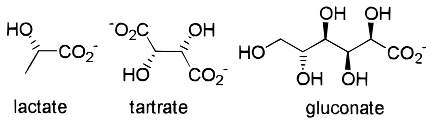
To deconvolute the reduction and stabilization roles of glycolate in morphology control in colloidal metal synthesis we carried out colloidal metal preparations in which glycolate can function only as a stabilizing agent, by the use of zerovalent metal complexes as precursors in a metal-colloid preparation. This method, which involves the reactive displacement of stabilizing ligands from a complex of the relevant metal, has been known for some time,[22,23] and by using such precursors the metal reduction step is eliminated. For example, the decomposition of polymer-containing solutions of nickel bis(cyclooctadiene-1,5), $Ni(COD)_2$, in either the presence or absence of hydrogen, has been used to prepare polymer-stabilized colloidal nickel.[24,25] We therefore used $Ni(COD)_2$ as a precursor for colloidal nickel, in the presence of glycolate, to determine whether glycolate influences the morphology of the colloidal metal particles solely by adsorption on the metal surface or by some other mechanism linked to its redox potential. Since nickel in $Ni(COD)_2$ is already in the zerovalent state, glycolate could act not as a reducing agent but solely as a colloid stabilizer.

$$Ni(COD)_2 + (n\text{-}C_8H_{17})_4N^+(HOCH_2CO_2)^- \xrightarrow[60\ °C]{H_2} \text{Ni-colloid}$$

The addition of hydrogen to a rapidly stirred solution of $Ni(COD)_2$ at 60 °C resulted in the formation of cyclooctane over a period of several hours due to reduction of the COD ligand in the starting material. TEM analysis of the resulting colloidal suspension of nickel revealed an average diameter of 4.5 nm, with a preponderance of trigonal cross-section particles (Figure 3a). The spherical and trigonal colloids are crystalline. In the high-resolution image in Figure 3b the lattice planes of the nickel are evident and the spacing of 0.249 nm corresponds to the [111] plane of the face-centered cubic modification, proving the presence of nickel in the zero-valence state. No evidence for significant amounts of nickel oxides was found in samples prepared in the complete absence of oxygen. Due to the fact that the colloid was prepared from a zerovalent nickel complex under a reducing atmosphere of hydrogen, we in fact expect essentially all of the resulting nickel particles to be in a reduced state.

Since TEM images always display the projection of the atoms onto the observation plane, no information can be obtained by this method concerning the third dimension. Indeed, a trigonal image is consistent with both a tetrahedral and a trigonal prismatic shape. We then turned to scanning tunneling microscopy (STM),[20] being aware of the possibility of artifacts that have been suspected in special cases.[26] Under specific conditions STM can resolve this problem, and Figure 4a shows STM images of spherical and trigonal Ni-particles adsorbed onto a Au single-crystal surface. A comparison of the different particle shape by means of line-scan-analysis demonstrates the extended flat character of the trigonal particle surface versus the spherical particle, ruling out a tetrahedral morphology for the trigonal particle (Figure 4b).

Control experiments using $(n\text{-}C_8H_{17})_4N^+Br^-$ or $(n\text{-}C_8H_{17})_4N^+NO_3^-$ as stabilizers led to the formation of Ni-colloids having exclusively spherical morphology, ruling out a role for these anions in shape selectivity. In complete contrast the use of lactate, tartrate, or glyconate as stabilizers provided Ni-colloids in which a substantial amount of particles having trigonal shapes were observed. Thus, the common structural element, namely α-hydroxy carboxylate, seems to dictate shape selectivity.



The mechanism by which glycolate and other α-hydroxy carboxylates influence the morphology of the growing metal

