The color rendering and near infrared reflection properties of coated iron oxide green pigments

Minhong Xu, Yuhua Guo, Guoxiang Pan[*], Qiang Shen, Mengyu Zhou, Qiu Liang

Department of Materials Engineering, Huzhou University, Huzhou 313000, P.R. China

Abstract

In this study, a novel iron oxide green pigment (FePc), composed of phthalocyanine blue (CuPc) and iron oxide yellow pigments (FeOOH), was prepared by intermittent stirring. The FePc was coated with the hydrolysate of sodium metasilicate and silane coupling agent KH602. The structure and properties of prepared pigments were characterized by TEM, SEM, XRD, FT-IR, XPS, and TG-DTA techniques. The aspect ratio of FePc decreased compared to FeOOH. XPS analysis showed that CuPc and FeOOH were bound by hydrogen bonds. The thermal decomposition temperature of the coated pigments increased from 266 ^{o}C to 314 ^{o}C, and the color difference ΔE of pigment was 1.623 after baking at 240 ^{o}C for 30 min, indicating the prepared pigments had excellent heat resistance. The surface modification of FePc improved their hydrophobicity and dispersibility in organic media. The pigments with CuPc/FeOOH ratio of 0.2 exhibited well color properties (L^*=55.44, $a^* = -9.9$, $b^* = 6.63$), and green tone. The coating and surface modification had little impact on a^* value. Particularly, all the newly prepared green pigments displayed high NIR reflectance. The prepared pigments have high heat resistance and dispersion properties, and are expected to be used in fields such as plastics and high-temperature coatings.

---

* Received

Corresponding author, Guoxiang Pan, Email: pgxzjut@163.com

1. Introduction

The existence of natural dyes and pigments makes the world rich and colorful. However, natural dyes or pigments extracted from plants and animals exhibit a lack of stable color tone, poor chemical durability and thermalstability when subjected to heating, light, and chemical substances [1]. As a result, people have also attempted to synthesize pigments with different colors through various methods. Various shades of green pigment are reported such as uvarovite ($Ca_3Cr_2(SiO4)_3$)[2], Cr-doped $BiPO_4$[3], Cr_2O_3/SiO_2 composite pigments [4]. These green pigments contain chromium ions. More importantly, chromium ions exhibit five valence states from +2 to +6, which transition to divalent or trivalent cations as the environment changes, ultimately leading to uncertainty in the color of the pigment [5]. In addition, among various oxides, chromium has multiple oxidation states, and Cr single bonds and O valence bonds can change under changes in temperature and/or oxygen partial pressure, thereby affecting the color tone of Cr based pigments. In actual production, the color tone of Cr based pigments is also difficult to control [6]. Other green pigments such as Scheele's green ($CuHAsO_3$) and Emerald green ($Cu(CH_3CO_2)AsO_3$), despite their high light-fastness, excellent price-performance ratio, brilliant hue, and high thermal stabilities [7], contain arsenic, making them undesirable. More importantly, inorganic green pigments are difficult to use in the high-temperature paint coating field. In addition, organic green pigments mainly consist of phthalocyanine green, which has well light and weather resistance, strong coloring power, bright color, small color difference, good color spreading and fluidity [8, 9]. However, the price of phthalocyanine green pigment is relatively high. Therefore, there is an urgent need to

2

49   develop environmentally friendly and cost-effective green pigments.

50   Preparing green pigments through color blending is also a new approach. Through

51   the subtractive method in the principle of color mixing, it is found that green pigments

52   can be prepared by blending yellow and blue pigments. Commonly used yellow

53   pigments include doped ZrO_2, $(Bi,Ca,Zn)VO_4$, $BiVO_4$-$GdPO_4$, Ce substituted $SrMoO_4$

54   [10-13]. Goethite (α-FeOOH) is a common and stable iron oxide present in natural

55   environment [14]. So far, due to the advantages of chemical stability, non-toxic and

56   low cost, α-FeOOH has been extensively studied in water purification, organic

57   pollutant degradation, coatings, pigments and other fields [15-18]. Regarding blue

