



Review Review on Fabrication of Structurally Colored Fibers by Electrospinning

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Abstract: Structural color derived from the physical interactions of photons, with the specific chromatic mechanism differing from that of dyes and pigments, has brought considerable attention by the conducive virtue of being dye-free and fadeless. This has recently become a research hot-spot. Assemblies of colloidal nanoparticles enable the manufacture of periodic photonic nanostructures. In our review, the mechanism of nanoparticle assemblies into structurally colored structures by the electrospinning method was briefly introduced, followed by a comparatively comprehensive review summarizing the research related to photonic crystals with periodically aligned nanostructures constructed by the assembly of colloidal nanoparticles, and the concrete studies concerning the fabrication of well-aligned electrospun nanofibers incorporating with colloidal nanoparticles based on the investigation of relevant factors such as the sizes of colloidal nanoparticles, the weight ratio between colloidal nanoparticles, and the polymer matrix. Electrospinning is expected to be a deserving technique for the fabrication of structurally colored nanofibers while the colloidal nanoparticles can be well confined into aligned arrangement inside nanofibres during the electrospinning process after the achievement of resolving remaining challenges.

Keywords: structural color; electrospun nanofibers; nanoparticle assemblies; polymer; photonic crystal

1. Introduction

Structural color arises from photonic crystals possessing a periodic modulation assembled by colloidal nanoparticles; this has invited great interest since their introduction in the late 1980s [1–3]. The different mechanisms for controlling and manipulating light provided by the self-assembly of photonic crystals could be analyzed on the basis of the photonic bandgap [4]. Light refraction, diffraction, and scattering exist in the periodic nanostructures that contain regularly repeating internal regions [5]. Colloidal nanoparticles used to assemble photonic crystals with closely-packed structures play an important role in generating structural color to act on the transport and manipulation of light, owing to the Bragg diffraction [6]. Photonic crystals that exhibit brilliant structural colors are usually prepared by self-assembly of inorganic colloidal nanoparticles like silicon dioxide or silica (SiO₂) [7,8], titanium dioxide (TiO₂), core-shell colloids containing metallic nanoparticles like gold (Au)@SiO₂ colloids [9], polymeric nanoparticles including colloidal homopolymer nanoparticles [10,11], polystyrene (PS) [8,12,13], and copolymer nanoparticles like poly(styrene-methyl methacrylate-acrylic acid) [14]. Electrospinning is one of the favorable fabrication techniques that utilizes electrostatic forces to prepare polymer filament networks as scaffolds in nanometer scale, since it emerged in the early 1930s [15]. The periodically arranged nanostructures constructed by electrospinning have shown the potential of generating brilliant colors with the addition of photonic crystals, leading to a wide range of prospects in a novel biomimetic field.

In terms of the electrospinning technique, with the advantages of easy access to the adjustment of morphology of nanofibres and fast continuous preparation process [16], various kinds of electrospun nanofiber assemblies with desired properties could be prepared for myriad specific applications [17]. Unlike the dip-coating method [18], the electrospun nanofibers could be prepared without adhesion between the substrate and coating layer. No high thermal fulfillment tends to be required for the fabrication process, which is dissimilar to the melting and shear ordering method [19–21]. Electrospinning possesses high efficiency of manufacturing than the combined approach of microfluidic emulsification and solvent diffusion [22]. The electrophoretic method [23–25] has served as a fabrication technique for structurally colored fiber that has been examined on colloidal crystal growth with ordered arrangement for several decades, but the limitation of the substrate requirement with good electrical conductivity to form functional nanostructures cannot be neglected. Accordingly, electrospinning is conducted as a more effective approach for the production of structurally colored nanofibers of polymers compared with such template-directed assembly methods in which the subsequent removal of the sacrificial templates requires a troublesome and time-consuming process [26].

Even through structural color has been introduced into colloidal systems for a long time, researches regarding structurally colored electrospun nanofibers in combination with the assembly of nanoparticles are still quite sparse. Herein, this paper reviews highly relevant and significant research on structurally colored fibers with periodically aligned nanostructures by a promising electrospinning technique.