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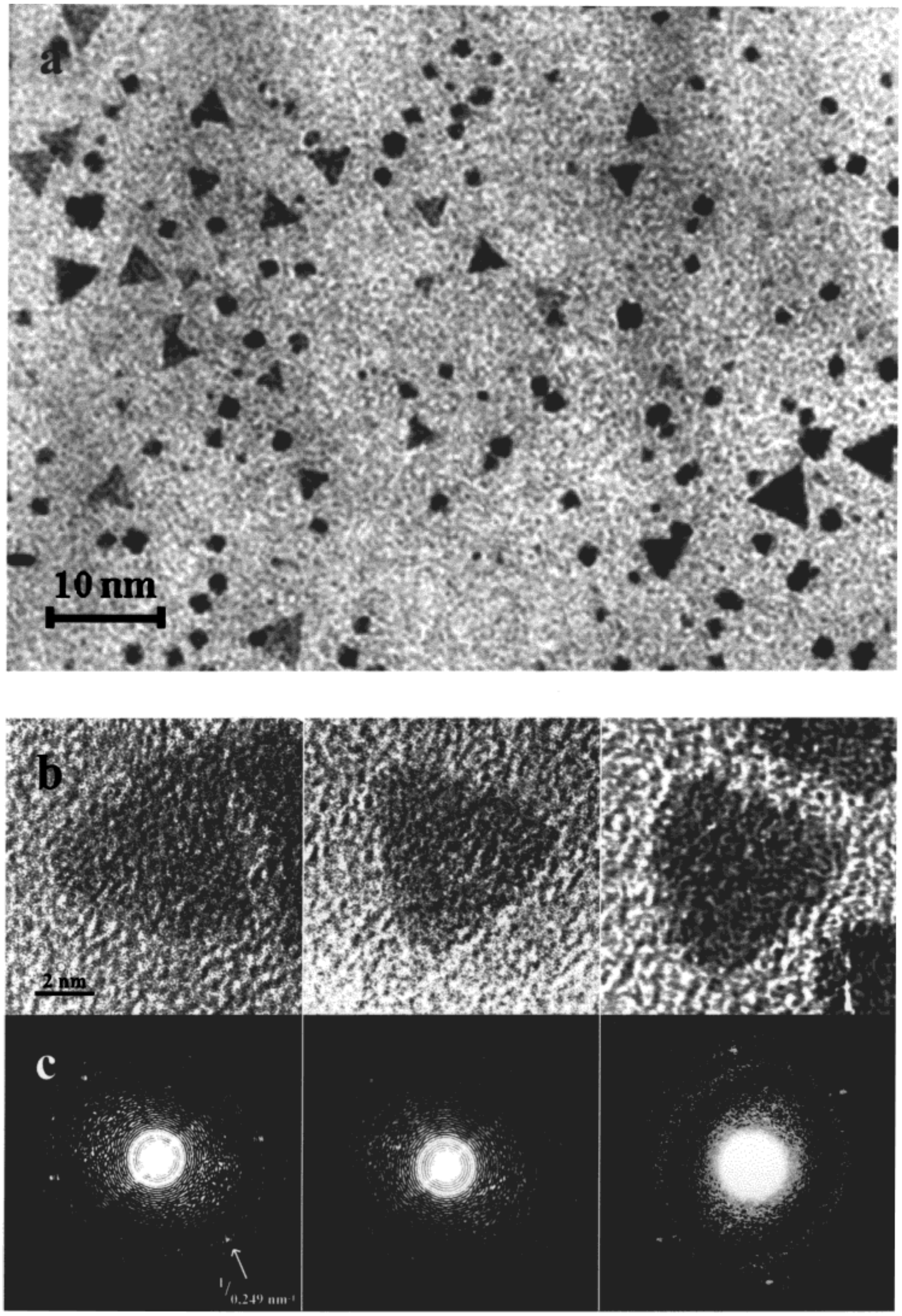

Figure 3. (a) TEM image of colloidal nickel particles prepared from $Ni(COD)_2$ in the presence of tetraoctylammonium glycolate. The trigonal cross section is evident. (b) High-resolution micrographs from several single trigonal colloidal nickel particles from part a. (c) The Fourier transforms showing the lattice plane spacing to be 0.249 nm corresponding to the [111] plane of the face-centered cubic modification.

particle may involve the selective adsorption of the anion on certain crystal faces of the growing nanocrystallite. If this mechanism were operating, one would expect the interaction of the glycolate with the surface of the Ni-nanoparticle would have spectroscopic consequences. It is to be expected that IR absorptions associated with vibrational transitions of the glycolate anion would be significantly affected by adsorption on the colloidal metal. We therefore investigated the possible adsorption of glycolate by means of in situ FTIR spectroscopy, a technique that we have previously applied to the analysis of CO adsorbed on the surface of metal colloids.[21,23,27]