58   pigments, there are Han blue ($BaCuSi_4O_{10}$) and Maya blue used a long time ago [19],

59   as well as Cerulean blue ($CoSnO_3$) and Prussian blue ($Fe_4[Fe(CN)_6]_3$) used in

60   currently[20-22]. Another type of blue pigment is organic blue pigment, such as

61   phthalocyanine blue. Phthalocyanine blue is an important organic pigment with bright

62   colors and strong coloring power [23, 24]. The preparation of green pigments using

63   inorganic iron oxide yellow pigment and organic blue pigment phthalocyanine blue as

64   raw materials is very challenging. It is necessary to consider the combination between

65   organic and inorganic pigments and the color rendering performance.

66   It's important to note that ordinary iron oxide yellow pigment α-FeOOH begin to

67   dehydrate at 177 ^{o}C and continue to dehydrate to become Fe_2O_3 between 270 ^{o}C and

68   320 ^{o}C, thus changing the color of pigment and affecting its application in high

69   temperature occasions [25, 26]. Therefore, it is necessary to improve the heat

70   resistance of the new green pigments synthesized from α-FeOOH, so that it can meet

71   the requirements of the coating of the coil material with the heat-resistant temperature

72   between 210 and 250 ^{o}C. On the other hand, it is also necessary to improve the

73   compatibility of synthesized green pigments with organic matrix and the wettability

3

74   of the matrix in order to broaden the application of synthesized green pigments in

75   high temperature coating industry such as plastic processing and coil coatings.

76   Recently, the focus of pigments formulators has shifted to develop materials with high

77   near-infrared reflectivity (NIR) while maintaining their appropriate spectroscopic

78   features that impart colour in the visible spectrum [27, 28]. The NIR refective

79   pigments have significant advantages in thermal protection of containers, ceiling

80   coatings, and storage room surfaces to reduce the use of air conditioning.

81   In this work, inorganic FeOOH was used as the core, organic phthalocyanine blue

82   pigment was coated externally to prepare composite green pigment (FePc). The FePc

83   was modified to improve its heat resistance, and finally surface modification was

84   carried out with a coupling agent to improve the dispersion performance of pigments

85   in organic media. Besides, the prepared pigments were characterized by multifarious

86   tools to study crystal structure, morphological characteristics, color coordinate values

87   and optical performance. In addition, studied the heat resistance, coloration, and

88   dispersion properties of pigments to evaluate their application. More importantly, the

89   coloration mechanism and near-infrared reflectance performance based on spectral

90   analysis have been further investigated.

91

92 **2. Experimental Section**

93 *2.1Materials*

94   Phthalocyanine blue pigments (CuPc, C.I.pigment bule 15：3), were purchased

95   from Shandong Yousuo Chemical Technology Co., Ltd. Iron oxide yellow pigments

96   (FeOOH), were provided by Zhejiang Huayuan Pigments Co., Ltd. Sodium silicate,

97   dilute sulfuric acid, silane coupling agent KH602, etc. were analytical purity and were

98   purchased from East China Pharmaceutical Co., Ltd. All solutions were prepared with

4

99   distilled water.

100   *2.2 Preparation of coated iron oxide green pigments*

101   Weigh the pigments according to the mass ratio of FeOOH to CuPc was 5:1. The

102   pigment was put into a high-speed pulverizer for mixing. After mixing for 1min, stop

103   for 1 min, and then continue mixing. The final mixing time was 10 min. The iron

104   oxide green pigment was obtained and marked as FePc.

105   The preparation of coated FePc was follows: FePc (10g) was added in 350 mL

106   distilled water, then dispersing for 10 min with ultrasound to get suspension. Under

107   water bath at 70 °C, the aboved suspension was stirred at 300-400 rpm. Certain

108   quality of sodium silicate solid, which was calculated by the mass of silicon dioxide

109   and the mass was 8% of the mass of FePc, was put into another beaker, and 200 mL

110   of water was added to make it completely dissolved. Then the above solution was

111   placed in a constant pressure funnel and dropped into the FePc suspension at a

112   constant rate of 1 d/s, with a dripping time of about 60 min. After dropping, adjust the

113   pH value of the solution to 8 with sulfuric acid, and continue stirring for 0.5 h. During

114   this process, the pH value remained unchanged. Finally, the precipitate was filtered,

115   washed with distilled water for three times and then dried at 70°C for 15 h. After that,

116   the above product was identified as FePc@SiO$_2$.