2. Mechanism of Nanoparticle Assemblies into Structurally Colored Nanofibers

While propagating the periodic structures, the wavelength of reflected light on the nanoparticleassembled nanofibers is predicted by a Bragg equation [27].

$$\lambda = 2dn_{eff} = (8/3)^{1/2} D_p (0.74n_p^2 + 0.26n_m^2 - \sin^2\theta)^{1/2}$$
(1)

where, λ , d, n_{eff} , D_p , n_m , n_p , θ refer to light wavelength of the reflected color, the periodicity of lattice spacing, effective refractive index, nanoparticle diameter, the refractive index of polymer matrix, the refractive index of nanoparticle, and light incidence angle, respectively.

If the light wavelength that fulfills the Bragg condition, incident light would undergo diffraction and hence the color of specific reflected light would appear on the surface of the ordered structures as demonstrated in Figure 1. The periodically ordered structures with aligned nanofibers are established by electrospinning, in which the round spheres represent the nanoparticles while the polymer matrix that surrounds the nanoparticles is mainly removed. Inserted image means cross section of part of the aligned nanofibers within a range around several microns made of nanoparticles. The periodicity and sizes of nanoparticles closely correlate to the color of reflected light, which is mainly controlled by modulating electrospinning parameters and emulsion polymerization conditions, respectively. Structural colors primarily depend on morphology of the material with certain properties, such as refraction index, playing a significant role of determining the color as well as color intensity [28]. The differences between density in amorphous and crystalline phases of the same polymer lead to differences in the refractive index, which means the ratio of the velocity of light in a vacuum to that in the polymer is closely related to the generation of structural color due to the significant role of polymers in the development of materials for photonics [6]. The width and frequency of the reflection tend to be determined by refractive index as well as the layer or film thickness in the photonic crystal film [7]. Hence refractive index has been identified as one of the fundamental optical properties of a polymer that is regarded as an input parameter for assessing many other optical properties [29,30]. A readily feasible method for changing color is to modulate the refractive indices of the nanostructures constructed by polymers [31]. Enlarging the difference between refractive index and colloidal nanoparticles and polymer binder tends to be accessible to strength the intensity of structural color. The surface polarity between the photonic crystal nanoparticles and polymer binder is shown to



exert great significance in the preparation of spinning solutions for establishing electrospun nanofibers, and subsequently it would be routinely considered while producing the electrospinning solution.

Figure 1. Demonstration of generating structural color according to Bragg's law.

A schematic representation of the preparation of nanoparticle assemblies into nanofibres with photonic crystal structures exhibiting brilliant color is given in Figure 2, which is similar to the given work [32]. Like conventional electrospinning setup, a spinneret with needle and syringe, a high voltage power supply, and a conductive collector including rotating drum (Figure 2a) or parallel collector (Figure 2b) are constructed for manufacturing well-aligned nanofibres, and the working principle of electrospinning is similar to the previous studies [33]. Syringe pump filled with spinning solution is used to provide the liquid to the tip of the needle in a certain flow rate. Due to the surface tension, a liquid droplet could form, where charges would generate while imposing a high voltage at the spinneret. A Taylor cone would exist when charge repulsion is strong enough to conquer the surface tension. Then the liquid could be ejected to the collector under the driving forces based on the electrostatic repulsion. Finally, the nanofibers align perpendicular to the axis of the drum or parallel electrode with the evaporation of solvent [34]. The mechanism that modeled and simulated the corresponding electrostatic field distributions between the needle and the collector in a three-dimensional (3D) space is shown in Figure 2c,d. The typical target collectors utilize a rotating drum and parallel collector, respectively. The electrostatic driving forces have no fixed direction that can be ascribed to the unstable electric field. In order to obtain the highly aligned nanofibres fabricated by electrospinning [34,35], it has been found to apply high rotating collectors, parallel electrode collectors [36,37], and auxiliary electrodes [38,39]. The gap width between the as-spun nanofibers reached the values ranging from centimeters to several micrometers as investigated in [40], which resulted in the uncontrollable orientation of electrospun nanofibers, and hence the deep investigation of suitable electrospinning conditions is required to build the scaffolding of aligned nanostructures that exhibits structural color. For instance, Li et al. [40] have analyzed the electrostatic forces using continuous conductive collector without and with an insulating gap, they found that a parallel collector had the priority of enabling the nanofibers in an uniaxial alignment.



