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# One-dimensional assemblies of silica-coated cobalt nanoparticles: Magnetic pearl necklaces

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## Abstract

Silica-coated cobalt nanoparticles were found to organize into chains when driven by a weak external magnetic field. Strong dipole–dipole magnetic interactions are believed to be the driving force of the self-organization once the cobalt nanoparticles undergo the superparamagnetic to ferromagnetic (SP–FM) transition, as increasing their size during the synthesis process. The method, although simple, produces structures resembling pearl necklace-like structures, comparable to one-dimensional species obtained in more laborious processes. Molecular dynamic simulations taking magnetic dipolar forces into account reproduce the observed self-assembled structures. The nanoscale engineering of this type of colloids is expected to extend the spectrum of magnetic effects and functionalities.

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**Keywords:** One-dimensional assemblies; Colloids; Molecular dynamic simulations

## 1. Introduction

One-dimensional nanocolloids, such as nanorods and nanowires have received considerable attention over the last years owing to their high potential for specialized optical and magnetic applications [1,2]. The high sensitivity of nanorods and nanowires to surface conditions is an advantage for instance, for sensor devices, but the same property can cause their instability and loss of desired properties. These considerations lead to the necessity of insulated one-dimensional nanoscale colloids with environmentally stable polymerized coatings. It was demonstrated that encapsulation of semiconductor, metal and/or magnetic nanoparticles [3] and rods [4] with silica in the form of amorphous inorganic polymer prevented their aggregation in a liquid and improved their chemical stability.

In a wide range of applications [5,6], it is of primary importance to control the surface properties of the nanoparticles. Moreover, magnetic nano-assemblies require a high degree of understanding of the interactions between neighboring nanoparticles and the magnetism of the individual entities. Control of the distance between particles, their size and magnetic properties allows tailoring the magnetic properties of the whole structure. Herein, we report the first synthesis of unique silica-coated chains of 32 nm cobalt nanoparticles resembling nanoscale pearl necklaces in colloidal suspension, which may be used as a first step in the processing of novel macroscopic magnetic materials. Additionally, a quantitative model based on molecular dynamics (MD) simulation is presented confirming the importance of magnetic dipolar interactions for the formation process.

Kobayashi et al. [3h] reported the synthesis of silica-coated cobalt nanoparticles which permits the preparation of Co cores of various sizes in aqueous solution and their coating with well-defined silica shells. Varying the process led us to produce silica-coated chains of 32 nm cobalt nanoparticles.

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## 2. Experimental section

The synthesis of these silica-coated chains of cobalt nanoparticles was performed as follows: 0.1 mL (0.4 M) of cobalt chloride hexahydrate (Fluka) in H<sub>2</sub>O was added to an aqueous solution (100 mL) of NaBH<sub>4</sub> (4.4 mM) (Riedel de Haen) and citric acid monohydrate (Riedel de Haen) ( $2 \times 10^{-6}$  M) under magnetic stirring. Previously deaerated Milli-Q water (18 M $\Omega$ cm) was used and nitrogen was bubbled during the whole process. Immediately after cobalt reduction, 400 mL of an ethanolic solution containing 15  $\mu$ L of APS (3-aminopropyl trimethoxysilane) (Aldrich) and 15  $\mu$ L of TEOS (tetraethoxysilane) (Aldrich) was added. 15 minutes later, the solution was centrifuged and the precipitate redispersed in ethanol (40 mL).

## 3. Results and discussion

Fig. 1 shows transmission electron microscopy (TEM) images of pearl necklace-like structures, formed by silica-coated cobalt nanoparticles with an average diameter of  $32 \pm 5$  nm and a silica shell thickness of 3–5 nm. The images were taken after evaporating a drop of the suspension directly after synthesis. Our experimental process, which presents slight differences compared to the previous one, leads to a bigger average size of cobalt nanoparticles ( $>20$  nm) and offers the deposition of thinner shells of silica (2–3 nm) since the hydrolysis and condensation of a smaller amount of TEOS are allowed to take place in a shorter period of time.

