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Fabrication of cobalt nanowires from mixture of 1-ethyl-3-methylimidazolium chloride ionic liquid and ethylene glycol using porous anodic alumina template

Peixia Yang[a,b,*], Maozhong An[b], Caina Su[b], Fuping Wang[a]

[a] *Research Station on Material Science and Engineering for Postdoctoral Fellows, Harbin Institute of Technology, Harbin 150001, China*
[b] *Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China*

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ABSTRACT

Porous anodic alumina template is synthesized by electrochemical anodization of aluminum and used to grow cobalt nanowires. The cobalt nanowires produced by direct current electrodeposition are characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction and physical property measurement system. Test results indicate that the average diameter of cobalt nanowires is about 45 nm, which is generally the same as the pore diameter of porous anodic alumina template, and the cobalt nanowires electrodeposited from mixture of 1-ethyl-3-methylimidazolium chloride ionic liquid and ethylene glycol have a smoother surface and better magnetic properties than cobalt nanowires electrodeposited from aqueous solution, and they show a better squareness. Therefore it can be concluded that the cobalt nanowires electrodeposited from mixture of 1-ethyl-3-methylimidazolium chloride ionic liquid and ethylene glycol using porous anodic alumina template can be used as a perpendicular magnetic recording film.

1. Introduction

One of the traditional methods used to fabricate nanowires and nanotubes is based on electrodeposition of various materials in porous anodic alumina (PAA) template [1–4]. PAA template is now a key material for fabrication of devices on nanoscale, such as ultrahigh-density magnetic recording devices, and electronic and optoelectronic devices [5–8].

It was reported in recent years that different magnetic nanowires have been fabricated using PAA template from aqueous solution by electrodeposition [9–12]. Hydrogen evolution is an issue, when metals are electrodeposited from aqueous solution. It is difficult to discharge hydrogen bubbles which are held up inside nanopores. The presence of these hydrogen bubbles has its adverse effect on the uniformity and the performance of nanomaterial. It is a new development trend in recent years to use room temperature ionic liquids for electrodeposition of various metals. Ionic liquid can be conveniently referred to as a compound composed entirely of ions, it has the merits of organic electrolytes and high-temperature molten salts, such as wide working temperature range, good electrical conductivity, wide electrochemical windows, and no steam press [13]. To sum up, ionic liquid is a promising electrolyte for electrodeposition of various metals. Ionic liquid is normally an aprotic medium, and so, it does not have the problem of hydrogen evolution, which frequently occurs in aqueous solutions. Cobalt has become very attractive for its special magnetic properties. It was reported that metal cobalt coating has been electrodeposited from ionic liquids. Carlin et al. [14] found that the electrochemical reduction of cobalt(II) in 1.5:1.0 $AlCl_3$:EMIC (1-ethyl-3-methylimidazolium chloride) room temperature ionic liquid leads to cobalt metal at potentials positive of +0.4 V and to $CoAl_x$ alloys at potentials negative of +0.4 V. Chen and Sun [15] reported that the electrodeposition of cobalt and zinc–cobalt alloys on the nickel electrode was conducted 40.0–60.0 mole percent (mol%) $ZnCl_2$–EMIC containing cobalt chloride at 80 °C.

It was reported that Kazeminezhad et al. [16] recently fabricated silver nanowires using a commercial nuclear track-etched polycarbonate template from 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) ionic liquid. However, the average diameter of Ag nanowires they produced was much larger than the nominal pore diameter of the template. To the best of our knowledge, not much work has been done on the electrodeposition of magnetic nanowires using PAA template from ionic liquids. So we synthesized PAA template by electrochemical anodization of aluminum and used PAA template to grow Co nanowires. The Co nanowires were fabricated from mixture of 1-ethyl-3-methylimidazolium chloride ionic liquid and ethylene glycol and

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* Corresponding author at: Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China. Tel.: +86 451 86413721; fax: +86 451 86415527.
E-mail address: yangpeixia@hit.edu.cn (P. Yang).

