

SOLUTION SYNTHESIS OF MONODISPERSED NANOCRYSTALLINE FCC-, ϵ - AND HCP-COBALT PARTICLES³

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RESUMEN

Se presenta la investigación sistemática realizada del 'proceso polyol' aplicado a la producción de partículas metálicas de cobalto. En esta primera aproximación, se logró controlar la cinética de la reacción y el tamaño de las partículas metálicas a través de una selección apropiada de la química de la solución en el sistema glycol etileno (EG) - o Trimetileno glycol (TMEG) - Cobalt(II). Al añadir iones hidróxidos en la solución de Co en EG se recorta el tiempo de reacción. Esta reducción del tiempo de reacción permitió un control conveniente del tamaño sub-micrón de las partículas de Co, con una gran uniformidad. Un ajuste adicional del tamaño de las partículas fue obtenido con el uso de iones acetatos. Bajo esta última condición, fueron producidas partículas uniformes de Co de un diámetro de aproximadamente 220 nm. Las partículas de Co, fueron policristalinas con una estructura de fcc y hcp. La magnetización de saturación (M_s) y la fuerza coercitiva (H_c) a temperatura ambiente, fueron en el rango de 65 a 162 emu/g y 35 a 199 Oe, respectivamente. En la presencia de iones de Pt, se pudo sintetizar nanopartículas de Co tan pequeñas como de 25 nm. Dependiendo de las condiciones de sintetización, a escala de manómetros, se estabilizó partículas de ϵ -Co metaestables y/o de hcp-Co. La fase hcp, con alta fuerza coercitiva, fue producida sin necesidad de recocido. El M_s y H_c de las partículas de Co sintetizados en presencia de iones de Pt, variaron en el rango de 53 a 77 emu/g y 222 a 535 Oe, respectivamente.

Palabras claves.- Polyol, nanopartículas metálicas, ϵ -Cobalto, partículas uniformes, química de soluciones, caracterización magnética.

ABSTRACT

The systematic research of the 'polyol process' applied to the production of metallic Cobalt particles is presented. In this approach, the control of the reaction kinetics and the metal particle size were achieved through a suitable selection of the solution chemistry in the ethylene glycol (EG)- or Trimethylene glycol (TMEG)-Cobalt(II) system. The addition of hydroxyl ions into the Co solution in EG caused a dramatic shortening of the reaction time. This shortening in reaction time permitted a convenient control of the size of sub-micron Co particles with a high monodispersity. A further tailoring of the particle size was achieved by using acetate ions. Under the latter condition, monodispersed Co particles of about 220-nm in diameter were produced. The Co particles were polycrystalline and their structure consisted of either fcc or fcc/hcp mixtures. The saturation magnetization (M_s) and coercivity (H_c) at room temperature ranged from 65 to 162 emu/g and 35 to 199 Oe, respectively. In presence of Pt ions, Cobalt nanoparticles as small as 25 nm were synthesized. Depending on synthesis conditions, metastable ϵ -Co and/or hcp-Co were stabilized at the nanosize level. The high coercivity-hcp phase was produced without need of any annealing. The M_s and

H_c of the Co particles synthesized in presence of Pt ions, varied from 53 to 77 emu/g and 222 to 535 Oe, respectively.

Key words.-Polyol, nanocrystalline metal particles, ε-Cobalt, monodispersed particles, solution chemistry, magnetic characterization.

INTRODUCTION

Magnetic nanoparticles are of great technological importance because of their use in magnetic recording media or production of permanent magnets. In the ideal case, the particles should be single domain, monodispersed and magnetically hard. On the other hand, the preparation of monodispersed magnetic particles will also permit a better understanding of the magnetic behavior as a function of the particle size.

Among various synthesis options, the chemical routes offer the possibility of a tailored design of materials at the molecular level coupled with the viability to control the particle size and size distribution. Moreover, a cost-effective scale-up for processing and production can also be expected. In the conventional polyol process¹, metallic powders can be prepared by making use of the reducing properties of liquid diols or polyalcohols.

These polyols act also as a solvent due to their high dielectric constant. Moreover, the polyol may also behave as a protecting medium for transition metal particles against oxidation. In the conventional approach, the reduction of transition metal ions and subsequent homogeneous nucleation towards micron-sized metallic particles take hours to occur even under boiling conditions of the polyol. Furthermore, there is little or no size control, particularly in the sub-micron size region.

