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Effect of Surface modified of $SiO_2@TiO_2$ Core-Shell particles on the Structural Colour under Electric Field

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Surface modified colloidal $SiO_2@TiO_2$ core-shell particles were chosen to study their responsive photonic properties and the effect of surface on structural colour under low electric field. The surface of $SiO_2@TiO_2$ core-shell particles were controllably coated by PDDA, PVA and SiO_2. Corresponding colloidal suspension of the modified $SiO_2@TiO_2$ showed a completely different reflection spectrum. The dielectric spectrum was employed to explain the effect of surface properties on the assembly.

1 Introduction

Responsive photonic crystals are periodical structures, which can change their structure under external physical or chemical stimulus. The preparation and modulation of responsive photonic crystals have increasingly attracted the interest of researchers due to their unique applications in areas such as display units, biological and chemical sensors, and active optical components.[1-3] Synthetic responsive photonic crystals are frequently produced using monodisperse colloidal particles crystallized into different ordered arrays in suspensions and tunable structural colours come from these arrays.[4-6] The key to a successful assembly and large tunability in photonic property is establishing long-range repulsive and attractive interactions that can cooperate to order the particles into periodical structures. Interparticle spacing of particles in these systems can be controlled by varying the intensity of stimulus and modification of colloidal particles surface. Many studies have focused on the use of magnetic fields to change the assembled structures of superparamagnetic colloidal particles to form structural colour. The driving force can be understood as the interaction of a magnetic dipole with the external magnetic field. Besides magnetic forces, the long-range electrostatic force is also essential in assembling magnetic colloidal particles into ordered arrays. This strong interparticle repulsion can be used to counterbalance the magnetic dipole-dipole attraction to induce the formation of periodic structures. The establishing of long-range repulsion has a lot to do with the surface properties in aqueous and nonaqueous solvents. In the case of superparamagnetic iron oxide particles in aqueous solution, electrostatic repulsive forces are introduced to the particles by coating them with a layer of polyelectrolytes containing high density negative charges[2]. While in nonaqueous solvents, the electrostatic forces are usually greatly diminished. To establish strong and long-range repulsive forces to balance the attractive force, some researchers have make use of the short-range solvation force which is originated from the overlap of two relatively thick solvation layers on the hydrophilic silica[3] or hydrophilic carboxyl covered particle surfaces.[4] Others address the challenge by modifying the surface of the particle by introducing modifying agent.[5-7] Guan etc have synthesized monodisperse superparamagnetic particles by a modified polyol process in the presence of glucose and poly (vinyl pyrrolidone) (PVP). They show a long-range steric repulsion sufficiently strong to counteract the magnetic attractive force[8]. The nature of repulsion between particles is electrostatic or steric according to the surface properties.

Recently, we have demonstrated an electrically tunable photonic crystal system through the assembly of $SiO_2@TiO_2$ colloidal particles in propylene carbonate[9]. In these systems, when particles have like charges, they repel each other through electrostatic interactions and minimize the total repulsive energy by forming ordered structures known as crystalline colloidal arrays (CCAs). By changing the strength of the external electric field, we can conveniently tune the diffraction wavelength. But, the exploitation of the effect of different modification of non-magnetic colloidal particles on the structural colour under electric field remains rather unexplored however.

In this work, we modify the surface of $SiO_2@TiO_2$ particles by introducing Poly Diallyldimethylammonium Chloride (PDDA), Polyvinyl Alcohol (PVA), because they can induce electrostatic and steric respectively. For comparison, $SiO_2@TiO_2@SiO_2$ (STS) double-shell particles have been prepared by the hydrolysis method. Previous research had suggested that the reflection peak of the modified TiO_2 nanoparticles did not move under different voltages. $SiO_2@TiO_2$ colloidal particles in propylene carbonate show obvious structural colour in external electric field. And interestingly, the position of reflection peak maximum is maintained of STS double-shell particles under different voltages. The relation between surface properties of

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the above-mentioned particles and optical properties are systematic investigation in this work. The reflectance spectrum of the suspension was measured under different electric field. A simple and unilateral increase of the charges on the colloidal particles surface is not a good solution for tunable structural colours. The external electric field will induce the highly colloidal particles moves toward glass substrate and aggregate each other. Meanwhile, we use the dielectric spectrum to explain the effect of surface properties on the assembly because it provides critical insight into the electrokinetic properties of colloids, including their surface charge and electrophoretic mobilities, key properties that determine a suspension's stability and its response to an applied electric field[10].

