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Modeling and evaluation for encapsulation efficiency of zircon-based heteromorphic encapsulation pigments

Binglong Lei, Wu Qin, Guilan Kang, Cheng Peng, Jianqing Wu*

School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

Zircon-based heteromorphic encapsulation pigments have been widely investigated and applied since 1970s and the issue concerning their low encapsulation efficiency has however not been intensively explored by researchers. In the current investigations, we established a heteromorphic encapsulation modeling upon series of hypotheses and preconditions and correspondingly proposed a theoretical function $\alpha_{max} = [1 - (k + 1)(D/L)]^3$ for encapsulation efficiency evaluation. The function has presented different encapsulation efficiencies for the pigments with varying *k-D-L* constitutions and meanwhile indicated a most effective approach for efficiency elevation by size reduction of pigmental cores. Demonstrations for higher efficiency were comparatively conducted by two representative CdS@$ZrSiO_4$ pigments, in which finer pigmental cores had endowed the semi-products and final pigments with remarkable encapsulation elevation by 64.39% and 24.65% respectively. The modeling has also exhibited that it is approachable for higher efficiency in excess of 12% if superfine pigmental cores can be guaranteed during the encapsulation process.

1. Introduction

Zircon-based pigments were initially revealed by C. A. Seabright before 1970s [1–3]. Since then numerous high-temperature inorganic pigments have been developed and most have acquired widespread industrial applications for their excellent thermal stability, strong tinting strength, brilliant hues and abundant chromaticity. According to the correlation between coloring centers (chromophores or pigmental cores) and the encapsulating body, zircon-based pigments can be classified into two categories as zircon-based ion-substituted pigments (ZBIS, such as Pr–$ZrSiO_4$ yellow and V–$ZrSiO_4$ blue pigments) [4–7] and zircon-based heteromorphic encapsulation pigments (ZBHM, namely encapsulated or inclusion pigments) [8–10]. The latter kind of pigments are also denominated as heteromorphic pigments [11] mainly due to the coloring effect deriving from nano-to-micron sized chromophores other than from doped ions' entry into zircon lattice as in the ZBIS pigments [11–13]. This property has given rise to distinct differences in synthetic procedures between the two kinds of pigments. Delicate control should be guaranteed for ZBHM pigments so that pigmental cores can be well preserved against oxidation and pyrolysis before zircon formation at high temperatures and more cores as possible are included into zircon matrix for sufficient tinting strength.

According to literatures and current industrial applications, ZBHM pigments have primarily comprised ZnS/CdS@$ZrSiO_4$ for brilliant yellow hues, CdS_xSe_{1-x}@$ZrSiO_4$ for series of bright red-to-yellow hues [9,14], Fe_2O_3@$ZrSiO_4$ for pink hues [8,15–18], carbon-black@$ZrSiO_4$ for black hues [19,20], SnS/MoS_2@$ZrSiO_4$ for gray hues, *etc*. These pigments commonly function with sulfides or sulfoselenides, metal oxides, carbon-black or the other high-temperature unstable colorants as pigmental cores that can selectively adsorb and reflect visible light to generate varying hues but usually themselves can not withstand temperatures above 800 °C. A subsequent encapsulation of these chromophores into zircon matrix, as a robust protecting body, will produce numerous pigments with super thermal stability. If more chromophores should be encapsulated into per unit volume of matrix, resultant pigments will possess stronger tinting strength even when they are less applied for ceramic-ware decoration. Meanwhile, higher encapsulation efficiency also makes it possible to further reduce pigment sizes for more saturated hues and also qualify these pigments for advanced applications, such as digital decoration instead of noble metal pigments [21–23].

Among the ZBHM pigments, sulfide or sulfoselenide pigments have acquired most widespread industrial applications, whereas

* Corresponding author. Tel.: +86 20 87111669.
E-mail address: imjqwu@scut.edu.cn (J. Wu).

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the chalcogenide pigmental cores usually possess inferior thermal stability to oxide pigmental cores or carbon black. The representative chalcogenide ZBHM pigments, $CdS_xSe_{1-x}@ZrSiO_4$, are still stagnating at a low encapsulation efficiency of about 7–12% since it was first revealed by A.C. Airey [24,25]. The dissatisfactory efficiency is mainly attributed to the random and probabilistic encapsulation of zircon matrix to pigmental cores and it has not only restricted pigments' tinting quality from further promotion but also caused excessive consumption of raw synthesis materials. It is of great significance to elevate encapsulation efficiency for ZBHM pigments and eliminate their current disadvantages for further advanced applications.

It has been reported that for the red-to-yellow $CdS_xSe_{1-x}@ZrSiO_4$ pigments there exists an extreme encapsulation efficiency of about 7.48% obtained by a polyhedron modeling.[22] However, the efficiency retrieved from the modeling can not justify the existing higher values from industrial or experimental pigment products since it had applied over-simplified preconditions and omitted the correlation of zircon matrix and pigmental cores. Except this initiative research, to date, comprehensive and systematic investigations into encapsulation efficiency for ZBHM pigments are still in scarcity, though some researches [10,25–27] have involved a few sporadic and brief mentions or interpretations to some specific ZBHM pigments such as $Fe_2O_3@ZrSiO_4$ and $CdS_xSe_{1-x}@ZrSiO_4$. Meanwhile, the unique and nearly irreplaceable ZBHM pigments have acquired ever-increasing demands in recent years and manufacturing under improved encapsulation efficiency will be extremely desirable for both industrial manufacturers and pigment consumers. It is therefore highly urgent to investigate encapsulation efficiency and propose practical improvements for pigment production and application hereafter.