117   Coated FePc@SiO$_2$ was modified with silane coupling agents KH602. 5g

118   FePc@SiO$_2$ was added in 250 mL distilled water, then dispersing for 10 min to get

119   suspension. In water bath 80 °C, the aboved suspension was stirred at 300-400 rpm.

120   The KH602 (8%, based on the quality of FePc@SiO$_2$) was dissolved in 50mL

121   distilled water, slowly dropped into FePc@SiO$_2$ suspension, and stirred for 90 min.

122   Finally, the precipitate was filtered, washed with distilled water for three times and

123   then dried at 70°C for 15 h. After that, the above product was marked as

5

124　FePc@SiO$_2$-M.

125　*2.3 Characterizations*

126　　Scanning electron microscopy (SEM) analysis was performed on a Hitachi Model

127　S-3400N electron microscope operated at an accelerating voltage of 15 kV.

128　Transmission electron microscopy (TEM) images were taken on a FEI Tecnai G2 F20

129　electron microscope. X-ray diffractometer (Cu Kα, λ=0.1545 nm, pipe voltage 36 kV,

130　pipe current 20 mA) (Beijing Purkinje General Instrument Co., Ltd., China). Infrared

131　spectra were recorded using the KBr disc method on a 5700 FT-IR spectrophotometer

132　(Nicolet, USA). X-ray photoelectron spectroscopy (XPS) spectra of the solids were

133　collected using a 250XI K-alpha spectrometer (Thermo Fisher Scientific), with a

134　monochromatic Al Ka radiation source and a hemi-spherical electron analyzer.

135　Survey scans were recorded with a 500 μm spot size and a fixed energy pass of 100

136　eV, where energy step size was 1.000 eV. The thermal properties were measured by

137　simultaneous thermal analyzer SDT Q600 (TA instruments, USA), heating from the

138　room temperature up to 400 ℃ with a heating rate of 10 ℃/min. The wettability of

139　sample is evaluated by SZ-CAM series contact angle tester (Xuanzhun instrument).

140　Water droplets were deposited directly on the surface of the material and the water

141　contact angles (WCA) were measured. Three measurements were performed per

142　sample and averaged. The volume of the water droplet was 5 μL and the tip used was

143　a precision stainless steel tip.

144　*2.4 Color and UV-Vis-NIR measurements*

145　　The visible light absorption spectrum and NIR region (700–2500 nm) was recorded

146　by the UV-Vis-NIR spectrophotometer (Lambda 1050+, Perkin-Elmer). The CIE

147　LAB color data (*L**, *a**, and *b**) were calculated from the visible light reflection

148　spectrum by color CIE software (Perkin-Elmer, CIE D65 photo source, and 10

6

149 observation angle; the calculated spectrum range was 400–700 nm)[30]. The NIR

150 reflectance (R) in the wave□length range of 700 nm to 2500 nm can be calculated by

151 the following formula:

152
$$R = \frac{\int_{700}^{2500} r(\lambda)i(\lambda)d\lambda}{\int_{700}^{2500} i(\lambda)d\lambda} \tag{1}$$

153 where $r(\lambda)$ is the spectral reflectance ($W \cdot m^{-2}$) obtained from the UV–Vis–NIR

154 spectrophotometer and $i(\lambda)$ is the solar spectral irradiance ($W \cdot m^{-2} \cdot nm^{-1}$) obtained

155 from ASTM standard G159-98 [29]. NIR reflectance value was used to quantify the

156 solar radiation, evaluate their refective performance.