2 Experimental section

2.1 Chemicals

Tetraethoxysilane (TEOS, AR), titaniumtetraisopropanolate (TTIP, AR), ethanol (AR), $NH_3 \cdot H_2O$ (25%, AR), Polyvinyl Alcohol (PVA) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Propylene carbonate (99%) and ethylene glycol were purchased from Aladdin Chemicals. Poly Diallyldimethylammonium Chloride (PDDA) was purchased from Arich. Indium tin oxide (ITO) coated glasses with a resistivity of 7 Ω·cm was purchased from Corning Corp. All chemicals were used as received without further purification. The water used in this work was deionized (DI) water from a Millipor-Q purification system (Millipore, USA) of resistivity 18.2 MΩ·cm.

2.2 Synthesis procedures

$SiO_2@TiO_2$ (ST) and $SiO_2@TiO_2@SiO_2$ (STS) were synthesized by the hydrolysis of TEOS and TTIP under alcohol–ammonia conditions[9]. This approach is similar to the ammonia-catalyzed Stöber method[11]. The obtained core–shell particle (0.0648 g) was purified with repetitive centrifugation and re-dispersion at 8000 rpm and finally dispersed in water (10 mL). To the dispersion of 10 mL, Polyvinyl Alcohol (PVA) (0.0065 g) or Poly Diallyldimethylammonium Chloride (PDDA) (1.5 mL) was added in the dispersion solution. After reacting for 6 h, the colloid particles were purified again with a centrifugation and re-dispersion process.

2.3 Preparation of devices

The photonic display cell consists of transparent top and bottom electrode separated by 200 μm thick epoxy spacers. Unmodified and modified $SiO_2@TiO_2$ suspension (5.4 v% in propylene carbonate) was injected in between those electrodes by using the conventional injection syringe，then we apply an electric field to the photonic display cell.

2.4 Characterizations

The morphology and grain size of the samples was examined by FEI Tecnai G2 F20 transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) was used to measure the properties of particles before and after the modification. Zeta potential was measured by particle size analyzer (Malvern, Zetasizer nano zs). The reflection spectra of these silica colloids suspensions in electric field were measured by an Ocean Optics HR 2000CG-UV-NIR spectrometer coupled with a six-around-one reflection/backscattering probe. Electric field was applied to $SiO_2@TiO_2$ core-shell colloids suspensions by a function generator (Agilent, 33220A) for DC power supply. Fourier transform infrared spectrum (FT-IR) of the samples was recorded using Intelligent Fourier transform infrared spectrometer (NICOLET 6700). The change of $SiO_2@TiO_2$ core-shell colloids suspensions under different electric field was measured on a semiconductor inspection microscope (LEICA DM2500, Germany).The dielectric spectra of suspensions was measured by an impedance analyzer (HP 4284A) in the frequency range of 10^1~10^6 Hz using a measuring fixture (HP 16452A) for liquids at room temperature.

3 Results and discussion

Fig.1 shows TEM images of SiO_2, ST, STS particles. The diameter of SiO_2 core is about 90 nm. The thickness of the TiO_2 is about 7 nm. Fig.2 is the line scanning along the diameter of STS, It turned out that STS particles have a three layer construction.