Figure 2. Schematic diagram of electrospinning setup using (a) rotating drum, (b) parallel electrode; representative simulation of electrostatic field distribution between the needle and (c) rotating drum, (d) parallel electrode using COMSOL software. Red arrows refer to electrostatic forces.

3. Photonic Crystals for Fabricating Structurally Colored Fibers

The construction of photonic crystals with three-dimensional periodic geometry is a crucial part when it comes to fabricating structurally colored fibers. Coherently diffraction and scattering by the photons of specific wavelengths could occur on the periodic lattice planes of photonic crystals, which has a spacing that is similar to such wavelengths [28,41]. Prior to the preparation of three-dimensional photonic crystal structural color materials, the self-assembly of colloidal nanoparticles of spherical or cylindrical shapes into a close-packed and periodic array tends to enable the photonic crystal as an attractive candidate for generating structurally colored fibers. Colloidal nanoparticles can act as building blocks for constructing photonic crystals as a result of the superiority that includes multiple choices of chemical composition, cost-effective products, as well as tunable particle sizes [5]. The size dimension of nanoparticles mainly controlled by the adjustment of the reaction conditions during synthesis process, including the different amounts of reactants [42,43], precursor type, reaction temperature, and time [44], causes a shift of color that enlarges the potential applications of promising areas.

3.1. Inorganic Nanoparticles for Photonic Crystals

Since Iler [45] first carried out the research that multilayers assembled by colloidal nanoparticles could be formed on rigid substrates by the layer-by-layer (LBL) deposition method, many researchers have studied different nanoparticles, including inorganic nanoparticles for constructing photonic

tunable structural colors in organic solvent by assembling SiO₂ nanospheres, and the experimental results indicated that carbon black dopant remarkably increases the chroma and enhances the intensity of the structural colors. Structural color changes of colloidal crystal films from red to violet were determined by the assembly of SiO₂ nanoparticles with different particle sizes from 207 to 350 nm using the Stöber process [43]. A recent study by Zhang [47] disclosed vivid structural color coatings from atomization deposition of SiO₂ nanoparticles with poly (vinyl alcohol) additive on silk fabrics, which can possess robust mechanical properties as depicted in Figure 3.



Figure 3. Schematic illustration showing the fabrication process of amorphous SiO₂ nanoparticles into photonic crystals with noniridescent colors on various substrate materials by atomization deposition. Reprinted with permission from [47] American Chemical Society, 2018.

Several conventional techniques have been employed to produce TiO₂ films, including conventional sol-gel method [48,49], vapor deposition method [50,51], and liquid phase deposition [52,53]. Chen and co-workers [54] successfully used an effective method named the atomic layer deposition (ALD) technique to fabricate TiO_2 coatings with vibrant and uniform structural colors using black carbon fibers as substrates, showing excellent laundering durability. These have many potential applications in the field of optical and color-display devices. Because the use of single inorganic particles is significantly limited to the formation of periodically arranged photonic structures, core-shell colloidal particles have become desirable materials. Metal nanoparticles like gold (Au) or silver (Ag) are extraordinarily efficient at strongly absorbing and scattering light to enhance the intension of reflected light for exhibiting brilliant color, due to the optical property known as localized surface plasmon resonances [55,56]. SiO₂ nanoparticles incorporated with gold has been prepared to form colloidal spheres (Au@SiO₂) with core-shell shapes, which can serve as the building blocks for photonic applications [9]. Yuan et al. [50] reported structural colors on polyester fabric with the coating of silver(Ag)/TiO₂ films made by magnetron sputtering. The resultant samples with diverse colors of purple, light blue, blue, pink, and dark red could be displayed by controlling different thickness of TiO₂ thin films. Luo et al. [57] reported electrically induced structural color alteration of core-shell (SiO₂@TiO₂) photonic crystals for electric field applications.

3.2. Polymeric Nanoparticles for Photonic Crystals

Since the discovery of an approach for synthesizing monodisperse polymer colloids by Vanderhoff, this synthetic method has been used to prepare diverse polymeric colloids, including homopolymer colloidal nanoparticles as well as copolymer nanoparticles, besides inorganic colloidal nanoparticles [58,59]. These monodisperse polymeric colloidal nanoparticles prepared by some mature synthesis techniques, such as emulsion polymerization, dispersion polymerization, precipitation polymerization, or seeded polymerization, can be incorporated into polymer solution for electrospinning [5]. Among the synthetic routes, emulsion and dispersion polymerization are the most commonly used.