157   Calculation of the color diference (ΔE) after baking was used to evaluate the color

158 stability of pigments. The sample (2.0 g) was put into crucible, and baked at 240 ^{o}C

159 for 30 min. Then taken out and cooled to room temperature to measure the value of

160 color difference. According to Hunter's color difference formula [31]:

161
$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \tag{2}$$

162   Usually, ΔE is the value of color difference, ΔL is the lightness axis (positive is for

163 white and negative is for black). The parameters Δa (positive is for red and negative is

164 for green) and Δb (positive is for yellow and negative is for blue) indicate the hue or

165 color of the pigments.

166

167 **3. Results and discussion**

168 *3.1 Morphology analysis*

169 **Insert Fig. 1**

170   SEM images of FeOOH and the prepared FePc are displayed in Fig.1. The color of

171 FeOOH (Fig.1a) is obvious yellow, and it has a typical needle-like structure with a

172 length of about 2 μm, and a small amount of agglomeration between particles. When

7

173   CuPc and FeOOH are blended to prepare FePc, the FePc pigment shows obvious

174   green. The FePc are mostly rod-shaped, with a reduced aspect ratio and a reduced

175   agglomeration phenomenon. Comparing the morphology, the particle size and length

176   of FePc decreased, which may be caused by high speed stirring and shearing during

177   the preparation process.

178   Fig. 1c shows the multi-elemental EDS mapping images of C, N, O, Fe, and Cu in

179   FePc. The O and Fe elements come from FeOOH, the N element mainly comes from

180   N in the molecular structure of CuPc. Apparently, the corresponding N and Cu maps

181   illustrate a homogeneous distribution of these elements in the field of the

182   cross-section view. At the same time, it is also certified that the uniform distribution

183   of CuPc in iron oxide green pigment.

184   To further confirm the formation of the FePc@SiO_2 interface before and after

185   modification, the TEM analysis were performed. Fig. 2(a) is the TEM diagram of

186   FePc coated with silica. The surface of FePc is uniformly coated with a thin coating

187   layer, and the thickness between 3.2 and 4.3 nm. This layer may be SiO_2, indicating

188   that SiO_2 has been uniformly coated on FePc surface.

189   The lattice fringes of FeOOH are clearly visible, and the spacing of (110) planes is

190   calculated to be 0.42 nm (Fig. 2b). From Fig.2c and Fig.2d, the KH602 is modified

191   successfully on FePc@SiO_2 surface, the coating layer is uniform, and the thickness of

192   coating layer is about 6 nm. In conclusion, the coating modification of FePc is

193   successfully realized using SiO_2 and KH602.

194   **Insert Fig. 2**

195   *3.2 XRD Characterization*

196   **Insert Fig. 3**

197   The XRD patterns of FePc, FePc@SiO_2 and FePc@SiO_2-M are shown in Fig.3.

8

198   The diffraction peaks at about $2\theta=17.8^{\circ}$, 21.2°, 34.7°, 35.5°, 36.6°, 53.1° and 59.0° are

199   correspond to crystal planes (020), (110), (021), (101), (111), (221) and (151),

200   respectively, which are consistent with the characteristic diffraction peaks and crystal

201   planes of FeOOH[32]. Using the Bragg's formula ($2d\sin\theta = n\lambda$) to calculate the

202   interlayer space d_{110} value of FeOOH, the d_{110} value is 0.4199nm. The diffraction

203   peaks of FePc and FeOOH are basically the same, and there are strong diffraction

204   peaks near 22 °(2θ), 33 °(2θ) and 37 °(2θ), with sharp peak patterns. This shows that

205   FePc has well crystal form and high crystallinity, which means that the original

206   crystal structure of FeOOH is not changed after compounding with CuPc.

207   Compared with the diffraction peak of FePc, there is no obvious characteristic peak

208   of SiO_2 in FePc@SiO_2, which means that coating layer SiO_2 exists in amorphous state

209   [33]. Furthermore, the positions of diffraction peaks of FePc@SiO_2-M are basically

210   the same as that of FePc@SiO_2. The crystal structure of FePc did not change during

211   the coating and surface modification processes.