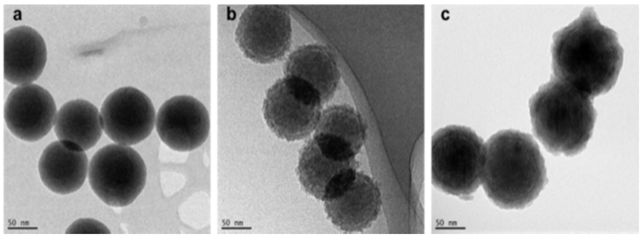

Fig.1 TEM images of a) SiO_2, b) $SiO_2@TiO_2$, c) $SiO_2@TiO_2@SiO_2$.

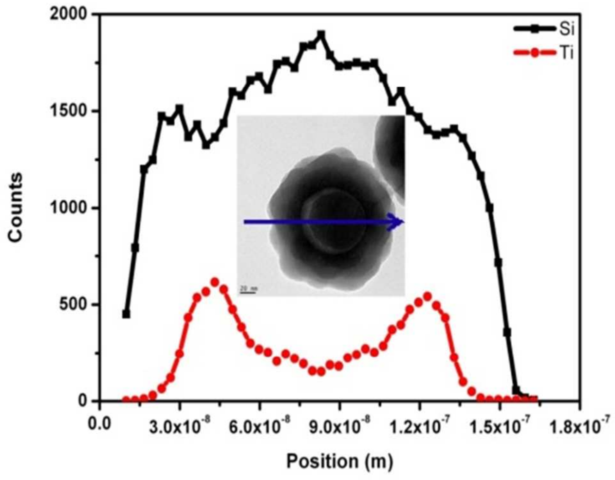

Fig.2 Line scanning along the diameter of $SiO_2@TiO_2@SiO_2$.

We use the X-ray photoelectron spectroscopy (XPS) to measure ST and $SiO_2@TiO_2$ modified by PVA (ST-PVA). From Fig.3 we can see that the combination modes of C in the ST include C-Ti

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(282.2 eV)，C-H (283.93 eV)，C-Si (282.6 eV)，C-O (286.2 eV) by means of XPS peak differentation, while there exists C-Ti (282 eV)，(C*H_2-CH_2)n (283.5 eV)，C-C，C-H (284.6 eV)，C-O (286.2 eV) in the ST-PVA. By comparing the combination modes of C in the ST and ST-PVA, there are significantly more bond of C-C, C-H and C-O in ST-PVA, because the structure of PVA is mainly made by C-C, C-H, C-O, so we can safely conclude that ST has been modified by PVA successfully.

The surface zeta potential of the SiO_2@TiO_2 particle was found to be around –40 mV. When SiO_2@TiO_2 particle was modified with PDDA, the zeta potential value reached about +70 mV, which proves SiO_2@TiO_2 was effectively covered with PDDA. After coating with silica again, the zeta potential value was about –40 mV. In addition, the zeta potential value of ST-PVA was about –40 mV.

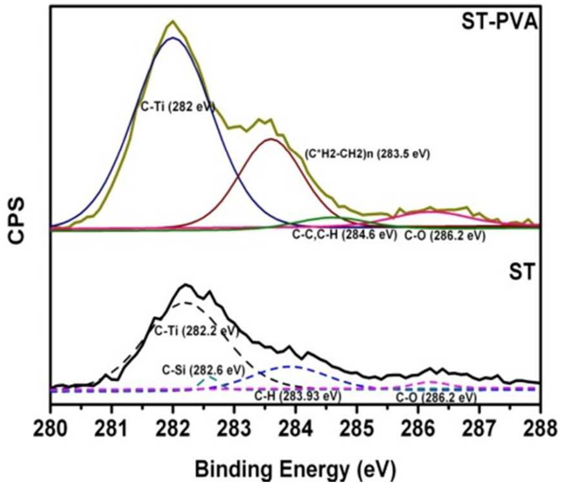

Fig.3 X-ray photoelectron spectroscopy of ST and ST-PVA. (Color on the line)