Although the works of other groups suggested an improvement on the capability of the polyol route to produce not only submicron but also nanometric sized particles, the provided information did not consider a systematic discussion on the relationship between synthesis conditions, solution chemistry, phase stability and particle size of the products. In this paper we discuss the factors conducive to the enhancement of the formation rate of Co particles in polyol medium, achieved through a suitable selection of the solution chemistry and synthesis conditions, and how the control of these factors permitted the tailoring of particle size in the sub-micron and nanosize levels.

The suitable control of the mentioned parameters was also tightly related to the stability of Co phase, including the formation of, otherwise, metastable ε- and hcp-Co phases. The high-coercivity hcp-Co nanoparticles were produced in large amount and without necessity of post-synthesis annealing.

Experimental

Materials.- All reagents of chemical grade were used without any further purification. Ethylene glycol, C₂H₆O₂ (EG, boiling point 195°C) or trimethylene glycol, C₃H₈O₂ (TMEG, boiling point 214°C) were used as the solvent and reducing agents. Co(II)-acetate tetrahydrate salt was used as the cobalt source. When needed, Pt ions were added into the reacting solutions as hexachloroplatinate salt, H₂PtCl₆. Sodium hydroxide, and sodium acetate trihydrate were used as the source for hydroxyl and acetate ionic species, respectively.

Synthesis of nanocrystalline Cobalt particles.- Suitable amounts of sodium hydroxide and/or sodium acetate were dissolved in the cobalt solution in polyol (EG or TMEG) as described in our previous work¹. When needed, Pt-salt was dissolved into the Cobalt polyol solution. This solution was then heated-up at constant rate under a gentle mechanical stirring ('heating stage'). During this stage, the precipitation of a gel-like and non-magnetic solid was observed. Once the suspension reached the specific temperature, typically 200±5°C, it was refluxed for an additional time while maintaining the temperature constant. This further heating at boiling condition favored the progress of the following reactions: precipitation of the intermediate phase, dissolution of the intermediate, reduction of metal ions by polyol.

The time required for the formation of a strongly magnetic gray solid after the reactants reached the selected reaction temperature was defined as the 'reaction time'. Metal powder products were washed several times and stored in ethanol. The structure, morphology and magnetic properties of the products were analyzed by XRD, SEM, HRTEM and VSM techniques.

RESULTS

Effect of the OH-/Co mole ratio in starting solutions

The 'reaction time' required to get a complete reduction and precipitation of cobalt ions decreased for any increase of the OH-/Co mole ratio. The reaction time was reduced from 6.5 hours in the test without OH⁻ ions to 2 minutes for an OH-/Co ratio of 45. This systematic shortening in reaction time could be attributed to the speeding up of the slowest step ('rate controlling step') involved with the metal formation. According to related works²⁾, and considering that the reduction reaction itself should take place without any kinetic restriction, the dissolution of the intermediate could be considered as the rate-controlling step.

Therefore, the excess of hydroxyl ions would have increased the solubility of the intermediate, favoring a very quick generation of dissolved cobalt species that finally get reduced into metal. Moreover, analogue to aqueous systems, highly alkaline conditions would have promoted more reducing conditions favorable for cobalt formation. However, an extremely large excess of hydroxyl ions, e.g., OH-/Co mole ratio of 60, would have increased the solubility of cobalt particles.

The corresponding supernatant sampled right after the end of the reaction was dark blue, suggesting the presence of dissolved cobalt species.

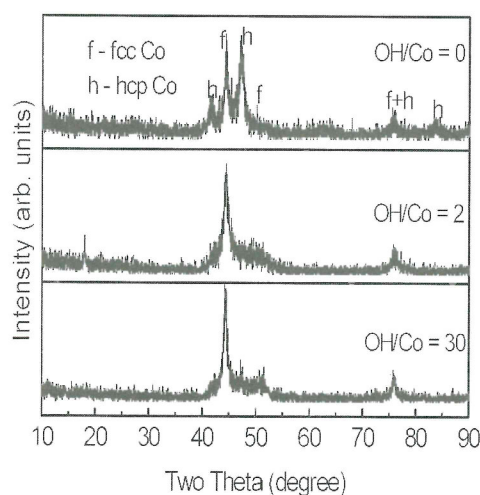


Fig. 1 XRD patterns of Co samples produced at various OH-/Co mole ratios.