Figure 5 shows the evolution of the IR spectrum in the region corresponding to the asymmetric CO_2^- stretching mode of dissolved glycolate during the hydrogen reduction of $Ni(COD)_2$. As shown in Figure 5a, the band at 1621 cm^{-1} (ν_{as} CO_2^-) in the initial reaction mixture, before hydrogenation, decreases while a new band at 1604 cm^{-1} develops over a period of 2 h. Figure 5b shows IR spectra of the reaction mixture recorded over a period of 22 h after subtracting the spectrum at $t = 0$. At the beginning of the colloid synthesis, the reaction mixture solely contains dissolved glycolate resulting in a baseline for subsequent spectra. With additional adsorption of glycolate (22 h) the band at 1621 cm^{-1} due to dissolved glycolate decreases,

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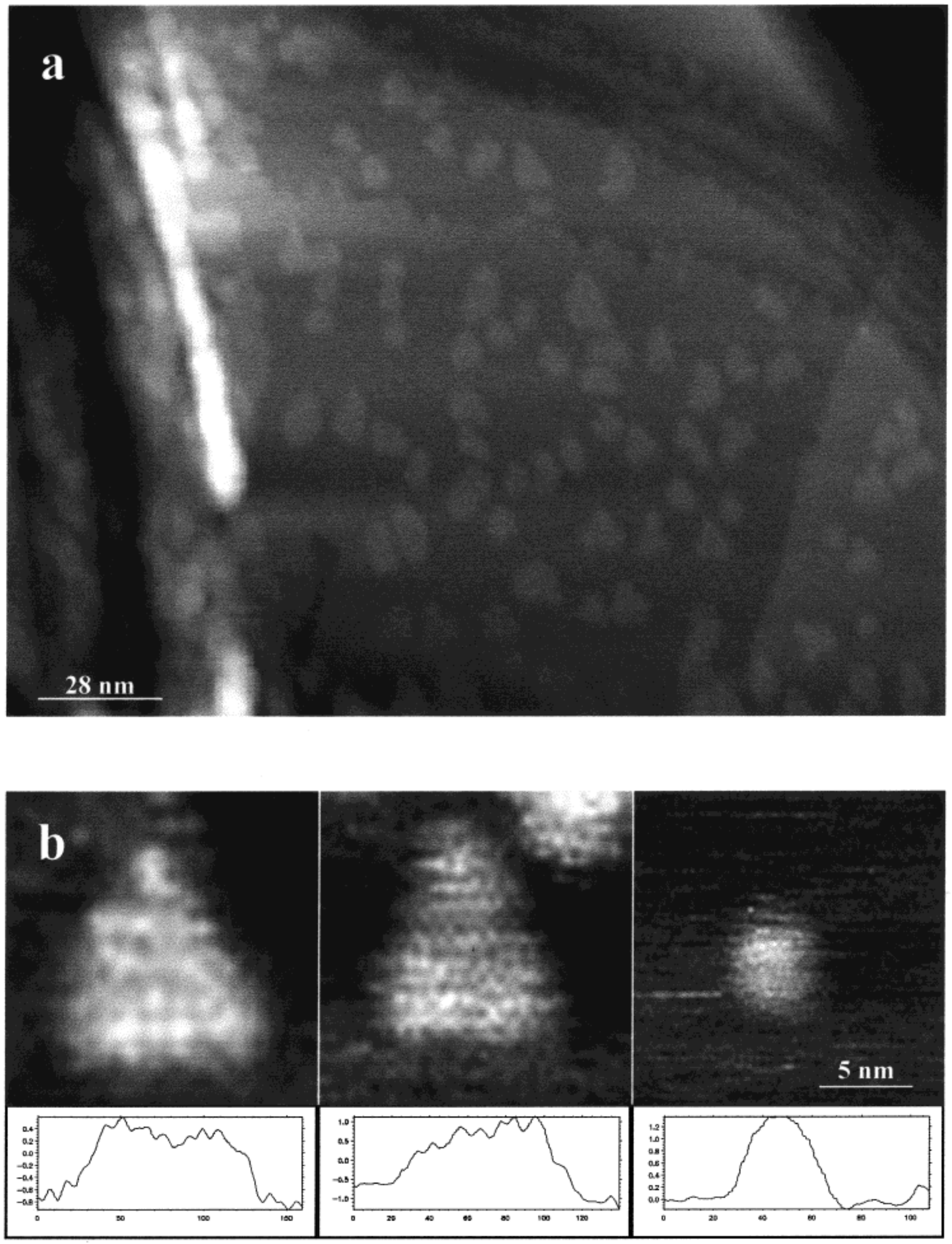

Figure 4. (a) STM image of spherical and trigonal colloidal nickel particles immobilized on a Au single-crystal surface. (b) Line scans across spherical and trigonal particles, demonstrating the flat three-dimensional structure of trigonal colloids.

giving a negative absorbance, whereas a new band at 1604 cm^{-1} develops, resulting in an S-shaped curve in the spectrum.