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from aqueous solution by direct current (dc) electrodeposition, respectively, and they were characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction and physical property measurement system. Test results indicate that the average diameter of Co nanowires is about 45 nm, which is generally the same as the pores diameter of PAA template, and the Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol have a smoother surface and better magnetic properties than the Co nanowires electrodeposited from aqueous solution, and they show a better squareness. Therefore it can be concluded that cobalt nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol using PAA template could be used as a perpendicular magnetic recording film.

2. Experimental

2.1. Instruments

The surface and cross-sectional morphology of PAA template and cobalt nanowires were characterized by field emission scanning electron microscope (FE-SEM, Hitachi S4700). Co nanowires were characterized by transmission electron microscopy (TEM, JEM200CX) and selected area electron diffraction (SAED). X-ray diffraction patterns were recorded using a D/Max-3B X-ray diffractometer (Rigaku). The magnetic properties of Co nanowires at room temperature were determined using a physical property measurement system (PPMS, Quantum Design).

2.2. Preparation of porous anodic alumina template

Aluminum sheets (thickness: 0.5 mm; purity: >99.99%) were obtained from Joinworld Co., Ltd. (Xinjiang, China). PAA template was synthesized using a two-step anodization technique described in Ref. [17]. The first step anodization and the second step anodization were performed in 1:1 sulfuric/oxalic acid mixture at 26 V and 5 °C for 3 h each. After the first step anodization, the formed alumina was etched off in aqueous solution containing 1.8% CrO_3 (wt%) and 6% H_3PO_4 (wt%) at 60 °C for 2 h. After the second anodization, the remaining aluminum substrate was removed by soaking in a $CuCl_2$-based solution (100 ml of HCl (38%) + 100 ml of H_2O + 3.4 g of $CuCl_2{\cdot}H_2O$) at room temperature for about 10 min. The perforated porous alumina template was prepared by removing the bottom part (barrier layer) of the template in 5 wt% H_3PO_4 at 35 °C. A platinum layer of ~100-nm thick was sputtered on one side of PAA template, which served as the working electrode in the subsequent metal electrodeposition process.

2.3. Preparation of cobalt nanowires from mixture of EMIC ionic liquid and ethylene glycol

The platinum layer on one side of PAA template and the cobalt sheet with a purity of 99.99% were used as the cathode and the anode, respectively. Co nanowires were fabricated by dc electrodeposition at 80 °C for 1 h from the electrolyte containing EMIC, anhydrous $CoCl_2$ and ethylene glycol = 2:1:18 (by molar). After the experiment, the PAA template embedded with cobalt nanowires was washed in ethanol and deionized water, and then stored in the desiccator.

2.4. Preparation of cobalt nanowires from aqueous solution

Co nanowires were fabricated in a conventional three-electrode electrochemical cell. The platinum layer on one side of PAA template was used as the working electrode. A cobalt sheet with a purity of 99.99% and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. Co nanowires were electrodeposited from the aqueous solution containing 120 g L^{-1} $CoSO_4{\cdot}7H_2O$ and 45 g L^{-1} H_3BO_3 at room temperature. Cobalt nanowires were fabricated by dc electrodeposition at 1.0 V (SCE) for 2 h, the pH value of electrolyte was adjusted to 2.0–3.0.

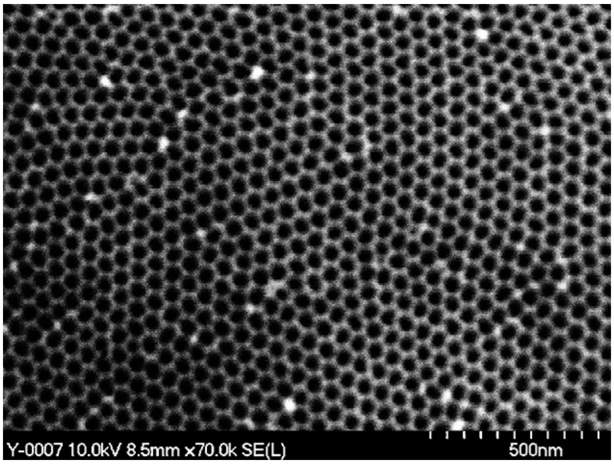

Fig. 1. FE-SEM image of surface of PAA template prepared in 1:1 sulfuric/oxalic acid mixture at 26 V and 5 °C.