Based upon series of preconditions and hypotheses, a tridimensional modeling of core–shell ZBHM pigments has been established. Further demonstration for higher efficiency was conducted by one particular but representative ZBHM pigments, $CdS@ZrSiO_4$, in which much smaller pigmental cores were applied from a delicate step-by-step sol–gel route. The encapsulation efficiency in this system has been significantly promoted. We correspondingly extended the encapsulation efficiency modeling and conclusions to the other ZBHM pigments which share the common core–shell heteromorphic property with $CdS@ZrSiO_4$ and involved less synthesis restrictions.

2. Experimental

2.1. Chemicals and materials

Sodium silicate pentahydrate ($Na_2SiO_3\cdot5H_2O$), zirconium oxychloride octahydrate ($ZrOCl_2\cdot8H_2O$), sodium sulfide nonahydrate ($Na_2S\cdot9H_2O$) and cadmium sulfate hydrated ($CdSO_4\cdot8/3H_2O$) were purchased from China Guangzhou Chemical Company. These starting materials were directly used without any pretreatment. A liquid surfactant PAAS (Polyacrylic acid sodium salt, Mw ≈400–600) was purchased from China Tianjin Chemical Company and had been modified by HCl before usage. Deionized water with resistivity of 18.2 MΩ was applied from a water purifier.

2.2. Syntheses of ZBHM pigments

Two kinds of synthesis approaches for $CdS@ZrSiO_4$ were applied according to the encapsulation efficiency modeling for ZBHM pigments. The former synthesis below applied a delicate sol–gel route which had been designed for ultrafine chromophores to be encapsulated, whereas the latter synthesis had applied the typical co-precipitation route which as an established method had been widely applied for industrial ZBHM pigments.

2.2.1. Synthesis by the step-controlled sol–gel route

A 400 ml solution (N) with 86.91 g $Na_2SiO_3\cdot5H_2O$ was first prepared and then 2.4 g PAAS as surfactant was added in and homogenization was maintained for 5 min by magnetic agitation. Another solution (M) was meanwhile prepared by mixing 21.94 g $CdSO_4\cdot8/3H_2O$ and 120.00 g $ZrOCl_2\cdot8H_2O$ into 700 ml deionized water, and then Solution N was pumped into M at a slow rate. Another solution of 20.58 g $Na_2S\cdot9H_2O$ in 300 ml deionized water was meanwhile prepared and afterwards slowly pumped into the above white sol. The reddish yellow sol (labeled as A-Semi, hereinafter also referred to its dehydrated product) obtained was subsequently washed for 5–6 times till chloride's depletion and dried at 110 °C overnight. The semi-product was mixed with 7.0 wt% LiF and then directly calcined at 1050 °C for 30 min, followed by washing with nitric and sulfuric acids for 3–4 times around. The final pigment product of $CdS@ZrSiO_4$ after drying was labeled as ZA. The molar ratio of Zr/Si was invariably maintained at 1.0:1.1 for the current and below syntheses.

2.2.2. Synthesis by the coprecipitation route

Four 250 ml solutions respectively with 86.91 g $Na_2SiO_3\cdot5H_2O$, 21.94 g $CdSO_4\cdot8/3H_2O$, 120.00 g $ZrOCl_2\cdot8H_2O$ and 20.58 g $Na_2S\cdot9H_2O$ were simultaneously added into the reaction container with 400 ml deionized water as base solvent while in agitating (one of the four solutions can also directly serve as the base solution). After depletion of the four solutions and homogenization for 10 min, the yellow sol (labeled as B-Semi) obtained was subsequently washed for 5–6 times and dried at 110 °C overnight. The semi-product was identically treated with A-Semi and the final pigment obtained was labeled as ZB.

2.3. Characterization

X-Ray diffraction (XRD) patterns were recorded in the range of 10–90° on an X-ray diffractometer (PANalytical X'pert PRO, Almelo, Netherlands) by Cu Kα radiation (40 kV, 40 mA). The morphology was observed by SEM (EVO 18, Carl Zeiss AG, Oberkochen, Germany). Size distributions of sample particles diameters were measured by a laser scattering particle size analyzer (BT-9300S, Dandong, China). A visible spectrophotometer (D65 illuminant, X-Rite Color 8200, Grandville, USA) was applied for chromaticity characterization and reflective optical spectra were measured from 400 nm to 700 nm and hues were evaluated according to Commission Internationale de l'Elcairage (CIE) system and the $L^*a^*b^*$ parameters (L^*, lightness; a^*, red hues from green (−) to red (+); b^*, yellow hues from blue (−) to yellow (+)).

3. Results and discussion

3.1. Preconditions and hypotheses for modeling

For ZBHM pigments, chromaticity and encapsulation efficiency are two of most significant indexes for pigments' performance in decoration. With the increase of chromophores encapsulated in zircon matrix and sufficiently protected by it, final pigments will be endowed with higher content of pigmental cores and better chromaticity. Higher encapsulation efficiency makes it possible to reduce consumption of raw materials and also enables final pigments to be pulverized into finer products for advanced applications. It is of remarkable significance to explore the correlation between zircon matrix and pigmental cores such as ZnS, CdS, MoS_2, CdS_xSe_{1-x}, Fe_2O_3 and carbon-black, *etc* [25]. We established the