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ABSTRACT

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Nature has a lot of creature which possess exceptional color effect without the presence of any colorants. The vibrant color of butterfly wings or the glittering color of opal gemstone is the result of interaction of light with the structure present within colored area. Replicating those color effect paved the way of researching assembly of periodic nanostructured materials. In this particular paper, synthesis of polystyrene nanospheres has been discussed. Different parameters of emulsion polymerization were exploited to get particular size and distributed nanospheres which were then allowed to assemble. Substantial color effect was observed. For the characterization purpose scanning electron microscopy (SEM) was applied.

Key words: nanostructured materials, emulsion polymerization, SEM

INTRODUCTION

The manipulation of light is one of the unique characteristics of nature. In addition to functionality, most of the surfaces present in nature often produce vivid and iridescent colors. Nature has been producing photonic structures for producing brilliant color which is also known as structural color (Eadie and Ghosh, 2011). The unique vividness, transparencies, strongest white and deepest black shown by nature rely on ordered, quasi-ordered or dis-ordered structure, which have lattice constants or scattering element sizes on the order of the wavelength of the visible spectrum (Kolle *et al.* 2013). These sub-micrometer structures are referred to as biological photonic crystals (Kenkichi 2005). Usually structural color results from interference or diffraction. The main characteristic which is the determining factor for photonic crystals is the type of periodic structure with a band gap which forbids the propagation of a certain frequency range of light. So it always reflects the specific band width of visible light (Kertész *et al.* 2006). The natural structures which suits in this regard are butterfly wings, some plant species, marine creature (brittlestar) opals etc. (Vukusic and Sambles, 2003). Ordered assembly of colloids or colloidal microspheres has been studied extensively to mimic the opal structure as a route to photonic crystals and photonic band gap materials (Meseguer 2005) (Xia *et al.* 2000). Synthesis of polystyrene nanospheres of particular size and distribution has been optimized through emulsion polymerization parameters. After the colloidal particles were self-assembled the color appearance was observed. The assurance of particle size and distribution was obtained through SEM analysis.

Diffraction and color:

Diffraction is a form of scattering. Interaction of light with randomly ordered small particles makes the output rays less close in relationship. If the light interaction is with a more organized structure then the output waves have a close relationship to each other. In this criterion there is a chance for the waves to interfere constructively or destructively which is called diffraction. The color found in the surface of a CD, reflected patterns on banknotes or security logos are the result of diffraction (Tilley 2011). According to Nassau there are fifteen causes of color and diffraction covers a (Nassau 2001) huge potential area.

Bragg's law:

Determining the diffraction effect of crystals or crystal like structures needs the implication of Bragg's law. Atoms arranged in ordered array and forming a 3D grating is similar to small particles found in crystals. Diffraction of X-ray from the atoms has been studied to understand the diffraction feature of many crystals like structures. The main outcome of the law is the separation of atoms in crystal is similar to the wavelength of X-ray (Tilley 2011).

Photonic crystals:

Photonic crystals can be defined as materials where a periodic spatial modulation in the refractive index leads to coherent scattering of light and alters the propagation of wavelengths of light in proportion with the length scale of the periodicity (López 2003). In three dimensional photonic crystals there is a sufficiently high value of refractive index mismatch between the constituent phases, which delivers a full photonic band gap. This results in the inhibition of propagating specific wavelength range. The selection of material for photonic crystals is an important parameter. For polymer nanophotonics the low value of the refractive index difference results in full band gap material. Polymers are relatively cheap and can be functionalized for different end uses (Paquet and Kumacheva, 2008).

Opals:

These are mainly precious gemstones found in nature that diffracts light in the same way that ordinary crystals diffract X-rays. Colors found in opals are described as structural color in biology and physicists define them as

photonic crystal interaction with light. However there is a difference between photonic crystals and opals. Opals can be defined as the prototype of photonic crystal as they do not possess complete photonic band gap (Joannopoulos *et al.* 2008). In opals ordered packing of submicron particles can be found. As discussed earlier, 3D arrangement is mostly found in opals. When light interacts with such face-centered and closed packed structures, strong diffraction from each sphere plane can be observed. The propagation of light may be allowed or forbidden depending on constructive and destructive interference of diffracted beams respectively. The photon energies which lead to destructive interference resulted that light is diffracted backwards (photonic band gap). This is observed as a reflection in the reflectance spectrum and is responsible for the color (Stein *et al.* 2007). Core-shell structure is very popular for the manufacturing of opals. For the core particles, polystyrene is widely used because it can produce uniform spherical shape, high monodispersity and large particle size range (Deng and Marlow, 2012).