The X-ray diffraction patterns of the solids produced at different OH-/Co mole ratios are shown in Figure 1.

With the exception of the test in absence of hydroxyl; i.e., OH-/Co=0, at which a mixture of fcc- and hcp-Co was detected, all other solids mainly consisted of fcc-Co phase.

Furthermore, the average crystallite size estimated from the XRD pattern for the fcc-Co was around 13-20 nm in all cases.

Although the stable structure at room temperature for bulk cobalt is the hcp phase, and the fcc structure being stable only at temperatures above 420°C, it is well documented that fcc-Co will become the most stable phase for Co nanoparticles^{3), 4)}.

This behavior is explained, at least in part, by considering that for very fine crystallites the variation in the surface free energy would be large enough to reduce the driving force of the allotropic transformation from fcc to hcp.

However, more recent works on synthesis of Co nanoparticles by different routes^{5), 6)}, indicate the possibility to produce nanocrystals (less than 20nm in diameter) consisting of hcp-, ϵ -Co or amorphous Co phases.

A common point in the considered options was the simultaneous control of the particle size and the reaction kinetics. XRD analyses also suggest that besides the probable influence of crystallite size on the phase stability condition, the presence of OH⁻ ions could also be related to the inhibition of the development of hcp planes through some preferential adsorption of hydroxyl ions.

The affinity of metal sites in the solid for free hydroxyl ions is thermodynamically feasible under our experimental conditions.

Furthermore, this adsorption phenomenon can also be involved with the monodispersity of the particle size (negatively charged particle surfaces) as shown in Figure 2 for samples produced at various OH-/Co mole ratios.

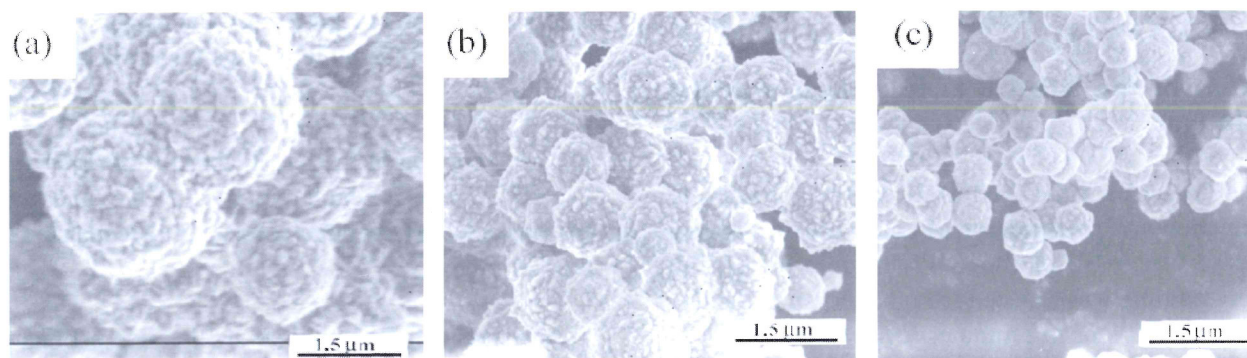


Fig.2 SEM micrographs of the cobalt particles produced at OH/Co mole ratios of (a)0, (b)10, and (c)30.

The above commented shortening in the reaction time went in parallel with the decrease in the size of spherical particles. Moreover, the particles were highly monodispersed, especially in the OH/Co range from 10 to 30 where the size of the polycrystalline aggregates varied from a few microns to 0.5 μm.

The decrease in particle size and the improved monodispersity for the rise in the amount of hydroxyl ions should be related to the kinetic enhancement previously commented; faster and larger availability of Co species avid for their reduction might have promoted higher nucleation rates. Under this condition, a major fraction of cobalt ions was consumed for the nuclei formation leaving only a minor part for further growth by incorporation into the already existing particles.

The previous interpretation should be considered together with the effect of adsorbed OH⁻ ions that would have promoted stronger electrostatic repulsive forces between metal surfaces protecting them against excessive aggregation.

