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Preparation of large-scale and angle-independent structural colors by additive of black polypyrrole

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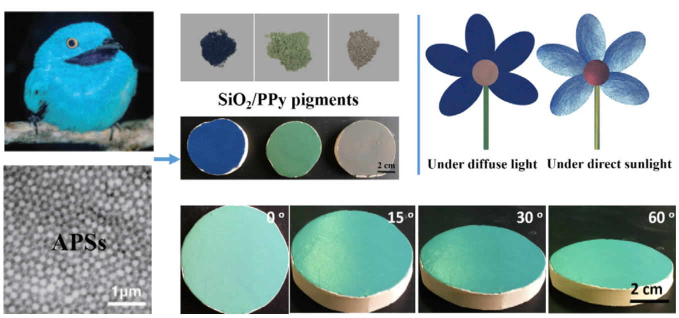
GRAPHICAL ABSTRACT

The large-scale films exhibit identical colored appearances with its pigments and have the presence of metallic texture under direct sunlight.



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ABSTRACT

Vividly structurally colored pigments with a non-iridescent character produced by APSs (amorphous photonic structures) have attracted great attention recently. However, these artificial APSs usually have a low color visibility. Here, a new strategy based on a drop-coating method for creating large area 3D APSs by using polypyrrole (PPy) as an additive is proposed. The bright and non-iridescent structural colors were obtained by self-assembling the mixture of monodisperse SiO_2 spheres and PPy particles. The color hues of the APSs are strongly related to the diameter of the SiO_2 spheres while their spectral purity can be controlled by the proportion of the SiO_2 spheres to the PPy particles. Surprisingly, these structurally colored films applied on ceramic substrate have the presence of a metallic texture under direct sunlight. To the best of our knowledge, such bright and non-iridescent structural colors obtained by simple but effective coating method may facilitate the development of special functional industries for various applications.

1. Introduction

Color plays a crucial role in nature, it can be roughly divided into two broad categories of pigmentary color and structural color [1]. Pigmentary color is the intrinsic property of materials, produced by the electron selective absorption of light which is the electrons of molecules embedded in materials. In contrast, the structural color is the result of the fundamental optical processes of diffraction, interference or scattering [2–6]. Structural colors usually have a distinctive appearance which is shiny, metallic property with an angle-dependent apparent color. They generally

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suffer little dissipative loss, and do not fade like chemical pigments, which are sensitive to change in chemical and have relatively low environmental resistance [1,7].

Structural colors have an increasing demand in many fields such as colors display [2,8], sensor devices [9,10] and anti-counterfeiting labels [11]. But the structural color with highly ordered periodic materials often change along with the observer's angle because of the Bragg diffraction, so it's not conducive to the pigment, color display and related applications, etc. [12–17]. To solve this problem, scientists have developed an amorphous photonic structures (APSs) of disorder or quasi-disordered arrays, that exhibit the same color appearance which is independent of the viewing angle [18–22]. For example, Forster et al. [19] adopted two monodisperse colloidal particles with different size and then prepared the non-iridescent structurally colored films with disordered structure array by spinning methods on the glass substrate surface.

It is also noteworthy that the low-angle dependent structural colors of the APSs prepared by above-mentioned approaches usually have low color visibility due to strong incoherent light scattering [19–22]. Inspired by the chromogenic mechanism of living organisms in nature, the significant method for solving this problem is to add carbon black materials into colloidal systems [2,18,20]. However, the commonly used carbon black whose size is dozens of nanometers and have high surface energy is unstable and easily recombined, leading to a significant decrease in brightness.

In order to further improve the color saturation, it is important to employ new black materials, such as cuttlefish ink, and iron oxide black particles, which have high absorption in the visible region to enhance color saturation [23–27]. For instance, Teshima et al. [23] prepared monodispersed spheres assembled by SiO_2 and Fe_3O_4 by using a microflow-focusing device. Zhang et al. [25] reported non-iridescent structurally colored pigments and greatly improved visibility of pigments by using cuttlefish ink as an additive to absorb partial light scattering. Several researchers have designed a system with core-shell-like structures composed of materials with different refractive [27–30]. However, these methods is complex and the production is relatively low. From the above reports, it is still a great challenge to use a simple strategy to prepare large-scale structural colors with high color saturation.