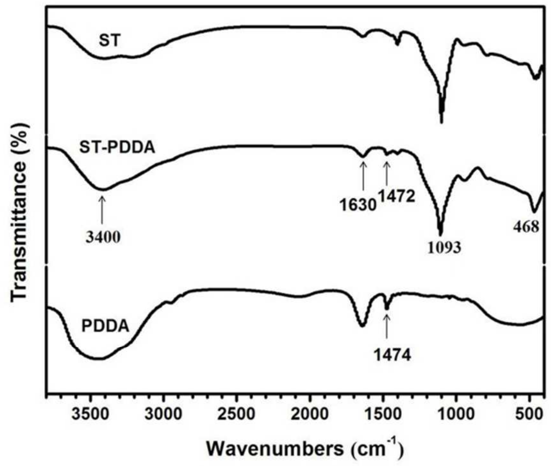

Fig.4 FTIP spectra of ST, ST-PDDA and pure PDDA

As shown in Fig. 4, the bands around 1093 cm^{-1}(ST and ST -PDDA) are originated from the stretch of Si–O–Ti ,and the absorption peaks for the ST and ST-PDDA at 468 cm^{-1} is assigned to the Ti-O vibration[12], whereas the peaks around 1630 and 3400 cm^{-1} are attributed to the absorbed water and hydroxy groups. The bands around 1474 cm^{-1}(PDDA) and 1472 cm^{-1}(ST-PDDA) are originated from the stretch of C–H, However, this kind of absorption peak doesn't exist in the FTIR spectra of ST, This result indicates the presence of PDDA molecules in ST-PDDA. Moreover, it is notable that the stretching band of C–H at 1474 cm^{-1} for pure PDDA is shifted to 1472 cm^{-1} for ST-PDDA, which suggests that PDDA molecules may be adsorbed on the surface of ST particles by chemical bonding.[13]

As seen from the reflection spectra in Fig. 5, it shows a dramatic difference between the four kinds of particles. For the ST and ST-PVA, the position of peak maximum is changed obviously with the increasing of the electrical field; the position of peak of ST-PDDA has a smaller variation. It is an interesting fact, however, the peak position of STS maintained almost during whole cycle.

The different response to the electrical field is due to the distinct surface properties of four kinds of nanoparticles which could be characterized by the zeta-potential. The zeta-potential of the ST-PDDA reached about +70 mV at a pH near 7, so the particles aggregate on the negative electrode after applying electric field at and beyond 2 v. Just as shown in Fig. 4b, the reflection peak maximum value is decreasing sharply after a positive voltage of 2 v was applied. While the zeta-potential of other three kinds of particles is about -40 mV at a pH near 7 which is not enough for the particles to aggregate on the relative electrode after applying electric field. Just as shown in Fig.6, when a 3 v electric field is vertically applied, a mass of aggregations of colloidal particles can be observed only for ST-PDDA. However, the other particles are still well dispersed at 3 v electric field, which is consistent with the result of Fig.5.

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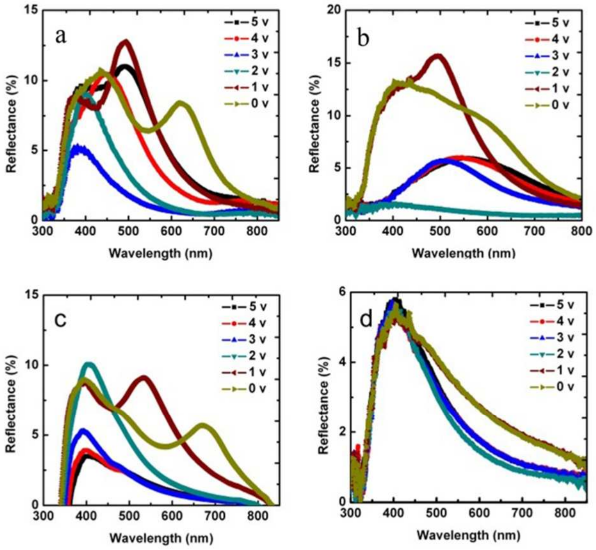