3.3 FT-IR Characterization

213   **Insert Fig. 4**

214   The FTIR spectra of FeOOH, FePc@SiO_2 and FePc@SiO_2-M are shown in Fig. 4.

215   The absorption peaks (Fig.4a) of FeOOH at 3420 cm^{-1} are owing to surface adsorbed

216   water, and the strong absorption peak at 3125 cm^{-1} is attributed to the stretching

217   vibration of –OH in FeOOH. Four absorption peaks near 899, 796, 615 and 475 cm^{-1}

218   are characteristic absorption peaks of FeOOH [34]. The absorption peaks of CuPc at

219   1723 cm^{-1} and 1606 cm^{-1} are belong to the vibrational absorption peaks of C=C and

220   C=N in the phthalocyanine ring [35]. By analyzing the infrared spectrum of FePc, it is

221   found that the above two absorption peaks shift to 1799 and 1663 cm^{-1}. This result

222   may be due to the change of the electron cloud in the phthalocyanine ring, which is

9

223   caused by the physical and chemical interactions of the CuPc on FeOOH. Moreover,

224   the absorption peak at about 3420 cm^{-1} disappeared, but the absorption peak at 3125

225   cm^{-1} does not change, indicating that there are still hydroxyl groups on FePc surface.

226   Compared with FePc@SiO$_2$ (Fig.4b.), the absorption peak position of

227   FePc@SiO$_2$-M at 3100 cm^{-1} changed slightly. This may be due to the change of the

228   hydroxyl group on the surface of FePc@SiO$_2$, resulting in the change of the stretching

229   vibration absorption peak of -OH group. However, the change of FT-IR spectrum

230   before and after modification with KH602 is not obvious, which may be caused by

231   less coating amount.

232   *3.4 XPS analyses*

233   The XPS spectra with full-scan of prepared pigments are shown in Fig.5a. The

234   binding energies at about 724.7 eV, 711.5 eV, 529.7 eV, 398.5 eV, 285.7 eV, 154.15

235   eV, 103.5 eV, 91.1 eV and 52.7 eV are consistent with the electronic states of Fe2p,

236   O1s, N1s, C1s, Si2s, Si2p, Fe3s and Fe3p, respectively [36]. The XPS spectrum of

237   FeOOH shows three elements: O, C, and Fe. According to the chemical formula, only

238   O and Fe belong to FeOOH, while C comes from excess hydrocarbons in the

239   environment. The Auger resonance peak of O is in Fig.5a, but the area of the peak is

240   not large, indicating that a small amount of O$_2$ is attached to FeOOH surface. The

241   characteristic peaks of N1s, Cu2p1 and Cu2p3 in CuPc molecule appeare in the XPS

242   spectrum of FePc, and the intensity of the characteristic peaks of C1s increases. This

243   is mainly due to the ring structure of C, N and the central metal Cu in CuPc. When

244   FePc is coated with sodium silicate (FePc@SiO$_2$), it can be clearly seen that the peaks

245   of Si2s and Si2p are between 100-200 eV. When coated with KH602, the percentage

246   of C and Si in FePc@SiO$_2$-M decreases clearly, but the percentage of O significantly

247   increases. This is probably related with the elements of KH602 and atomic

248   composition of the interface layer of FePc@SiO$_2$-M.

249   The XPS spectrum of Cu2p (Fig.5b) shows that the binding energys of Cu2p$_{3/2}$ in

250 FePc, FePc@SiO$_2$ and FePc@SiO$_2$-M are 935.05 eV, 935.11 eV and 935.21 eV,

251 respectively. It is found that the binding energy of Cu2p$_{3/2}$ increases slightly,

252 indicating that the density of electron cloud around Cu atom increases, which is

253 caused by the effect of SiO$_2$ and KH602. Furthermore, compared with the C1s

254 binding energy of 285.7 eV, binding energy of C1s in FePc@SiO$_2$ (Fig.5c) is almost

255 unchanged. It shows that the binding mode between CuPc and FeOOH remains

256 unchanged after SiO$_2$ coated. After modification with HK602, the binding energy of

257 C1s is changed from 285.7 eV to 285.4 eV, which is mainly attributed to the C-O in

258 HK602. This indirectly confirms that the success of surface modification of

259 FePc@SiO$_2$ with HK602.

260   The tested samples have N1s main nitrogen peak at about 398.6 eV (Fig.5c-e),

261 which belongs to C-N bond. In addition, there is a weak π-π* satellite feature of the