Once stable crystallites are formed, further aggregation among them would continue until an adsorption-assisted equilibrium is reached. The decreasing trend in particle size was observed even at OH/Co = 45, but now the particles consisted of a mixture of small individuals (below 150-nm) and lumps of bigger sizes. A closer observation of the SEM pictures suggested that those lumps consisted of the smaller spherical individuals, which may have coalesced due to the high surface free energy of the smaller particles that would have overcome the repulsive interaction energy between surfaces provided by adsorbed hydroxyl ions.

Effect of the acetate/Co mole ratio

On the consideration that the adsorbed hydroxyl ions would have protected the final particles from excessive aggregation, the effectiveness of other adsorbing entities was investigated. The ideal species would be the one with a strong affinity for surface metal atoms and minimum or null interference with the metal forming-reactions.

Among, systematically evaluated, citrate, phosphate, and acetate species, acetate ion CH₃COOH⁻, was found to be the most effective. The coexistence of acetate and hydroxyl ions in solution favored an even further shortening of the reaction time and tailoring of the particle size. When the OH/Co mole ratio was 45 and the total acetate/Co mole ratio 20, a reaction time as short as 20 seconds was enough to form the metal. The XRD analyses performed on the corresponding solids exhibited the predominance of fcc-Co peaks.

The estimated crystallite size, varied in the range from 15 to 20 nm. Figure 3 shows the SEM pictures for OH/Co 45 and acetate/Co = 2 (acetate in the cobalt salt), 20 and 30. The corresponding reaction times were 2 minutes, 20 seconds and 9 minutes. The pictures evidenced the drastic change in the morphology of the solids; the formation of agglomerates was suppressed in presence of excess of acetate ions. Moreover, the variation in the acetate/Co ratio from 6 to 20 permitted the formation of monosized particles as small as 220-nm in diameter.

As in the case of OH⁻ ions, adsorbed acetate species would have contributed to prevent further particle growth and aggregation by reinforcing the

electrostatic repulsion interactions. In turn, it was also found that larger values of the acetate/Co molar ratio (Figure 3-c) did not represent any further improvement on particle size control, on the contrary, the reaction time was prolonged and the particle size became larger. This suggests the existence of a critical acetate/cobalt ratio above which no enhancement of the surface charge takes place and only lead to a rise in ionic strength. The higher ionic

strengths would cause the compaction of the electric double layer surrounding the forming particles, favoring their coalescence and final aggregation in a similar way as observed in the coagulation of colloidal particles in aqueous solutions. A similar trend in particle aggregation was observed when the cobalt particles were formed in presence of acetate ions alone.

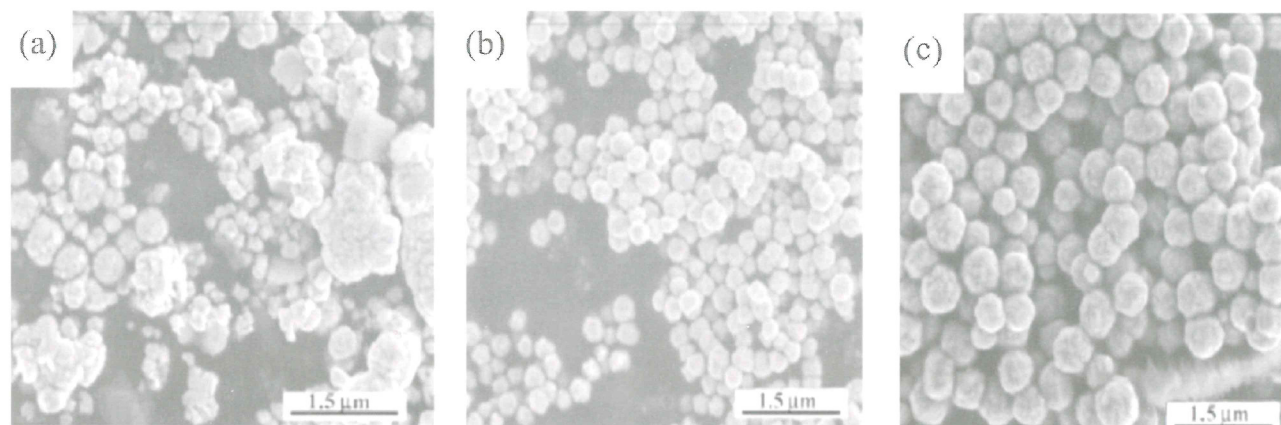


Fig. 3 SEM micrographs of the solids produced at OH/Co 45 and total acetate/Co mole ratios of (a) 2, (b) 20, and (c) 30.