2.5. Electrochemical measurement

Electrochemical experiments were carried out in a vacuum atmosphere glove-box system filled with dry nitrogen. EMIC–$CoCl_2$–ethylene glycol were poured into the self-made glass electrolytic cell in the glove-box. The electrochemical measurements were performed in a conventional three-electrode cell using a potentiostat/CHI630B. A platinum plate (0.5 cm^2) was used as the working electrode (WE), the counter electrode (CE) was a platinum electrode (1.0 cm^2), the reference electrode was a zinc (Aldrich, 99.999%) wire immersed in a $ZnCl_2$/EMIC ionic liquid contained in a glass tube having fine porosity frits at the tip. For the voltammetric experiments, the temperature was kept constant at 80 °C. Before every measurement, the working electrode was immerged in hydrochloric acid (1:1) for a few minutes, polished successively with increasingly finer grades of emery paper, followed by silicon carbide grit, and finally to a mirror finish with aqueous slurry of 0.15 μm alumina, rinsed with distilled water, and dried under vacuum.

3. Results and discussion

Fig. 1 shows a FE-SEM image of surface morphology of PAA template prepared in mixture acid electrolyte at 26 V.

It can be seen from Fig. 1 that the nanopores are uniform and highly ordered, and have an average diameter of about 45 nm. The space between nearest-neighboring pores is about 20 nm, slightly smaller than the pore diameter, the interspace is about 65 nm, and the pore density is about 10^{10} pore cm^{-2}.

A typical stationary staircase cyclic voltammogram recorded on platinum electrode in the 2:1:18 (by molar) EMIC–$CoCl_2$–ethylene glycol is shown in Fig. 2.

It can be seen from Fig. 2 that the cathodic current begins to appear at 170 mV (vs. $ZnCl_2$/Zn) in the EMIC–$CoCl_2$–ethylene glycol melt bath. There are a single reduction wave and a coupled oxidation wave on the CV curve, the corresponding potentials of reduction wave and oxidation wave are −150 and 395 mV (vs.

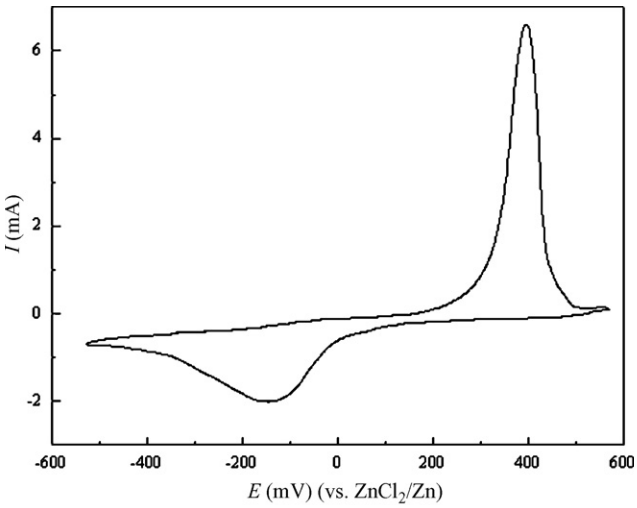

Fig. 2. Cyclic voltammogram for EMIC–$CoCl_2$–ethylene glycol (2:1:18) (by molar) on Pt electrode at 80 °C. Scan rate was 50 mV/s. Electrode area was 0.5 cm^2.

$ZnCl_2$/Zn), respectively. There is only a pair of redox waves which corresponds to the deposition and dissolution of Co.

Fig. 3 shows FE-SEM images of surface (a) and cross-sectional (b) morphology of Co nanowires after removing alumina partially using 0.5 M NaOH solution.