In previous studies, polypyrrole (PPy) is a common, environmentally friendly black material that absorbs light from visible light and it is biocompatible [31]. It has previously been used in fields including catalysis, chemical sensing, microelectronics and photoelectric devices [32]. PPy deposition on hydrophobic PS latex particles for the preparation of structurally colored films has been reported [29]. However, to polymerize hydrophilic pyrrole monomers on PS nanoparticles, the latter first requires surface functionalization.

In this study, we created a kind of bright and non-iridescent structural colors based on the drop-coating method by using PPy black particles as an additive to monodisperse SiO_2 spheres. The color could be tuned to blue, green and zinzolin simply by adjusting the size of SiO_2 nanospheres and their spectral purity could be tuned by the mass ratio of SiO_2 nanospheres and PPy particles. The large-area structurally colored films were formed on ceramic substrates by a sort of vividly paint combining structurally colored pigments and ethanol. And then the color maintain consistent with the corresponding powders after the solvent evaporated completely. It's amazing that these structurally colored films present metallic texture under direct sunlight. In addition, the synthetic route is relatively inexpensive and environmentally friendly, which obviates any complex fabrication steps, thereby it's a facile way and has the prospect of large-scale application.

2. Experimental section

2.1. Materials

Tetraethoxysilane (TEOS), ethanol, ammonia (28%), ammonium persulfate (APS), polyvinyl alcohol (PVA1788) and p-toluenesulfonic acid (p-TSA) were purchased from the Tianjin Chemical Reagent Co, Ltd of China. Pyrrole monomer (Py) dehydrated by calcium hydroxide for 24 h was distilled under reduced pressure before use. All others chemical reagents were analytical grade and used without further purification. Deionized water (18.2 MΩ·cm resistivity) was used in all experiments.

2.2. Synthesis of SiO_2 NPs

Monodispersed silica nanoparticles of the diameter ranging from 183 nm to 285 nm were synthesized according to the modified StÖber method [24]. Firstly, a mother solution containing aqueous ammonia (4 mL), and ethanol (44–50 mL) was prepared in a 100 mL glass beaker under vigorous stirring. When the temperature of the mixture reached to 40 °C, the mixture solution consisting of TEOS (3 mL) and ethanol (0–6 mL) was then added into the solution, drop wisely. The reaction was lasted for 4 h with constant stirring until the reaction completed. Finally, the product of SiO_2 was purified by centrifuging and re-dispersing in deionized water and ethanol for several times, followed by drying in 50 °C oven to obtain a white powder.

2.3. Synthesis of PPy NPs

The synthesis route of PPy particles by cryogenic polymerization way was as follows: First, 65 mL distilled water was added in a round-bottom flask including 0.1 g PVA, 0.1 g p-TSA and 0.5 mL Py, and then vigorously stirred for 1 h at room temperature. Next, 20 mL aqueous solution of 1.14 g APS was added drop by drop into the mixture, and kept stirring for 12 h in the ice-bath. The product of PPy was purified by centrifuging and re-dispersing in deionized water and ethanol for several times. Finally, the product was dried in a vacuum oven at 60 °C for 24 h to obtain a dark powder.

2.4. Synthesis of SiO_2/PPy structurally colored pigments and fabrication of colored films

Firstly, SiO_2 nanoparticles were dispersed into ethanol with the concentration of 10 wt%, and then ultrasonicated for 1 h. To study the relationship between the amount of PPy and color saturation, the amount of PPy suspended in the ethanol was varied from 0.1, 0.3, to 0.5 wt%, and then ultrasonicated for 1 h.

Secondly, a syringe was used to take 1 g of SiO_2 suspension while a fixed amount of 0.5 g PPy suspension was added drop by drop into the prepared SiO_2 suspensions and then the mixed suspension was ultrasonicated for 30 min. Finally, the mixed suspension was dried at room temperature to obtain the structurally colored pigments or a small amount of the mixed suspension was dropped onto ceramic substrate and left overnight for drying to obtain structurally colored films.

2.5. Characterization

The morphology of SiO_2/PPy structurally colored pigments and films of APSs were observed using scanning electron microscopy (SEM) (Hitachi S4800). The samples were sputtered with a thin Au layer (10 nm) before SEM observation.