Colloid Polym Sci 275:593–598 (1997)
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ORIGINAL CONTRIBUTION

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Preparation and properties of uniform amorphous and crystalline colloidal nickel sulfide

Received: 20 January 1997
Accepted: 21 January 1997

Supported by the NSF grant CHE-9423163

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Abstract Amorphous spherical particles of nickel sulfide of 10 nm in diameter were synthesized by the controlled double-jet precipitation (CDJP) technique using nickel sulfate and sodium sulfide. Cubic crystalline particles of ~200 nm were obtained by aging dispersions of amorphous particles at 80 °C for more than a week, as long as the pH was kept between 3 and 3.5. Electrokinetic mobilities of these particles are reported, as well as color properties of their dispersions in liquids and in poly(vinyl alcohol) films are described.

Key words Black pigment – double-jet precipitation – nickel sulfide, amorphous – nickel sulfide, cubic – nickel sulfide, nanosized

Introduction

Several studies dealt with the preparation of uniform metal sulfides using different procedures. In a two-step process cadmium or zinc sulfide "seeds" were first precipitated in acidic solutions containing the metal salt and thioacetamide (TAA), which in the presence of additional amounts of TAA were further aged at an elevated temperature [1, 2]. Another method was based on the phase transformation through a rapid dissolution of a metal hydroxide, caused by the reaction of metal ions with S^{2-} released from TAA [3]. In the described cases TAA served as the reservoir for the sulfide ion. Alternatively, several monodispersed metal sulfides were prepared by aging aqueous solutions of the corresponding metal complexes saturated with H_2S at room temperature [4–6]. The described procedures yielded particles in the submicron size range.

More recently, it was shown that nanosized palladium sulfide could be obtained by the controlled double-jet precipitation process (CDJP) [7]. In this work, uniform nickel sulfide particles of ~10 nm in size were prepared by the same process using different nickel salts and sodium sulfide. The so-generated amorphous nickel sulfide was converted to cubic crystalline particles of ~200 nm by aging the original dispersions at 80 °C for long periods of time. The original nanosized particles were also incorporated into polymer films and their optical properties were evaluated.

Recently, the interest in nickel sulfide has increased due to its color and electric characteristics [8, 9]. The same material may be used as a promising black pigment, which has some advantages over other such solids (e.g. carbon black), because uniform particles assure the color reproducibility.

Experimental

Materials

All inorganic chemicals were reagent grade and were not further purified. The $Na_2S \cdot 9H_2O$ solution was freshly prepared before each experiment. All solutions were filtered through 0.2 μm pore size membranes before use. The surfactant AVANEL S-150 CG (PPG Ind.) was received as a 35 wt% aqueous solution.

Preparation of particles

Nickel sulfide was prepared by the controlled double-jet precipitation (CDJP) which involves simultaneous addition of two reactant solutions by means of peristaltic pumps into a solution in a reactor [10]. In the present work, 50 cm^3 each of nickel sulfate and sodium sulfide solutions were introduced at a constant flow rate of 10 cm^3 min^{-1} into 100 cm^3 of an aqueous solution, containing surfactant AVANEL S-150 CG (S-150), followed by aging for 5 min. The entire process was carried out at the ambient temperature. The concentration of reactants, the nickel salt and sodium sulfide, was varied from 0.02 to 0.5 mol dm^{-3}, while the mole ratio $[Ni^{2+}]/[S^{2-}]$ was kept constant at 1, with 0–5 g dm^{-3} of the surfactant in the solutions used in these experiments. The stability of nickel sulfide dispersions was investigated over the pH range 8–2, which was altered with H_2SO_4, immediately after the CDJP was completed. Experiments with other nickel salts ($NiCl_2$, $Ni(NO_3)_2$) were carried out to evaluate the effects of different anions on the particle properties.

In aging experiments, the pH of dispersions of amorphous particles was adjusted with either H_2SO_4 or NaOH from 2 to 11, which were then kept at 80 °C for various periods of time in sealed containers with no stirring. In some cases, an open vessel was used to evaluate the possible effect of oxygen on the final solids during the aging process.