As shown in Fig. 3(a), the Co nanowires are uniformly distributed, highly ordered, and parallel to each other. As byproducts of the etching process, some residual etched alumina flakes can be seen on the top of the Co nanowires. As shown in Fig. 3(b), the well-paralleled nanowires suggest alumina matrix is not completely dissolved, and so, they remain parallel in the PAA template.

Shown in Fig. 4(a) and (b) are typical TEM images of Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol and from aqueous solution, respectively. Shown in Fig. 4(c) is the SAED pattern of Co nanowire electrodeposited from mixture of EMIC ionic liquid and ethylene glycol.

As shown in Fig. 4(a), the surface of Co nanowire is smooth, an average diameter is about 45 nm and an average length is about several micrometers. The average diameter of Co nanowires is generally the same as the pore diameter of PAA template. It can be seen from Fig. 4(a) and (b), the surface of Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol is relatively smoother than that of Co nanowires from aqueous solution. The SAED pattern of Co nanowire shown in Fig. 4(c) indicates that the Co nanowire is of a polycrystalline structure.

Fig. 5 illustrates the X-ray diffraction patterns of Co nanowires embedded within the PAA template from aqueous solution (a) and from mixture of EMIC ionic liquid and ethylene glycol (b), respectively.

The XRD patterns show the smooth amorphous broad peaks between 20° and 30° come from Al_2O_3 film. We can see from

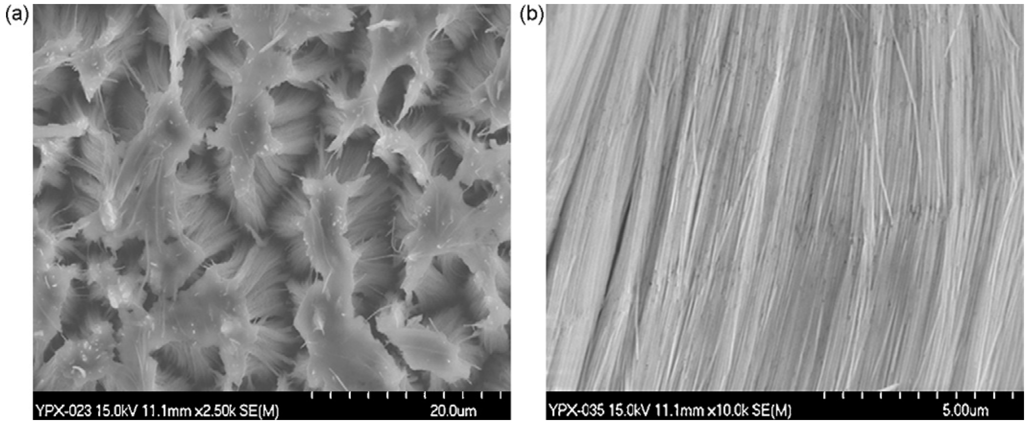

Fig. 3. FE-SEM images of surface (a) and cross-sectional (b) morphology of Co nanowires with alumina partially removed using 0.5 M NaOH solution.

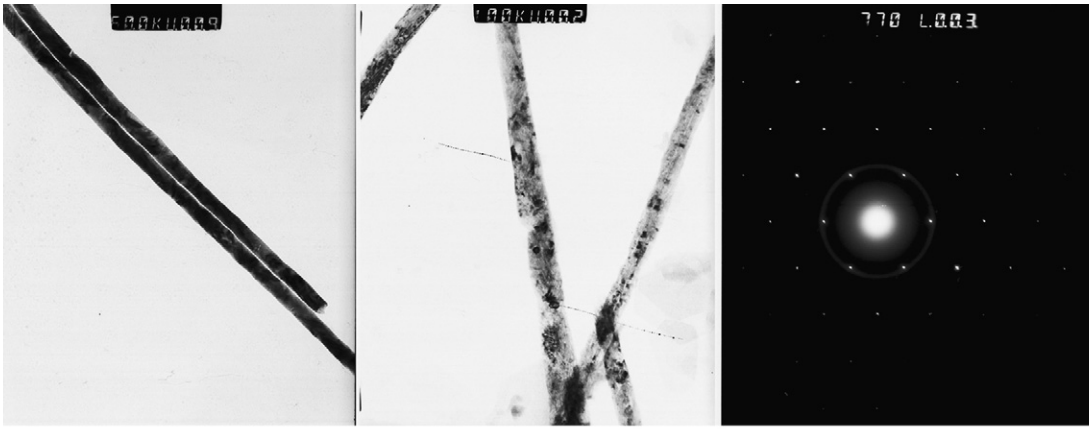
(a) (b) (c)

