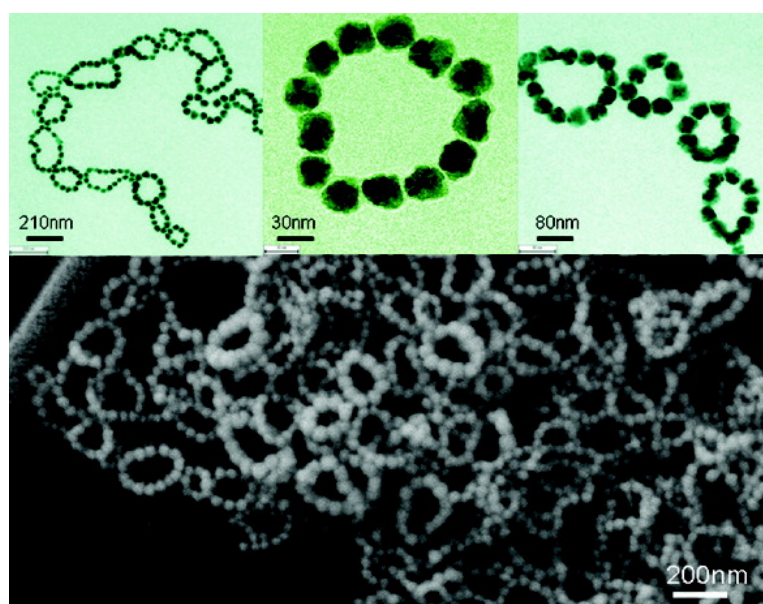


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High Yield Synthesis of Bracelet-like Hydrophilic Ni–Co Magnetic Alloy Flux-Closure Nanorings

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The synthesis of nanorings has drawn much attention in recent years because these unique, closed, one-dimensional (1D) nanostructures have intricate formation mechanisms and properties as well as special applications.¹ Various annular nanostructures such as Co,² Ag,³ Au,⁴ ZnO,^{1a} CuO,⁵ TiO₂,⁶ SnO₂,⁷ α -Fe₂O₃,⁸ Cd(OH)₂,⁹ CdS,¹⁰ PbSe,¹¹ and Ag₂V₄O₁₁¹² have been prepared via different routes. Flux-closure nanorings, a type of uniquely assembled nanoscale rings,¹³ were usually discovered in the self-assembly process of some ferromagnetic nanoparticles when cast and dried onto carbon-coated transmission electron microscope (TEM) grids.¹⁴ Owing to chiral bistable magnetic flux-closure states, this kind of ring has been an appealing candidate for ultradense information storage architectures.^{14d} However, this kind of self-assembled nanoring has poor stability as a result of the weak noncovalent interaction and strong substrate dependence. Thus, these rings lack free-standing capability, which could limit their further applications. Recently, synthesis, properties, and potential applications of multi-component magnetic nanoparticles have attracted much attention.¹⁵

Herein, we report a simple solvothermal method to synthesize single-walled flux-closure Ni–Co magnetic alloy nanorings in high yield. This kind of nanoring was directly fabricated in a reaction solution. In addition, this kind of nanoring is easier to manipulate and transfer without being disassociated, which is different from those reported previously.¹⁴

The Ni–Co nanorings were solvothermally prepared by a synchronous reduction of cobalt(II) acetylacetonate (Co(acac)₂) and nickel(II) acetylacetonate (Ni(acac)₂) at 240 °C for 3 h in a Teflon lined stainless steel autoclave with a capacity of 22 mL using triethylene glycol (TREG) as solvent in the presence of poly(vinylpyrrolidone) (PVP) (see Supporting Information). The yield can reach up to 80 wt%.

The X-ray diffraction pattern of the obtained samples is very similar to those of either Co or Ni with a face-centered structure (JCPDS 15-0806 and 01-1260). A slight variation in the peak position can be observed, and all the peak positions lie between the peak positions of pure Ni and pure Co (Figure S1). Energy dispersive X-ray spectrum (EDX) analysis performed on different selected areas containing many Ni–Co nanoparticles shows that the structures contained both Ni and Co with a mean molar ratio of 79:21 (Figure S2). The X-ray photoelectron spectrum (XPS) also shows the presence of Ni and Co elements (Figure S3). High-resolution transmission electron microscope (HRTEM) images show that a typical nanoparticle is mainly of the same lattice spacings with a lattice spacing of 1.02 Å, corresponding to the interplanar distance of {222} planes of *fcc* Ni or Co (Figure S4). These results indicate the formation of an alloy phase of nickel and cobalt.

The TEM image in Figure 1 shows that the particles are mainly bracelet-like nanorings and their interesting assemblies such as linearly linked rings, looped rings, and enclosed rings, each of which

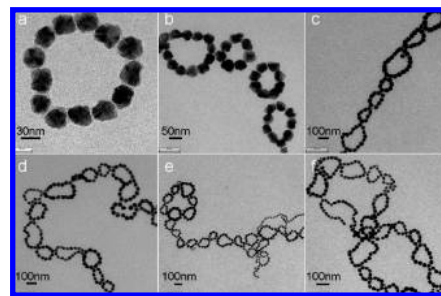


Figure 1. (a–f) TEM images of the bracelet-like Ni₇Co₃ nanorings with different assembled nanostructures.