Colloidal homopolymer nanoparticles such as polymethylmethacrylate and polystyrene monodispersed spheres, have been successfully synthesized to be used for fabricating structural color. The size of such nanoparticles influencing optical properties of electrospun nanostructures can be determined by synthesis conditions like concentration of initiator, reaction time, and temperature. The preparation of nanofibres containing polymeric nanoparticles by electrospinning has been examined [12]. Meng et al. [60] studied the mechanical stability and hydrophobicity of structural color films composed of PS microspheres, which was of great significance for potential architectural purposes in paint and decoration. According to Han et al. [61], the stability of switching performance of the tunable photonic crystals consisting of well-ordered PS colloidal arrays has been improved in long range for display applications. Tang and co-workers [62,63] presented a kind of polymer opal film with brilliant structural colors from PS nanospheres or crosslinked PS/polydimethylsiloxane (PDMS) with well-aligned structures by using the self-assembly method with thermal assistance for architectural applications. Gu et al. [8] described a kind of structural color with a lotus effect formed by mixing both PS spheres and SiO₂ particles to deposit an opal film on a glass substrate. Meanwhile, researchers have made much efforts to prepare poly(methyl methacrylate) PMMA nanospheres for many promising purposes, synthesized by a commonly used method called emulsion polymerization [10,64,65]. Tang et al. [66] developed a kind of heat-resistant photonic crystal film consisting of PMMA colloidal spheres with different colors by investigating the effect of methyl methacrylate (MMA) concentration on particle size as well as the distribution of PMMA particles.

Despite colloidal homopolymer nanoparticles, a variety of copolymer nanospheres commonly exhibiting core-shell nanostructures can be synthesized with other kinds of monomers by polymerization to achieve the desired functions. Liu et al. [67] developed a kind of photonic crystal named poly(styrene-methacrylic acid) coating on the textile fabrics exhibiting brilliant and variable structural colors, possessing better hydrophobic properties. Non-iridescent brilliant structural colors (blue, green and red) from photonic structures based on assembling polystyrene/poly(*N*-isopropylacrylamide-co-acrylic-acid) particles with core-sheath particle structure over the full-spectrum were demonstrated by Park [68], as displayed in Figure 4a,b.

Figure 4c,d shows that a kind of core-sheath colloidal poly(styrene-methyl methacrylate-acrylic acid) nanospheres was synthesized by emulsion polymerization using three monomers including methyl methacrylate, styrene and acrylic acid from [14]. Brilliant and monochromatic colors of colloidal crystal films covering the entire visible range from red to violet color on a glass substrate were obtained by assembling such nanospheres with various diameters. Yuan et al. [69] also successfully synthesized monodispersed poly (styrene-methyl methacrylate-acrylic acid) composite nanospheres and it was designed to be blended with a measured amount of PVA to produce a dye-free electrospun fibrous membrane with tunable brilliant structural colors by colloidal electrospinning. The schematic illustration of this process and the typical scanning electron microscope (SEM) images of the nanofibres are depicted in Figure 5. The SEM results demonstrated that the colloidal spheres are well-arranged on the surfaces of nanofibres in a cylindrical shape.



Figure 4. (**a**,**b**) Three structural colors (blue, green, and red) of photonic microcapsules prepared with various shell thicknesses of core-sheath particles under optical micrographs. (**a**) bright-field, (**b**) dark-field. Reprinted with permission from [68] Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2014; (**c**) Schematic diagram of poly(St-MMA-AA) nanostructure and the typical transmission electron microscope (TEM) image of the core-sheath nanospheres with the diameter of 173 nm; (**d**) Pictures of prepared films with different sizes deposited on the glass substrate. Reprinted with permission from [14] Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.



Figure 5. Schematic illustration of the fabrication process of electrospinning for preparation of colorful fibrous membranes. Reprinted with permission from [69] American Chemical Society, 2015.