For transmittance measurements, nickel sulfide precipitates were washed five times with water, separated by centrifugation, and dried in vacuum at 50 °C for 12 h. 0.1 g of the dry powder was dispersed in 500 cm^3 of a solution containing 0.3 g S-150 while in an ultrasonic bath for 1–2 h. For the preparation of films, 3 g of solid poly(vinyl alcohol) (MW ~ 2000) was added to 10 cm^3 of the dispersion, which was agitated overnight. The resulting highly viscous liquid was spin-coated at 500 rpm on thoroughly cleaned 5 × 5 cm glass plates as described elsewhere [11]. The transmittance spectra of nickel sulfide dispersions and films were recorded with a Perkin–Elmer Lambda 6 UV/vis spectrophotometer.

Characterization

The particle morphology was inspected by transmission (TEM) and scanning (SEM) electron microscopy and the size distribution was determined by dynamic light scattering with a DLS BI-200SM instrument. Energy-dispersive X-ray analysis (EDX) was used to examine the composition of the solids, while the crystal structure of the particles was established by X-ray powder diffraction (XRD) using CuKα radiation and identified by comparison with data for standard samples. Differential thermal (DTA) and thermal gravimetric (TGA) analyses were carried out at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. To evaluate the electrokinetic mobilities, the particles purified as before were dispersed in a 0.01 mol dm^{-3} NaCl solution. The mobilities were measured with the PenKem 3000 instrument 5 min after the pH of the dispersion was adjusted with HCl and NaOH, as needed.

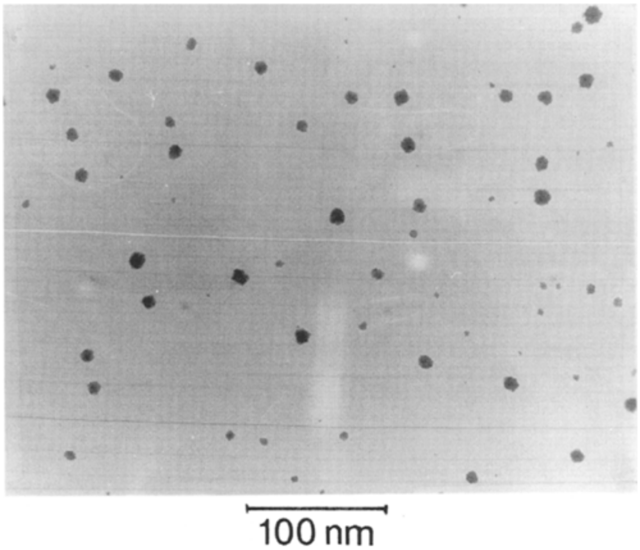
Results and discussion

Amorphous spherical particles

The precipitation of nickel sulfide by the CDJP process resulted in extremely small particles, the size of which was independent of the concentrations of reactants (0.02–0.5 mol dm^{-3}) and of the surfactant (0–5 g dm^{-3}), as well as of the kind of nickel salts employed. A typical TEM of such particles (Fig. 1) indicated diameters of 5–10 nm and the X-ray diffraction of these solids shows them to be amorphous (Fig. 2a).

The presence of a surfactant, such as S-150 used in this work, prevents aggregation of the dispersed matter. Enhanced stability could also be achieved by lowering the pH with H_2SO_4 to 3–4, immediately after the CDJP was completed. A dispersion that contained a high

Fig. 1 Transmission electron micrograph (TEM) of a nanosized amorphous nickel sulfide, prepared by the controlled double-jet precipitation (CDJP) using solutions of 0.02 mol dm^{-3} $NiSO_4$ and Na_2S each, that were introduced at the rate of 10 cm^3 min^{-1} into 100 cm^3 of an aqueous solution containing 0.525 g AVANEL S-150 surfactant at 20 °C



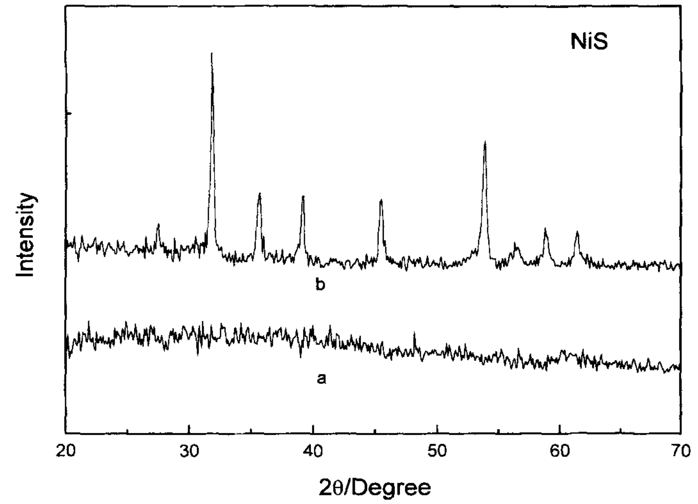


Fig. 2 XRD pattern of (a) amorphous particles shown in Fig. 1, and (b) cubic particles shown in Fig. 4b