The formation of chains of cobalt nanoparticles is attributed to the magnetic dipole–dipole interaction between neighboring particles as discussed in more detail below. The reduction of Co<sup>2+</sup> ions by NaBH<sub>4</sub> produces clusters of metallic cobalt, poorly stabilized by the citrate ions present in the solution, which become aggregated and form nanoparticles. When the volume of the nanoparticles further increases, one has to consider two different size regimes which are separated by a critical volume, i.e. critical diameter  $D_C$  which characterizes a blocking temperature above which the magnetization is fixed to the geometry of the particles and below which the

magnetization can freely rotate independent of the motion or rotation of the particle itself. One could loosely term this a transition from a superparamagnetic to ferromagnetic blocked (SP–FM) state. In the first case, the magnetization is oriented along the easy magnetic anisotropy axis, and in the later case, the time average of the magnetization of the particle is zero. This transition depends in a correlated way on the volume, magnetic anisotropy and the temperature of the particles. During the synthesis, the temperature is fixed and the magnetic volume of the Co particles increases. In the experiment we find that at approximately a critical diameter of 20–25 nm the formation of chains sets in. This process, as outlined schematically in Fig. 2, is possible only when the magnetization of the particle does not fluctuate during the time of magnetic interaction in the suspension. Due to the anisotropic nature of the dipolar interaction the formation of chains is favored, since the north and south poles of the dipolar nanomagnets attract each other while particles coming close to each other side by side with the magnetization direction parallel will repel each other thus favoring the formation of “pearl necklaces”.

For small enough spheres like the ones observed in this work, the formation of magnetic domains within the particle is energetically unfavorable. For hcp Co particles, for example, a critical diameter of approximately 15 nm has been calculated (see for example [7]), which increases when small magnetic fields are applied. This has been observed also in previous work on micron-sized core-shell colloids [8,9]. During the synthesis the suspension is stirred by a magnetic rod and a small magnetic field is present favoring the formation of chains. As a result of the dipolar interactions, the larger cobalt clusters form chains and sometimes closed loops in order to minimize the magnetostatic energy. The observed spontaneous self-assembly of the nanoparticles yielding unique structures such as chains resembling pearl necklaces and loops (Fig. 3) proves the importance of dipolar interactions even in wet-chemical synthesis.

Fig. 3 shows TEM images of closed loops and chains of silica-coated cobalt nanoparticles suggesting that the SP–FM transition took place at room temperature for  $32 \pm 5$  nm average diameter cobalt particles. The deposition

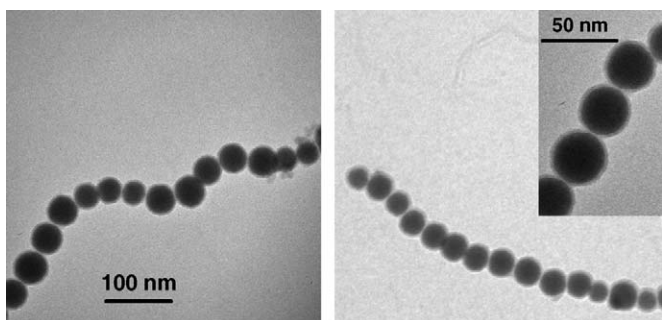


Fig. 1. TEM images of silica-coated cobalt nanoparticles self-assembled into one-dimensional-structures.

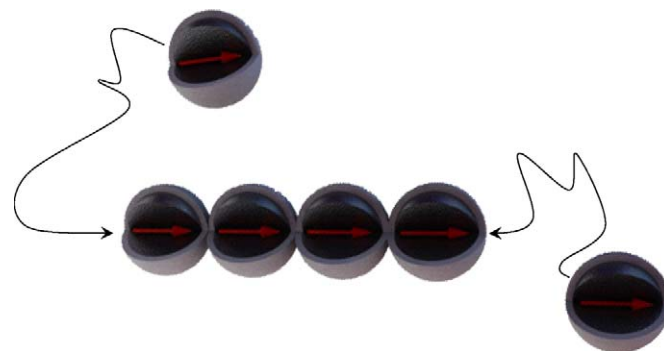


Fig. 2. Scheme of formation of chains of silica-coated cobalt nanoparticles.

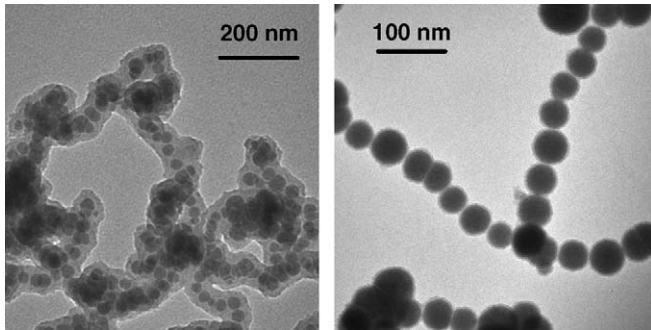


Fig. 3. Loops and chains of cobalt nanoparticles with different thickness of the outer silica shell.

of the silica shells avoids agglomeration and protects them (but not fully) against oxidation [3k]. Nevertheless, a further deposition of silica tends to form not only loops of nanoparticles but more fractal-like structures (Fig. 3, left). Bigger aggregates of cobalt nanoparticles were also found in the samples, which can easily be related to the poor citrate stabilization during the synthesis and therefore, a further optimization of the experimental method is needed toward a completed magnetic characterization of the silica-coated cobalt nanoparticles and their magnetic interactions leading to one-dimensional-structures.