Of synthesis temperature

Based on the above trends, the possibility to decrease the synthesis temperature was also investigated. For a 0.01M Co solution, the OH/Co and acetate/Co mole ratios were fixed at 4,5 and 20, respectively. The corresponding reaction times were 45 seconds, 32 minutes and 4.5 hours when the reaction temperatures were 200, 180 and 160°C. As confirmed by XRD analyses, the synthesis of cobalt was accomplished even at a temperature as low as 160°C, an impossible situation in absence of the coexisting ions. Nevertheless, the metal synthesis at low temperatures was achieved at expenses of prolonged reaction times and monodispersity. The trends observed here were in line with our findings discussed in section 3.1.

Effect of the relative proportions of Co(II) ions and ethylene glycol

The concentration of the cobalt salt in polyol solution was varied from 0,1M to 0,0025M. In all cases, the particles produced were in the micron-size range and strongly aggregated. The most remarkable

observation came from the XRD analyses, shown in Figure 4.

The stability of the hcp phase was enhanced for more diluted cobalt concentration; i.e., larger availability of EG.

Although the precise reasons involved with this behavior are not well elucidated yet, we believe that larger proportions of EG would have favored the reduction of Co and/or some specific adsorption of polyol molecules onto specific planes of the cobalt structure would have inhibited the development of the fcc planes.

Magnetic characterization of Co particles produced in EG.

The saturation magnetization M_s , and coercivity H_c , for the powder produced at OH/Co=0 were 135 emu/g and 161 Oe, respectively. In turn, M_s and H_c for the solids obtained in presence of OH⁻ ions (OH/Co>0) were between 140-150 emu/g and 35-98 Oe, respectively.

The comparative enhancement in the H_c for $\text{OH}/\text{Co}=0$ was attributed to the development of hcp-Co phase as evidenced by XRD analyses. The average M_s of 145 emu/g for $\text{OH}/\text{Co}>0$ could be attributed to the predominance of the fcc-Co phase. The saturation magnetization and coercivity of the metal particles produced in presence of hydroxyl and acetate ions ranged from 90 to 105 emu/g and 125-150 Oe, respectively.

These values, which represent a drop in M_s and a rise in H_c when they are compared with the results for the solids produced in presence of OH- ions alone, could be attributed to the development of dead layers on the surface of metal particles (Co-acetate like deposit) or surface oxidation. In turn, the magnetic properties of the metal produced for different relative proportions of Co and EG showed an antagonistic trend between M_s and H_c , the magnetization dropped from 162 to 138 emu/g while the coercivity rose from 72 to 199 Oe.

These trends corresponded to a variation in Co concentration from 0.0025M to 0.1M. The rising trend in coercivity was expected from the rising predominance of the hcp phase.

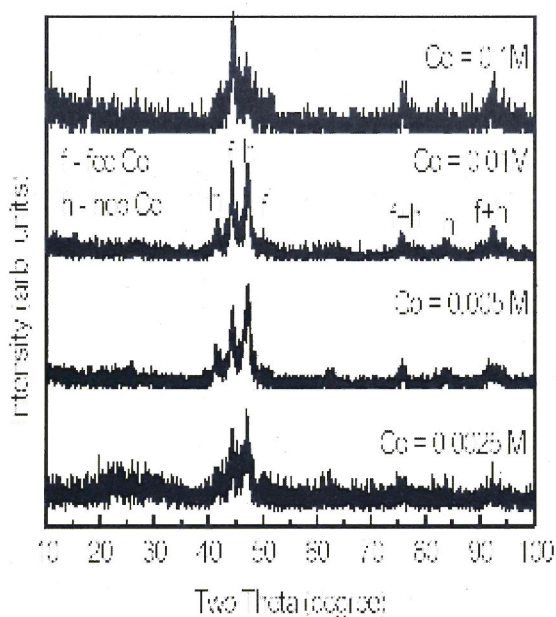


Fig. 4 XRD patterns of the solids produced at different initial concentrations of Co ions.

Synthesis of high coercivity hcp-Cobalt nanoparticles.