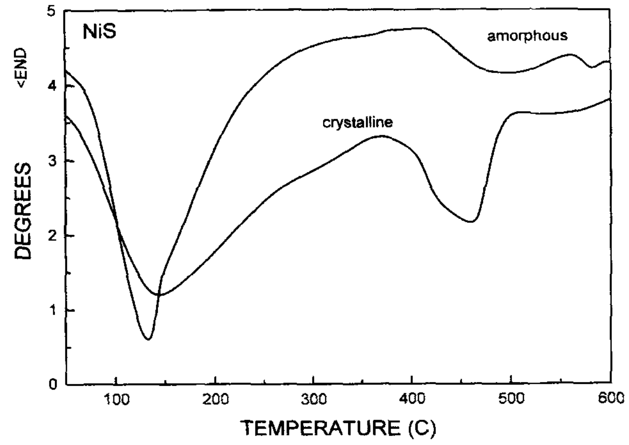


Fig. 3 Differential thermal analysis (DTA) of amorphous particles shown in Fig. 1 and of crystalline particles shown in Fig. 4b in nitrogen atmosphere at the heating rate of 10 °C min^{-1}

concentration of S-150 (e.g. 5 g dm^{-3}) at a low pH (e.g. 3) remained stable for more than two months without settling.

The EDX of amorphous particles obtained in a solution with pH 8.5 showed that, in addition to nickel and sulfur, there was a very small amount of oxygen in their composition. The TGA of the same particles in nitrogen gave a weight loss of 18.6% on heating to 230 °C and 51.7% to 580 °C. The DTA (Fig. 3) at the same condition as TGA indicated an endothermic process at ~130 °C, which can be attributed to dehydration of the sample, but no other thermal process was evident up to 600 °C.

It is generally accepted that the precipitation in aqueous solutions does not yield pure NiS. Various forms of nickel sulfide can be produced, depending on the pH of the solution. For example, in acidic solutions $Ni(HS)_2$ was initially formed, then transformed to α- and β-NiS [12]. In alkaline or neutral solutions α-NiS and Ni(OH)(HS) precipitated [13, 14]. The weight loss in TGA does not agree with any single composition described above, which suggests that the amorphous particles may be a mixture of two or more complexes of nickel sulfide.

Crystalline cubic particles

Colloidal cubic nickel sulfide was formed on aging dispersions of amorphous particles prepared as described above. Electron micrographs in Fig. 4 illustrate such solids obtained under conditions given in the legend, which have a mean size of 180 ± 12 nm. Actually, it was established that the crystallization process was completed sooner (after 3 days) with no further change in the particle size.

The chemical analysis with EDX shows that the cubic particles are composed of nickel and sulfur. The XRD pattern (Fig. 2b) of the collected solids displays five major peaks characteristic of NiS_2, confirming particle crystallinity. TGA of cubic particles in nitrogen gives a weight loss of 40% between 100 and 700 °C, while the DTA (Fig. 3) has two endothermic peaks around 140 °C and 450 °C, probably due to dehydration and sulfur sublimation.

These uniform cubic particles were formed under a narrow set of conditions, with the pH in the range of 3–3.5 being an essential parameter. In dispersions of $3.5 < pH > 4$ such particles appear very slowly, and at $pH > 4$, no cubes could be observed even after aging at 80 °C for two weeks. At $pH < 3$ irregularly shaped solids were produced in low yield, due to the removal of sulfide from the system as H_2S.

The described cubic particles were formed only when $NiSO_4$ was used in the preparation of the amorphous precursors. In systems with $Ni(NO_3)_2$–HNO_3, sulfide was oxidized to sulfur and its oxides in a short time, while those with $NiCl_2$–HCl yielded only a few cubic particles after 2 weeks of aging.