The band at 1604 cm^{-1} is assigned to the asymmetric stretching of CO_2^- in glycolate adsorbed on the surface of the Ni-colloid and clearly indicates the interaction of glycolate with the metal particle surface. The observed shift of 17 cm^{-1} is in line with surface-enhanced Raman spectroscopic investigations on the adsorption of citrate on Ag colloids carried out by Kerker et al.[28] In addition, the observed red-shift of 17 cm^{-1} gives rise to a minor decrease in the so-called *D*-value (the frequency difference between the symmetric and asymmetric $n(CO_2)$ bands) of the adsorbed glycolate. This is indicative of a non-chelating mode of coordination for the carboxylate group on the metal surface.[29] Whether the mode of coordination is monodentate or bridging remains uncertain from these data. While these experiments prove that the glycolate is adsorbed to the surface of the Ni-nanoparticles, they do not shed any light on the exact role of the α-hydroxy group, since IR absorption of this functionality is of no diagnostic help.

Summary and Conclusions

While an interaction between various stabilizers and suspended metal particles in a stable colloidal dispersion is traditionally assumed to involve adsorption at the colloidal metal surface, definitive evidence for this interaction is seldom presented.[1,20,26,30] The results we describe here support the hypothesis that in the nickel/glycolate system the carboxylate

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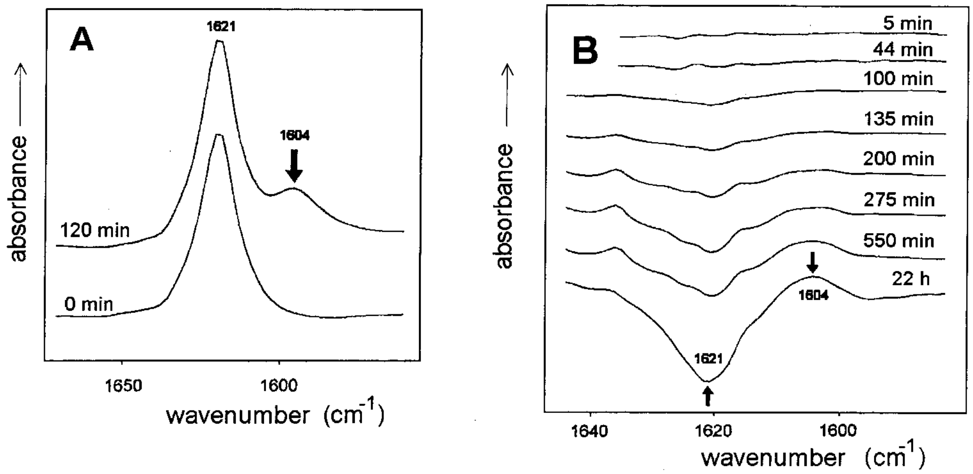

Figure 5. (a) IR spectra of dissolved glycolate (0 min) and development of a new band of adsorbed glycolate after colloidal nickel synthesis. (b) IR spectra of the reaction solution during colloid synthesis. The absorbances due to dissolved glycolate at $t = 0$ min were subtracted from each spectrum. Disappearance of dissolved glycolate (1621 cm^{-1}) and formation of adsorbed glycolate (1604 cm^{-1}) result in an S-shaped spectrum after 22 h.

exerts its stabilizing influence by adsorbing onto the surface of the colloidal nickel nanoparticles. More importantly, we have also demonstrated that the predominance of nonequilibrium trigonal morphology for colloidal Ni-particles prepared in the presence of glycolate can be ascribed to this interaction. Since the formation of the Ni-particles under the conditions we used in this study does not involve oxidation of the carboxylate but still gives a preponderance of trigonal cross-section particles, the morphology-determining role of glycolate (and of other α-hydroxy carboxylates) by adsorption on the particle surface appears likely. Finally, the presence of an α-hydroxy group in the carboxylate stabilizer is shown to be crucial to the formation of trigonal metal particles.

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