Fig.5 Reflection spectra of a) ST, b) ST-PDDA, c) ST-PVA, d) STS

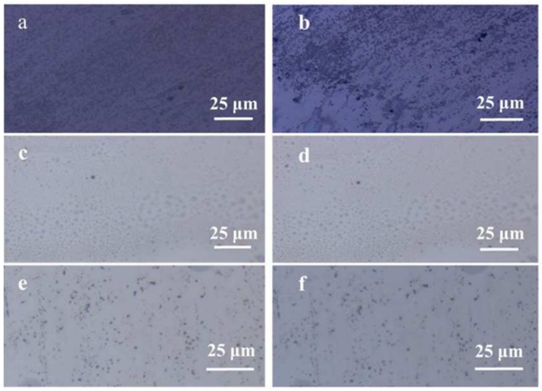

Fig.6 The photomicrograph of colloids suspensions at different electric field. ST-PDDA a) 0 v, b) 3 v, ST-PVA c) 0 v，d）3 v，STS e) 0 v, f) 3 v.

The peak maximum of ST-PVA is red shifted about 50 nm comparing with the reflection spectra of the ST particle suspensions. This data offers good evidence that the particle spacing increased after grafting by PVA. According to Fig.6 d, we can also come to this conclusion. It shows a long-range steric repulsion sufficiently strong to counteract the electrical attractive force. The other three kinds of particles are based on electrostatic repulsive forces which is weaker than the steric repulsion. The electrophoretic movement of colloids would lead to the flow of the medium and appear as boundary lines (Fig.6b, Fig.6d), but it doesn't exist in Fig.6f, this result indicates that electrode field has almost no effect on directed self-assembly.

There is interfacial polarization for the particles when applying electric field. STS has the most interfaces among the four kinds of particles, so the total polarization rate is the minimum because the masking will occur. The conclusion can be confirmed by the following dielectric spectra.

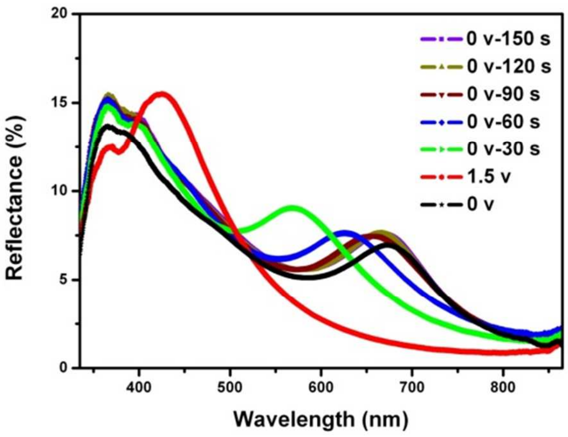

Fig.7 Time-dependent reflection spectra of $SiO_2@TiO_2$ modified by PVA after turning off the DC power supply at 1.5 v.

As shown in Fig. 7, the reflectance peak almost returned to its original position after turning off the DC power supply at 1.5 v after 150 s. It suggests that the structure under the electric field is reversible. It has been known that the main difference between the ST and the modified ST. We study the property between them deeply in terms of dielectric measurements.

The dielectric spectroscopy of colloidal suspensions can provide critical insight into the electrokinetic properties of colloids, including their surface charge and electrophoretic mobilities[14, 15], key properties that determine a suspension's stability and its response to an applied electric field. This interest extends to understanding the polarization of colloidal particles in electric fields for directed self-assembly[16, 17]. According to the previous literatures, the Cole-Cole equation shown in the formula,

$$\varepsilon^* = \varepsilon' + i\varepsilon'' = \varepsilon'_\infty + \frac{\varepsilon'_0 - \varepsilon'_\infty}{1 + (i\omega\tau)^{1-\alpha}}$$

where ε^* is a complex permittivity of suspension, $\varepsilon_0'$and ε_∞' are the limit values of the relative permittivity at the frequencies below and above the relaxation frequencies, respectively, ω is an angle frequency, τ is a dielectric relaxation time denoted by

$$\tau = \frac{1}{2\pi f_{\max}}$$

(Where f_{max} is the frequency of the dielectric relaxation peak.)[18], and α is the scattering degree of relaxation time. $\Delta\varepsilon'$ ($\Delta\varepsilon'=\varepsilon_0'-\varepsilon_\infty'$) is related to the magnitude of polarization and τ is related to the rate of polarization. The polarization rate was considered to have an effect on the stability of interparticle interaction under electric field[19, 20]. Whether or not the stable interparticle

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interaction was maintained under electric field is determined by the polarization rate of dispersed particles[21].