To confirm the role of the sulfate ion in the formation of cubes, a dispersion of amorphous particles was prepared with $NiSO_4$, and thoroughly washed four times with distilled water until no trace of sulfate ions could be detected with $BaCl_2$. This dispersion was then acidified with HCl to pH 3.2 and one part was aged at 80 °C for one week. To the other part was added Na_2SO_4 to yield 1×10^{-2} mol dm^{-3} of SO_4^{2-} and it was again aged as the

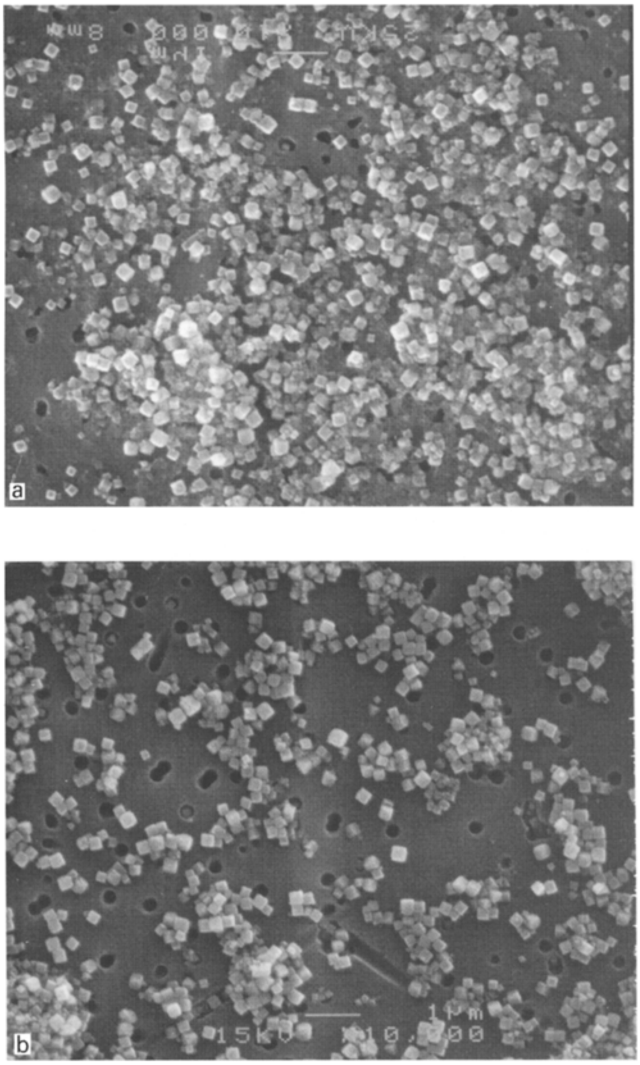


Fig. 4 Scanning electron micrographs (SEM) of nickel sulfide particles prepared by the CDJP using 50 cm^3 of 0.05 mol dm^{-3} solutions of $NiSO_4$ and Na_2S each, that were introduced into 100 cm^3 solution containing 0.14 g S-150 surfactant, after acidification of the obtained dispersion to pH 3.0, and aging it in a closed container at 80 °C for (a) 5 days, (b) 12 days

first sample. The dispersion containing only Cl^- ions remained essentially unchanged, while in the presence of Na_2SO_4 the particles turned into cubes, proving the critical role this anion played in the transformation process. Many research results on the formation of nickel sulfide indicated that in acidic solutions the action of sulfate ion led to solids less rich in the metal [15–17]. In view of the valence change of the sulfur ion, the following reaction may take place during aging at high temperature:

$$2NiS + 2H_2SO_4 \rightarrow NiS_2 + NiSO_4 + H_2SO_3 + H_2O \ .$$

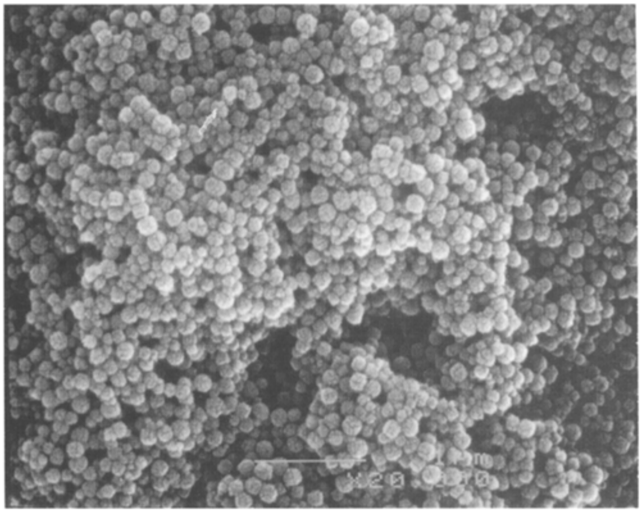


Fig. 5 SEM of nickel sulfide particles prepared under the same conditions as in Fig. 4b, except the precursor dispersion was kept in an open container for one hour before it was aged at 80 °C in a sealed container for 12 days

It would seem then that the original amorphous particles dissolved on aging at elevated temperature under the influence of sulfate ions, which produced disulfide resulting in crystalline NiS_2.