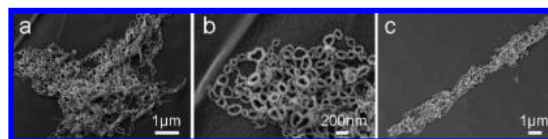


Figure 2. (a and b) SEM images of the Ni₇Co₃ bracelet-like nanorings with different magnification. (c) Alignment of the nanorings after applying a magnetic field.

is composed of 30 nm Ni–Co nanoparticles in varying numbers. A typical single ring was presented in Figure 1a, and these nanoparticles were surrounded and linked by a polymer with each other. The SEM images in Figure 2 show that a majority of nanostructures (~70%) are found in the form of bracelet-like nanorings. Besides those lying on the substrate, more rings lie on a higher layer and do not contact the substrate. When cast on the copper slice, even under an external magnetic field, these nanorings were still maintained and clearly appeared in a one-dimensional arrangement (Figure 2c). Apparently, the formation of these rings is not substrate-dependent. However, when a single-side magnet induced external magnetic field was introduced in the process of chemical synthesis, these nanoparticles will not assemble into ringlike nanostructures but form long nanochains instead (Figure S5). In addition, when the external magnetic field was changed into two-side symmetrical magnets (north pole and south pole) to induce a magnetic field, the particles are mainly long and straight microwires composed of many nanoparticles dozens of nanometers in size (Figure S6).

As-synthesized alloy nanorings in solution can be further coated by phenol formaldehyde resin in aqueous solution using a method we used to prepare silver@phenol formaldehyde resin core–shell particles.¹⁶ As expected, Ni–Co@phenol formaldehyde resin nanorings can also be produced, implying that this kind of nanoring can be further encapsulated with fluorescence matter and functionalized in a solution (Figure S7). These results indicate that these nanorings are formed directly in the reaction solution due to the

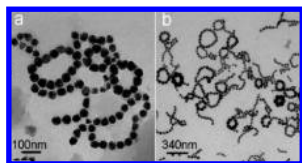
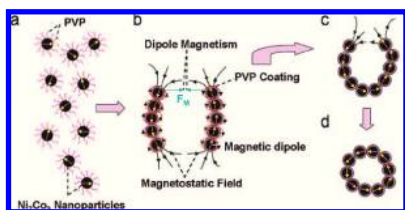


Figure 3. (a and b) TEM images of the Ni₇Co₃ assemblies with transitional morphologies which contain nanorings and dispersed short nanochains.

Scheme 1^a



^a (a and b) PVP-coated Ni₇Co₃ nanoparticles connect together by dipole-directed self-assembly and form a number of short nanochains stabilized by PVP. (c and d) Two short nanochains with opposite magnetostatic direction joining each other on two ends by dipole magnetism, consequently forming high-radian chains or bracelet-like nanorings. To further decrease the magnetostatic energy and spontaneous magnetostatic field, nanorings will be the preferred form.

dipole-directed self-assembly and the stabilization of PVP. Furthermore, these rings are still stable enough to prevent being disassembled even under drastic vibration, boiling solution, or in the presence of an applied magnetic field.

Figure 3 shows TEM images of observed Ni₇Co₃ assemblies with transitional morphologies. Some short and straight nanochains or curved nanochains and approximately closed ringy nanostructures can be found also. This provides some clues for the formation mechanism as proposed in Scheme 1. A number of short nanochains were first formed under the drive of magnetic dipole interaction¹⁷ and the stabilization of PVP (Scheme 1). For these stable short nanochains in the solution, the magnetostatic direction is disordered, but it is ordered for those nanoparticles which act as building units for a single nanochain. Two or more short nanochains with different magnetostatic directions will likely link together by dipole attraction to form high-radian nanochains or nanorings (Scheme 1b,c,d), to decrease the magnetostatic energy and the field outside of the rings.^{14d} Due to a lower energy state, nanorings will be the preferential form. These formed nanorings can be further stabilized by PVP and become integrated units. In solution, some nanorings with the same magnetostatic direction, clockwise or counter-clockwise, taken for chirality,^{14d} are easily linked together by a second magnetostatic field induced self-assembly, either to form long chains made up of nanorings or to form bigger rings composed of nanorings (Figure 1c–f).

Both PVP and magnetic dipole interaction play important roles in the formation of nanorings and their assemblies. The intensity of the magnetic dipole interaction can be regulated by adjusting the composition of alloy. A Ni–Co alloy with high nickel content has a tendency to form bracelet-like nanorings in higher yield (Figures 1 and S8), implying that the larger susceptibility is more suitable for the formation of nanorings. The influence of PVP concentration in the formation of nanorings was also studied. It is found that fabrication of nanorings at a PVP concentration lower than 0.1 g·mL⁻¹ is unfavorable.

As synthesized Ni₇Co₃ alloy nanoparticles show no hysteresis loop at 300 K and show a fast response to a foreign magnet and can be rapidly separated from the solution (see Figures S9, S10).

MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) cytotoxicity assay results show that the alloy nanoparticles are of good biocompatibility (Figure S11). As the concentration of the alloy Ni₇Co₃ nanoparticles increases from 0 to 1.25 mg·mL⁻¹, the signal intensity of the magnetic resonance (MR) image declines, indicating that this kind of alloy nanoparticle has the potential to be used as a T₂ magnetic resonance imaging (MRI) contrast agent (Figure S12).

In summary, we have reported here a straightforward solution route to synthesize stable bracelet-like hydrophilic Ni–Co magnetic alloy flux-closure nanorings in high yield. High nickel content in the alloy and high PVP concentration favor the fabrication of nanorings. In addition, the present synthetic method and growth mechanism might be extended to other ferromagnetic substances to direct large-scale synthesis of similar flux-closure nanorings and ring-based complex nanostructures, which may bring new nontrivial physical properties.

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Supporting Information Available: Characterization, XRD, EDX, XPS, HRTEM, TEM, SEM, M–H curve, MTT cytotoxicity assay, and T₂-weighted MRI image. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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