To obtain a quantitative understanding of the chain formation process due to magnetic dipolar forces, quantitative molecular dynamic simulations taking realistic magnetic parameters into account were performed. The simulations were completed for a model of magnetic hard spheres with dipolar interaction

$$U_{ij} = \frac{\mu_0}{4\pi r_{ij}^3} (\vec{\mu}_i \cdot \vec{\mu}_j - 3(\vec{\mu}_i \cdot \hat{r}_{ij})(\hat{r}_{ij} \cdot \vec{\mu}_j)) + U_{ij}^{(HS)}$$

between two particles  $i$  and  $j$  at distance  $r_{ij}$ , where  $\vec{\mu}_i$  denotes the magnetic moment of particle  $i$ , and a hard sphere potential  $U_{ij}^{(HS)}$ . A detailed description of this work will be published elsewhere [10]. The dipolar binding energy  $E^{(0)}$  of two spherical ferromagnetic particles with magnetic moment density  $\mu$ , volume  $V$  and non-magnetic shell to fully magnetized core radius ratio  $a$  is given by  $E^{(0)} = \mu_0 \mu^2 V / (12a^3)$ . Assuming a fully magnetically saturated core detailed MD simulations [10] show that the chain building transition takes place at  $k_B T_c / E^{(0)} \approx 0.056$ , from which we get the critical diameter  $D_c / a = 8.6$  nm at  $T_c = 300$  K for spheres with the magnetic moment ( $1.7 \mu_B$ ) of Co. Using  $a \approx 1.1$ , which corresponds to the experimentally observed average ratio of the diamagnetic silica shell to the ferromagnetic Co core, we calculate  $D_c = 11.4$  nm. Above this theoretical diameter the particles will form chains at room temperature which are stable against thermal excitations. It is not surprising that the calculated critical diameter is smaller than the one experimentally observed, since turbulence in the suspension and the Co silicides and Co oxides present at the Co/SiO<sub>x</sub> interface which reduce the magnetization of the core are

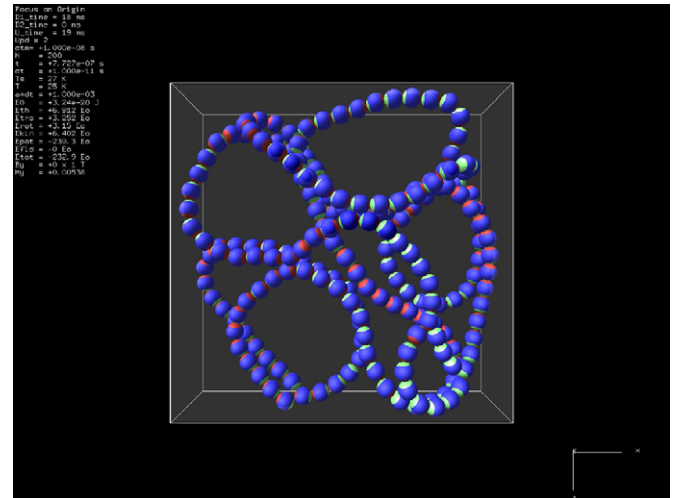


Fig. 4. Molecular dynamics simulation for the formation of Co pearl necklaces finding the same chain and loop-like structures as observed in the experiment.

not accounted for in the simulation. In the case of the experimentally found reduced magnetization, a larger critical volume is required to obtain the necessary magnetic interaction strength  $E^{(0)}$  for stable chains at room temperature. The configurations found in our simulations [10] (Fig. 4) are very similar to the experimental findings.

#### 4. Conclusion

In summary, the synthesis of one-dimensional nano chains and loops through dipole–dipole interactions between silica-coated cobalt nanoparticles is reported. The method which allows the stabilization of cobalt nanoparticles in water solution by a surrounding thin layer of silica was modified, producing chains of nanoparticles.

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