The amount of S-150 in the dispersions affected the formation of cubic particles. While a minimum concentration of S-150 (e.g. 0.2 g dm^{-3}) was necessary to keep the dispersion stable, high concentrations (e.g. 2 g dm^{-3}) inhibited the formation of cubic particles. In the latter case, the surfactant prevented the dissolution of the original amorphous particles, hence, the recrystallization did not take place, which may be due to their incorporation into micelles of S-150.

The oxidation of S^{2-} affected the nature of particles obtained on aging. Thus, the nickel sulfide dispersion obtained in an open vessel under stirring for 1 h before it was sealed and kept at 80 °C, consisted of nearly spherical nanosized particles (Fig. 5). On aging the system in an open container for 5 h, the sulfide was totally oxidized to sulfur and nickel ions were released into the solution.

Properties of the particles

Figure 6 gives the electrokinetic mobilities of aqueous suspensions of cubic particles as a function of the pH at a constant concentration of NaCl (0.01 mol dm^{-3}). The isoelectric point (i.e.p) was found to be at the high pH value of 9.9, which is close to that of the $Ni(OH)_2$ (pH 9.7) [18a, b]. Extensive work has been devoted to the study of surface chemistry of metal sulfides [19–21]. It was indicated that the complicated trend of these mobilities was

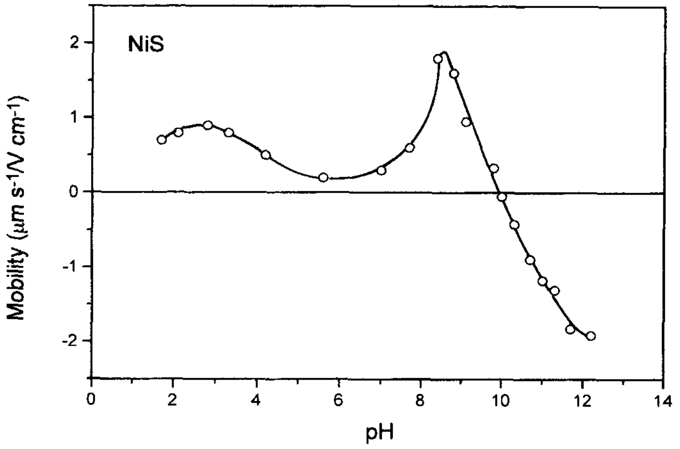


Fig. 6 Electrokinetic mobilities of cubic NiS_2 particles shown in Fig. 4b as a function of the pH in 0.01 mol dm^{-3} NaCl solution

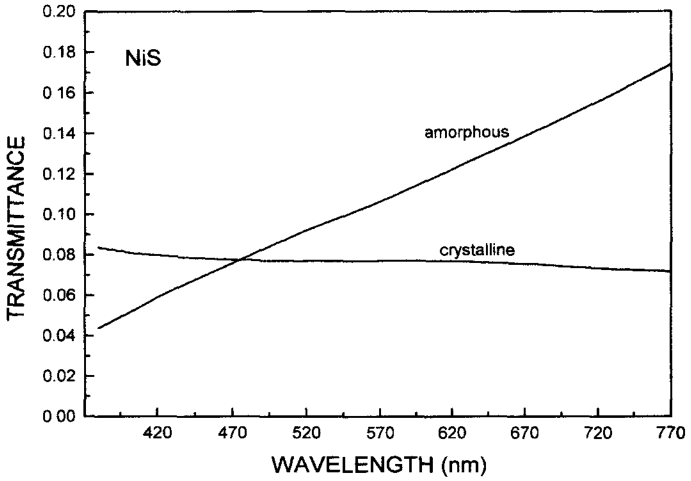


Fig. 7 Transmittance spectra of aqueous dispersions of amorphous and of crystalline particles containing 0.2 g dm^{-3} nickel sulfide

due to the oxidation of the sulfide surface and reabsorption/precipitation of the Ni^{2+}. Generally, S^{2-} ions are oxidized first to S^0, $S_xO_y^{z-}$ (e.g. $S_2O_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$), which are relatively soluble compounds. At the low pH, Ni^{2+} ions are released into the solution leaving the anions on the surface, which cause the mobility values to be less positive or even negative, depending on the extent of oxidation. With increasing pH, $Ni(OH)^+$ ions are adsorbed on the surface, leading to a maximum in the mobility curve. At the high pH, sulfide surface is coated with a hydroxide film, resulting in the electrokinetic behavior similar to that of nickel hydroxide.