Emulsion polymerization:

Polymerization is the most widely used technique for the synthesis of organic core shell structure (Ghosh Chaudhuri and Paria, 2011). As the particles should be designed to particular size, Mini, micro and emulsion polymerization are the major three techniques currently used for synthesis of purpose based nanoparticles. Emulsion polymerization is mainly known for using surfactant to produce polymer nanoparticles but problems regarding removing the surfactant in subsequent polymerization paved the way to increased popularity of surfactant free emulsion polymerization (Rao and Geckeler, 2011). Emulsion polymerization is a free radical initiated chain polymerization where a monomer or combination of monomers is polymerized in an aqueous medium. The basic ingredients which can be found in an emulsion polymerization are water, surfactants, initiators and chain transfer agent. Nucleation period is the main controlling part for particle size and distribution (Lovell and El-Aasser, 1997). Monomer droplet nucleation is considered for emulsion free polymerization rather than micelles nucleation in conventional emulsion polymerization (Baharvand *et al.* 2013). For emulsion free systems; four parameters have been found by which the size of the particles can be controlled:

- Concentration of the monomer;
- Concentration of the initiator;
- Ionic strength of the reaction mixture;
- Temperature.

With increasing concentration of monomer, the diameter of the particles increased. The ionic strength bore the same effect. Increased initiator concentration decreased the particle size. If both the initiator and ionic strength were increased then the opposite effect cancelled out. There is a maximum limit up to which the ionic strength of the mixture can be raised, beyond that the mixture can coagulate. It was found that particle diameter can be predicted with some level of accuracy from an equation based on these four parameters. The temperature range was found to be between 55 and 90°C, in which particles of uniform diameter were produced. The system was able to produce particle sizes between 100-900nm (Goodwin *et al.* 1978).

Characterization technique:

Scanning Electron Microscopy (SEM) is the most commonly used technique for size and shape analysis of nanoparticles (Ghosh Chaudhuri and Paria, 2011). Good depth of focus and ease of sample preparation makes SEM very popular for morphological analysis (Fan *et al.* 2002).

MATERIALS AND METHODS

Spheres have been synthesized according to a single stage polymerization process based on formation and growth of polymeric nuclei dispersed in an emulsion constituted by water, styrene, potassium persulfate (KPS). The polymerization was carried out in all-glass reactors of 500ml reaction volume. All glass ware were subjected to piranha solution cleaning prior to any reaction. The reactor was equipped with a shaft and blade type stirrer, a reflux condenser, a water bath to control temperature and argon gas inlet. The reaction temperature was controlled at 80°C. The stirring speed was selected at 240rpm. At first 140ml of de-ionized water was taken into the reaction vessel. The heating was started to reach the reacting temperature. Styrene and divinylbenzene (DVB) was added at 62°C rather than in the beginning. The amount of styrene and DVB was 4ml and 0.4ml respectively. The DVB was used as a cross-linking agent which helped to make the nanospheres stiffer. The KPS (0.0306gm) was added at 76°C. Then after reaching at reaction temperature, the reaction was allowed to continue for 4 hours. After that time the heating was stopped. The stirring was allowed to continue for 18 hours. Then colloid suspension was taken into a glass surface to assist self-assembly and evaporation of water. The dried sample was subjected to SEM analysis for characterization purpose. Philips XL30 FEG SEM was used for microscopic analysis of the produced particles. Platinum coating was done on the samples of 1nm in thickness. The parameters which were maintained during analysis are; Beam- 6-7kV, Spot-2.0, Aperture-2 and magnification up to x150000.

RESULT AND DISCUSSION

The SEM image analysis (Fig. 1) showed that the average particle size was 182nm with quite wide size distribution (Fig. 2). The distribution plot was manually done with the help of Image J software.