Fig.8 is the comparation of the permittivity and the dielectric loss of SiO_2, ST, ST-PVA, ST-PDDA, and STS at 2 v. From this Fig.6, $\Delta\varepsilon'$ and f_{max} reduced in the order of ST, ST-PVA, ST-PDDA, STS. This means that the magnitude of polarization and the polarization rate reduced in the order. In terms of the Cole-Cole fitting in Fig. 7, it is noted that $\Delta\varepsilon'$ of the suspension with PVA shell is slightly smaller than $\Delta\varepsilon'$ of the suspension with TiO_2 shell. However, the value of τ of the suspension with PVA shell is significantly bigger than that of the suspension with TiO_2 shell. This indicates that the magnitude of polarization of the suspension with PVA shell is close to that of the suspension with TiO_2 shell, but the polarization rate of the former is much slower, so there is enough time to assembly for the suspension with PVA shell. However, too slow polarization rate was difficult to maintain stable interparticle interaction just as the STS shown in Fig.7. The polarization rate of the STS is lower than the ST-PVA which is not strong enough to maintain stable interparticle interaction, so the position of peak maximum is maintained.

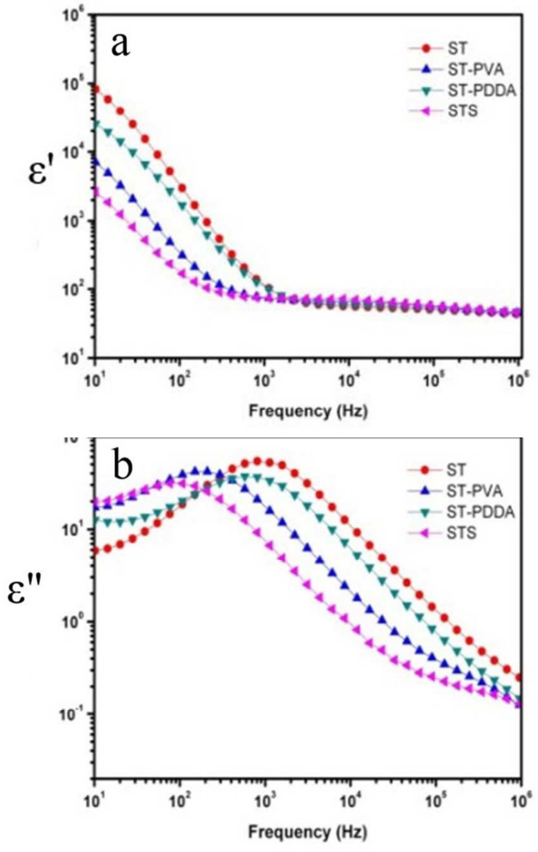

Fig.8 The comparation of the permittivity of ST (SiO_2@TiO_2), ST-PVA (SiO_2@TiO_2 modified by PVA), ST-PDDA (SiO_2@TiO_2 modified by PDDA), STS (SiO_2@TiO_2@SiO_2).

4 Conclusions

We obtain four kinds of particles with different surface properties by modifying the surface of particles by introducing Poly Diallyldimethylammonium Chloride (PDDA), Polyvinyl Alcohol (PVA), and silica. The reflectance spectrum of the suspension was measured under different electric field. It turned out that the suspension of particles with PVA shell has the best optical performance covers the whole spectrum. The dielectric spectrum is introduced to explain the effect of surface properties on the assembly deeply. It shows that the proper polarization rate is critical to the assembly of the particles under electric field. Too fast or too slow polarization rate was difficult to maintain stable interparticle interaction.

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