4. Electrospun Nanofibers Derived from Photonic Colloidal Nanoparticles

Many researchers have successfully achieved structural color films or photonic opals or coatings on substrates [43,70–72], and the electrospinning technique for generating common nanofibres has been proven. Electrospinning using a high-voltage electric field to spin polymer solutions into nanofibres with nanoscale diameters, tends to be a versatile technique for successfully manufacturing polymer nanofibres from various kinds of polymer materials, like poly (vinyl alcohol), poly(ethylene terephthalate), poly(vinyl phenol), polyurethanes, polyamide, poly(methyl methacrylate), polyacrylonitrile, poly (ether imide), poly (ethylene gricol) [73], which are treated as a polymer matrix, an indispensable element and the main component of the nanostructures exhibiting brilliant colors. More importantly, the fabrication of nanofiber membranes containing SiO₂ or TiO₂ colloidal nanoparticles by the electrospinning method has proven to be feasible according to previous works by Zhang [74], Im [75] and Pant [76]. A discovery of present work focusing on incorporating colloidal nanoparticles into electrospun nanofibers with well aligned morphology has been found as shown in Table 1 with detailed parameters. Different morphologies of electrospun nanofibers could be achieved from random packed, necklace-like to cylindrically hexagonal patterned structures by controlling several decisive conditions, which covers the different properties of the polymer matrix, including crystallinity, glass transition temperature, molecular weight, and spinning solution properties including surface tension, viscosity, conductivity, polymer solubility as well as the electrospinning processing parameters consisting of the feeding rate, applied voltage, receiving distance, effect of collector, and needle [15]. Besides, with the addition of photonic colloidal nanoparticles, more influencing factors are thought to be considered. The sizes and shapes of colloidal nanoparticles blended in polymer matrix is one of the indispensable factors determining the morphology of the as-prepared electrospun nanofibers. In the early 20th century, Yang et al. [26] presented the concept that colloidal particles can be confined and assembled inside nanofibres during the electrospinning process and they successfully fabricated polyacrylamide/SiO₂, poly(ethyleneoxide)/SiO₂ and poly(acrylonitrile)/SiO₂ nanofibers with close-packed SiO₂ particles formed in radial direction of the nanofibres. From SEM results in Figure 6, it can be documented that with the increasing size of SiO₂ particles from 100 nm to 1000 nm, the structure of polyacrylamide nanofibres transformed from less-aligned to assembled necklace-like structures.



Figure 6. Scanning electron microscope (SEM) images of the structures and morphology of polyacrylamide nanofibres with the increase of SiO₂ nanoparticle sizes: (**a**) 100 nm, (**b**) 300 nm, (**c**) 450 nm, (**d**) 700 nm, and (**e**) 1000 nm. Reprinted with permission from [26] American Chemical Society, 2006.

Another affecting factor is the weight ratio between photonic colloidal nanoparticles and polymer matrix. Yuan and his group members [12] investigated the morphology of polystyrene nanosphere(PS)/poly(vinyl alcohol)(PVA) electrospun fibers with the various structures. Polystyrene nanospheres were synthesized by emulsion polymerization using the monomer (styrene) with the addition of an emulsifier. The results showed that string-on-bead and necklace-like nanofibres were obtained with certain ratios of PS and PVA, as shown in Figure 7e. A common electrospinning factor named polymer concentration was also analyzed as can be seen in Figure 7g–n.

Despite the construction for morphology structures of electrospun nanofibers, extra factors may affect the color on the nanofiber surfaces according to Table 1. To evaluate the reason that most of the resulting nanofibers with uniform ordered structures were achromatous, the researchers found that it was attributed to the low refractive index. The subsequent exploration verified that after establishing the scaffolding in which electrospun nanofibers were in alignment, the polymer matrix could be removed without the destruction of the desired nanofiber structures that was conducive to yielding color. The dissolution of the PVA matrix of poly (styrene-methyl methacrylate-acrylic acid)/PVA nanofibers increased the refractive index contrast resulted in displaying structural color [69].