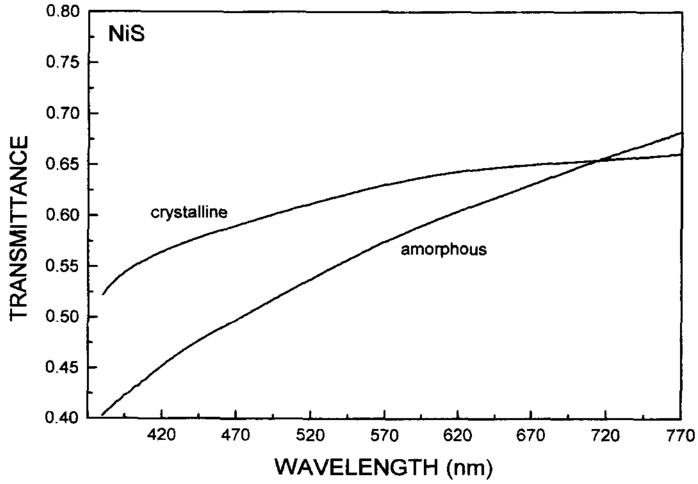


Fig. 8 Transmittance spectra of amorphous and of crystalline particles in poly(vinyl alcohol) films containing 0.07 wt% of nickel sulfide. The thickness of the film was 30 μm

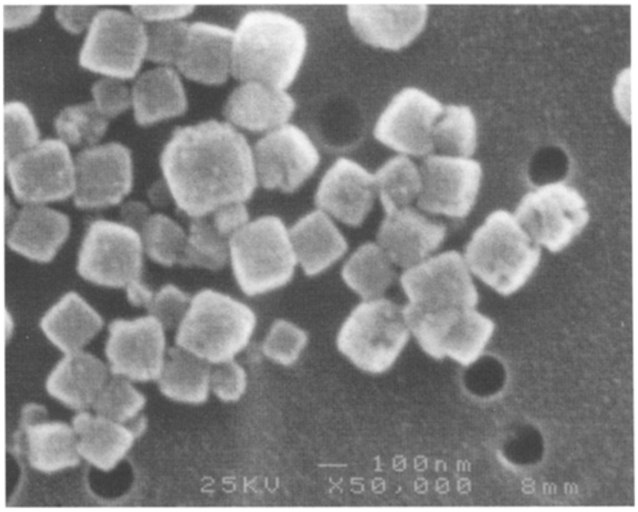


Fig. 9 SEM of the same NiS_2 particles as in Fig. 4b

The transmittance spectra of both amorphous and crystalline nickel sulfide aqueous dispersions, containing 0.2 g dm^{-3} solids, as well as of 30 μm thick poly(vinyl alcohol) films, containing 0.07 wt% particles indicated that light was absorbed over the entire visible range (Figs. 7 and 8). The dispersion and the film of amorphous particles showed a brown color, due to the small particle size. However, the color of dispersion of cubic particles was pure black. The extinction coefficient of aqueous dispersions of amorphous and cubic particles is estimated to be of the order of 10^3–10^4 mol^{-1} dm^3 cm^{-1} which is the same as that of carbon black [22].

Particle formation mechanism

The results presented in this work can be used to offer a mechanism of recrystallization of nickel sulfide particles from amorphous to cubic. The key role of the pH in the process can be explained by the dissolution of the nickel sulfide precipitate in acidic solutions. The dissolved sulfide formed crystallites of NiS_2, after an oxidation reaction under the influence of sulfate ions.

Recently, many studies [23, 24] indicated that the concept in LaMer's model for the formation of uniform precipitated colloids seems to be applicable only to the early stage of the solid phase formation. Figure 9 is the SEM of the same samples as in Fig. 4b, which shows that the final product was built up of nanosized subunits, obviously, by aggregation. The mean crystallite size calculated from the analysis of the XRD line broadening using the Scherrer formula [25] was 26 nm. One may conclude that nanosized crystallites were formed first, which aggregated into large uniform cubic solid.

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