Based on the above mentioned experimental evidence, the establishment of new phase stability conditions for Co nanoparticles should be achieved through suitable size control at the nanosize level coupled with an extremely fast reaction rate to stabilize the, otherwise, metastable phases. On the other hand, the use of nucleating agents to enhance the formation rate of solid phases from solution ('seeding') is a well-known approach. Accordingly platinum ions, which are easily reduced in polyol medium even at temperatures below 200°C, were selected as the source of nucleating agents. Suitable Pt/Co mole ratios and the use of trimethylene glycol (TMEG) instead of EG, accelerated the metal formation even further and promoted the formation of particles as small as 25 nm (Figure 5-a). The combined use of TMEG, apparently with a stronger reduction capability than EG, and Pt ions lead to the formation of a ϵ -hcp-Co mixture or, depending on the Co/TMEG ratio, hcp-Co particles (Figure 5-b).

The hcp-Co particles averaged 25 nm in diameter and were produced directly without the need for any annealing. The M_s and H_c of the Co particles synthesized in presence of Pt ions and at different Co concentrations as given in Fig. 2, varied from 53 to 77 emu/g and 222 to 535 Oe, respectively.

CONCLUDING REMARKS

The suitable combination of hydroxyl and acetate ions favored the formation of monosized cobalt particles in the size range from the micron and sub-micron levels (220 nm). The enhancement in the reaction kinetic through the addition of those ions permitted the decrease in the synthesis temperature down to 160°C, but only at expenses of the monodispersity obtained at 200°C. In turn, a direct dependence of the stability of the hcp nanophase with the initial concentration of Co ions in ethylene glycol as well as trimethylene glycol was also found.

The predominance of the hcp phase at more diluted Co concentration could be due to the high polyol/Co(II) ratio, which would have enhanced the reducing power and/or promoted adsorption of polyol species onto specific planes of the metal surface inhibiting the development of the fcc planes.

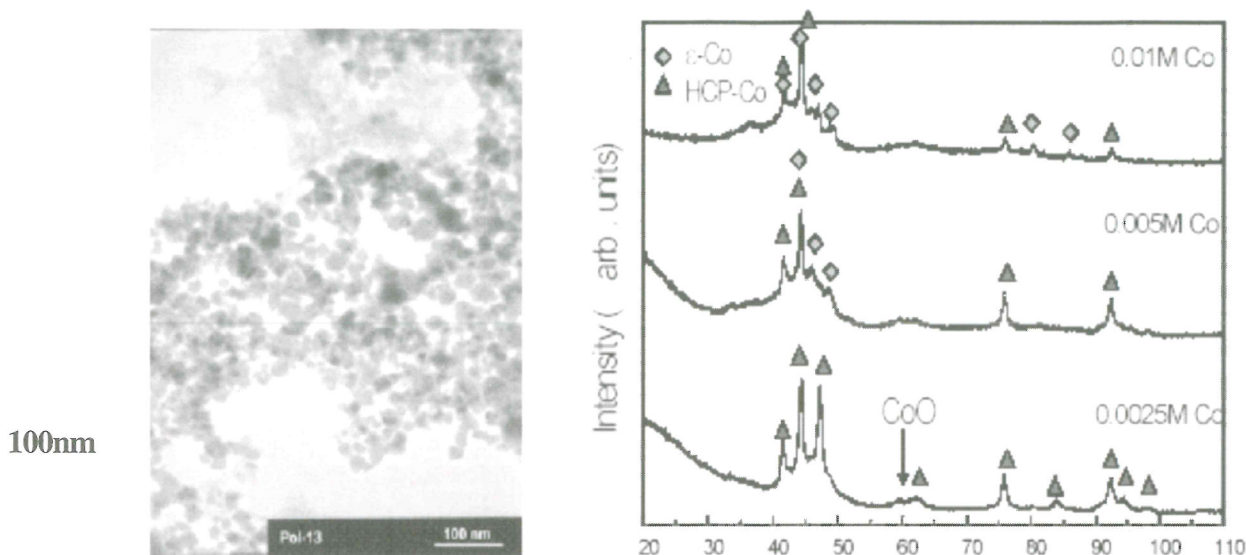


Fig. 5 (a) 25-nm Co particles produced at OH/Pt/Co mole ratio = 30/0.06/1 in TMEG, (b) XRD of cobalt nanoparticles produced at different Co(II) concentrations in TMEG.

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