	Colloidal Nanoparticles	Sizes (nm)	C1 (wt%)	Polymer Matrix	Mw	C ₂ (wt%)	R	Rf (mL/h)	V (kv)	D (cm)	T; H	Morphology	Ref.	
	silica	15, 50, 100	20	polyvinyl alcohol	Mn: 66,000	10	2:3	1	10	10	$25 \ ^{\circ}\text{C}$ $50 \pm 5\%$	grain-like singly aligned	[77]	
	silica	100, 300, 450, 700	20	Polyacrylamide poly(ethyleneoxide)	600,000–1,000,000 600,000	10	2:3	0.5–3	5–13	10	500 °C calcination	necklace-like	[26]	
	silica	143, 265, 910	12.2 21.6 13.1	polyvinyl alcohol	88,000	12 10 12	500:500 600:400 200:800 300:700	_	10–30	10	_	necklace-like blackberry-like	[32]	
	Silica polystyrene	700, 50 237	34 10	Polyacrylamide poly(ethyleneoxide)	600,000–1,000,000 600,000	10	—	0.5	5–13	10	calcination	stand-alone structures, superhydrophobic	[78]	
	polystyrene	100, 200, 335	40	polyvinyl alcohol	145,000 195,000	6	80:20	0.7	0–30	20	15-18 °C 30–50%	random to relative compact packing	[79]	
	polystyrene	225, 473	10, 15, 20, 30, 40	polyvinyl alcohol	14,500	13	1:1 2:1 4:1	0.2–0.8	10	15	$\begin{array}{c} 25\ ^{\circ}\mathrm{C}\\ 50\ \pm\ 5\%\end{array}$	blackberry-like to uniform	[12]	
	poly (styrene-methyl methacrylate-acrylic acid)	220, 246, 280	40	polyvinyl alcohol	14,500	13	4:1	0.5	10	15	—	green, red, purplish-red color cylindrically hexagonal ordered	[69]	
(N	poly f-isopropylacrylamide-co-tert-butyl acrylate)	226	40	polyacrylamide	146,000	16	1:4 2:3 1:1 3:2 4:1	0.5	10	15	20 °C 30 ± 5%	necklace-like blackberry-like	[16]	

Table 1. Fundamental	parameters of nanoparticle	s contained electrospun nanofibers	with well-aligned morphology.

Where, Mw and Mn are the weight-average and number-average molecule weight of polymer, respectively; C₁, C₂ denote the concentration of nanoparticles and polymer matrix, respectively; R is the ratio of nanoparticle and polymer; Rf is the feed rate; V is electrospinning applied voltage; D means the distance between needle and collector; T, H represent temperature and humidity. Rf, V, D, T, H represent the parameters in the electrospinning process.



Figure 7. SEM graphs of polystyrene nanoparticles into PVA nanofibres: (**a**–**f**) different weight ratios of PS and PVA of 1:4, 1:2, 1:1, 2:1, 4:1 and 6:1; The inserted images in each subfigure from a to **f** are measured under lower magnification. (**g**–**n**) different concentrations of PVA: 7, 9, 11, 13 wt%, while (**g**–**j**) PS:PVA is 1:4 and (**k**–**n**) PS:PVA is 4:1. Reprinted with permission from [12] American Chemical Society, 2012.

5. Outlook and Conclusions

Myriad studies have successfully produced well-ordered nanostructures on electrospun nanofibers with the blending of photonic nanoparticles, however, the research on nanofibres containing photonic nanoparticles endowing homogeneous and non-iridescent structural colors remains very few, which indicates that it seems to be difficult to achieve the well-ordered structure of electrospun nanofibers incorporating photonic nanoparticles as a result of the overall consideration of a multitude of factors and thereby it remains a daunting task.

Overall, tremendous achievements in structural coloration based on photonic crystals have been visible in many application areas, especially optical fields, but so far only a relatively small number of researchers have tried to prepare nanofibres with brilliant structural colors by electrospinning because of the difficult regulation of manufacturing conditions. Major efforts are still required to further develop and improve effective manufacturing approaches to structurally colored nanofibers. Researchers have presented electrospun nanofibers exhibiting vivid structural colors with the addition of polymeric particle colloids, however, inorganic spheres with higher reflective indices are expected be used to fabricate structurally colored fibers because the high refractive index contrast is beneficial for increasing the intensity of structural colors. Other properties of structurally colored fibers such as mechanical properties are supposed to be considered and examined for more promising applications. It could be concluded that electrospinning is a versatile approach that could be used for the generation of highly aligned electrospun nanofibers, showing the promise of paving the way for a revolution in the development of structurally colored materials for various dye-free applications.

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