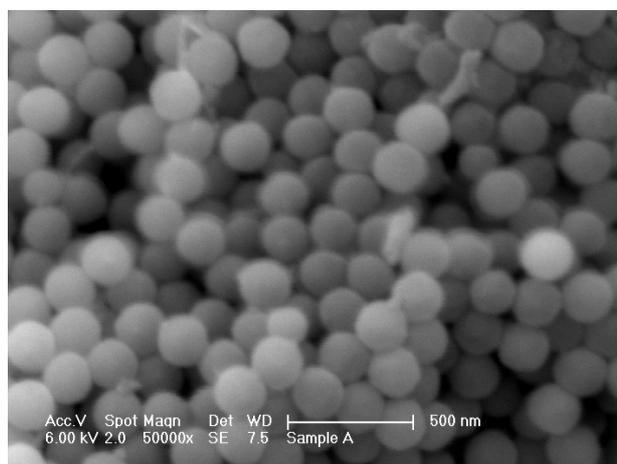


Fig. 1. SEM image of dried nanosphere assembly at 50000x

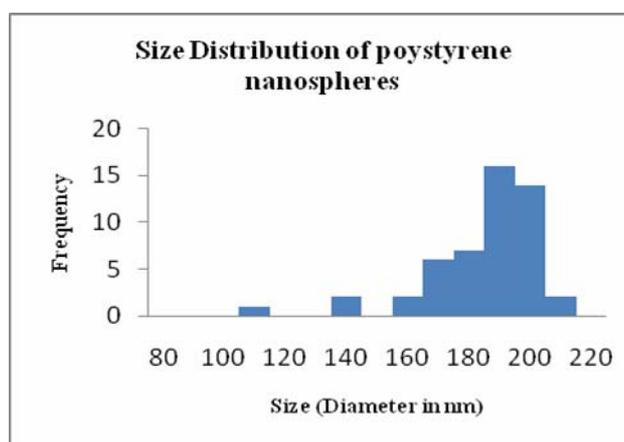


Fig. 2. Size distribution chart

The obtained result was output of combined optimization of some important parameters involved in emulsion polymerization. Surfactant free emulsion polymerization produces water resistant and adhesive particles, which cling to the glass wall of the reactor (Chern 2006). Particles are really difficult to remove from the glass walls. The mechanism of emulsion polymerization indicates that if any particle remains in the reaction area, it can change the rate of monomer consumption. The particle or contaminant can absorb the monomer and polymerization occurs. As a result fewer numbers of particles may be produced and size distribution becomes wide. To compensate for this, a piranha solution was used for cleaning the glass reactors prior to seed synthesis. A stricter control of the temperature is expected through out the reaction area lead to a narrow size distribution. In this approach a water bath was used. A large thermal mass works as a buffer for temperature. Small changes in different areas affect less in the reaction area. So the temperature is quite consistent in a water bath. The monomer/water phase ratio also has an effect on particle size and distribution. More available monomer can lead to large particle sizes (Smigol *et al.* 1992). A large thermal mass is known to have buffering properties against small temperature variations. A large volume of solvent therefore may act as an effective way to mask some of the temperature variations, unavoidable in the experimental set up and hence lead to an improvement in monodispersity. Large amount of solvent (water) was used in this method. The amount of monomer and initiator was standardized by changing ionic strength in different trials. Alongside these parameters some fine tuning of the process was also done which might had some effect in the monodispersed particle assembly. The monomers were added at 62^oC rather than the conventional system of adding them in the beginning. Heating while they are not reacting may change the surface tension in the droplets resulting in improper size and distribution. As KPS is dependent on heat to initialize the free radical reaction adding it just before reaching the reacting temperature can prevent secondary nucleation and proper utilization of monomers which is very essential for proper particle size and distribution. As the particle size was large enough to show color, a bright green appearance can be seen

(Fig. 3). Although the presence of milky white appearance is prominent in the dried assembly of structure due to the latex film formation. There might be some unreacted monomers because the initiator amount was at the minimum level. The improper size distribution was also liable for defective assembly of those nanospheres.



Fig. 3. Dried assembly of nanospheres in a watch glass

CONCLUSION AND FUTURE WORK

The color found through this process was encouraging. Further fine tuning may lead to increased particle size and narrow distribution of the particles which can produce brilliant color effect. At present the nano photonic materials are only used in electronics field. If this process develops further then other coloration areas may be exploited like textile coloration through nano photonics materials. The key finding of this work is, particle size and distribution is the key for producing structural color effect. The polymerization parameters can be optimized to obtain correct size and distribution.

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