Fig. 4. TEM images of Co nanowires from the electrolyte containing EMIC, anhydrous $CoCl_2$ and ethylene glycol = 2:1:18 (by molar) (a), from an aqueous electrolyte containing 120 g L^{-1} $CoSO_4 \cdot 7H_2O$ and 45 g L^{-1} H_3BO_3 (b) and selected area electron diffraction of Co nanowire electrodeposited from mixture of EMIC ionic liquid and ethylene glycol (c).

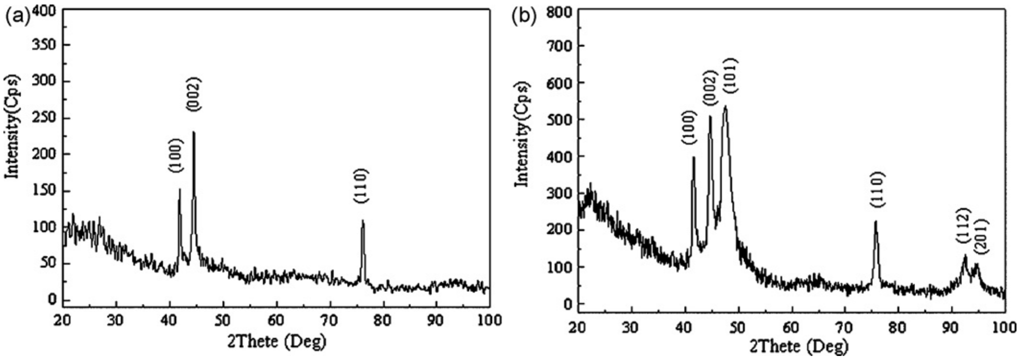

Fig. 5. X-ray diffraction patterns of Co nanowires from aqueous solution containing 120 g L^{-1} $CoSO_4 \cdot 7H_2O$ and 45 g L^{-1} H_3BO_3 (a), from the electrolyte containing EMIC, anhydrous $CoCl_2$ and ethylene glycol = 2:1:18 (by molar) (b).

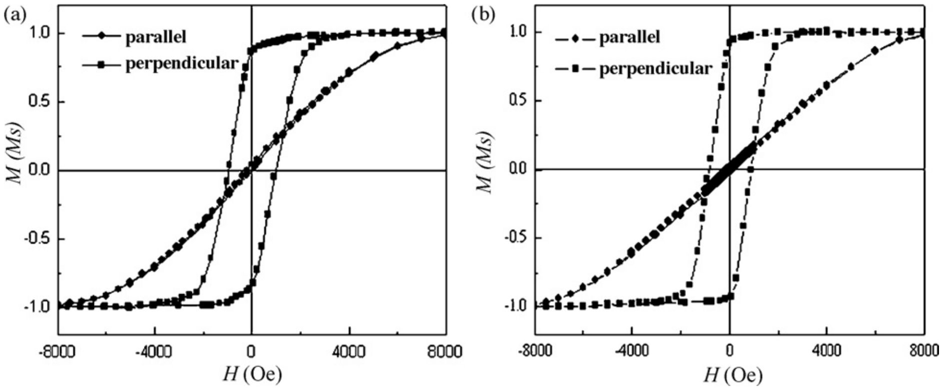

Fig. 6. Hysteresis loops of Co nanowires electrodeposited from aqueous solution containing 120 g L^{-1} $CoSO_4 \cdot 7H_2O$ and 45 g L^{-1} H_3BO_3 (a), from the electrolyte containing EMIC, anhydrous $CoCl_2$ and ethylene glycol = 2:1:18 (by molar) (b).

these two X-ray diffraction patterns that the diffraction peaks of Co nanowires electrodeposited in the nanopores of PAA template are consistent with those of bulk Co and Co nanowires are of a hexagonal close-packed (hcp) structure. As shown in Fig. 5(a), the Co nanowires electrodeposited from aqueous solution only exhibit three clear diffraction peaks, (0 0 2) diffraction peak is the highest, indicating that there is a preferred orientation along the (0 0 2) direction. However, Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol exhibit six clear diffraction peaks, indicating that there is not a preferred orientation direction (1 0 0), (0 0 2) and (1 0 1) diffraction peaks interconnect with each other. Therefore, it can be concluded that Co nanowires grow in a microcrystal structure. All these results indicate that Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol are a mixed phase of crystalline and microcrystalline, which display a polycrystalline structure. Co nanowires have a higher stress, so the size of Co crystalline grain embedded inside PAA template is not calculated by full-width half-maximum (FWHM), possibly because of the confinement of Co nanowires within PAA template.

Fig. 6 shows the hysteresis loops of ordered Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol (a) and from aqueous solution (b), respectively.

As shown in Fig. 6, the hysteresis loops exhibit a low coercivity (Hc) and squareness of hysteresis loop (Mr/Ms), when the field is applied perpendicular to the Co nanowires. When the field is applied parallel to the Co nanowires, the coercivity and squareness of Co nanowires are higher than those of bulk Co, i.e. the preferred direction of magnetization is always along the long axis of Co nanowire and the hard direction of magnetization is along the short axis of Co nanowires. These results indicate that Co nanowires inside PAA template show a strong perpendicular magnetic anisotropy, which can be used as a perpendicular magnetic recording film.

The values of coercivity and squareness of Co nanowires are summarized in Table 1.

As shown in Table 1, Co nanowires fabricated from mixture of EMIC ionic liquid and ethylene glycol possess the higher squareness of about 0.92, and Co nanowires fabricated from aqueous solution have a lower squareness. Co nanowires fabricated from mixture of EMIC ionic liquid and ethylene glycol have a strong perpendicular magnetic anisotropy and a moderate coercivity.

The differences in coercivity and squareness are thought to be related to such factors as the crystalline structure of nanowire, the crystalline grain size, and the defects in nanowires. Our TEM results given above indicate that over the entire length the surface of Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol is smoother than that of Co nanowires electrodeposited from aqueous solution. The defects reduce the Ms of Co nanowire. The difficulty of the magnetization reversal increases with the perfection of crystallite and the deterioration of coercivity. Moreover, small crystalline grain size leads to a low coercivity. All these properties show that the perpendicular magnetic anisotropy of Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol is enhanced, i.e. a good squareness is obtained.

Table 1
Magnetic properties of Co nanowires in PAA template

Electrolyte	Squareness (Mr/Ms)	Coercivity (Oe)
Aqueous	0.86	930
Ionic liquid	0.92	900

4. Conclusions

It can be seen from the results and discussion above that porous anodic alumina template is synthesized by electrochemical anodization of aluminum. Co nanowires are fabricated using PAA template by dc electrodeposition from mixture of EMIC ionic liquid and ethylene glycol and from aqueous solution, respectively. The Co nanowires produced are characterized by FE-SEM, TEM, XRD and PPMS. Test results indicate that the average diameter of Co nanowires is about 45 nm, which is generally equal to the pore diameter of PAA template. Two X-ray diffraction patterns show that Co nanowires fabricated from mixture of EMIC ionic liquid and ethylene glycol are of a polycrystalline structure. The Co nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol have a smoother surface and better magnetic properties than Co nanowires electrodeposited from aqueous solution, and they show a better squareness, so that cobalt nanowires electrodeposited from mixture of EMIC ionic liquid and ethylene glycol using PAA template can be applied to a perpendicular magnetic recording film.

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