262 shift several electronvolt of nitrogen-containing aromatic substances from the main

263 nitrogen peak near 400.3 eV [37]. The N1s binding energy in FePc@SiO$_2$ is 0.03 eV,

264 which is higher than that of FePc, implying the intermolecular force increases with the

265 increase of the electron cloud near N1s. The N element mainly comes from CuPc,

266 indicating that there is intermolecular force between the coating layer and CuPc after

267 coating. In additon, the binding energy of N1s about FePc@SiO$_2$-M continues to

268 increase (398.72 eV), which is due to the C-N bond in the molecular structure of

269 KH602. The above experimental results show that both coating and surface

270 modification can make the electron cloud near the N1s of FePc@SiO$_2$-M increases,

271 and the intermolecular force further increases.

272   **Insert Fig. 5**

273 **Insert Fig. 6**

274   As shown in Fig.6(a), about FeOOH, there are 3 peaks in the O1s fitting diagram,

275 and their binding energies are 529.65 eV, 531.05 eV and 533.21 eV, respectively.

276 Furthermore, the electron binding energy at 529.65 eV and 531.05 eV are ascribed to

277 the O in OH of FeO$\underline{O}$H and O in Fe$\underline{O}$OH, respectively, the results fit the feature

278 structure of FeOOH [38]. The binding energy at 533.21 eV is from the C-O bond of

279 air. Moreover, as shown in Fig.6(b), the O1s binding energy in FePc increases,

280 compared with that in FeOOH, which shows the ability of oxygen to lose electrons in

281 FePc is slightly reduced. According to the FT-IR analysis, the absorption peak of-OH

282 in FePc does not shift. Therefore, the shift of binding energy of O1s may be because

283 of the formation of hydrogen bond between O in Fe$\underline{O}$OH and H in the -C-H group of

284 CuPc ring, resulting in the change of electron cloud near the C=C and C=N groups in

285 phthalocyanine ring.

286   In Fig.6(c), there are also 3 peaks in the O1s fitting diagram in FePc@SiO$_2$, and

287 their binding energies are 529.9 eV, 531.21 eV and 532.58 eV, respectively. Also,

288 these 3 binding energies are respectively relative to the O in Fe$\underline{O}$OH, O in FeO$\underline{O}$H,

289 and O in C-O and Si-O bonds in the coating. Compare the C-O bond strength in Fig.6

290 (b), the binding energy of 532.58 eV is mainly attributed to the Si-O bond (SiO$_2$)

291 caused by SiO$_2$ coating on FePc surface. About FePc@SiO$_2$-M (Fig.6d), the binding

292 energy of Si-O in the O1s fitting peak slightly changes because of the existing of C-O

293 and Si-O bonds in KH602.

294   The binding energy of Si2p (102.77 eV) is less than that of SiO$_2$ gel which is

295 reported to be 103.5 eV. The change of Si2p binding energy implies that after coating

296 with SiO$_2$, there may be a large number of Fe–O–Si bonds on FePc surface. Base on

297 the fitting of Si2p of FePc@SiO$_2$ (in Fig.6e), there are 2 peaks at binding energy of

298   101.58 eV and 102.86 eV. The binding energies of 102.86 eV and 101.58 eV

299   respectively represent Si–O bond in SiO_2 and Fe–O–Si bond in the interface of layer

300   [33]. Fig.6(f) shows the curve fitting of Si2p of $FePc@SiO_2$-M. It follows that Si2p

301   has three peaks at 100.25 eV, 101.89 eV and 102.81 eV, corresponding to Si–C in

302   KH602, Si–O–Fe and Si–O in coated FePc, respectively [39].

303   *3.5 Thermal analysis*

304   The thermogravimetric curves of FeOOH, and FePc before and after coating are

305   shown Fig.7(a). The thermal behaviour of FeOOH can be divided into two stages

306   during the entire heating process. One is the removal of adsorbed water on surface of

307   FeOOH within the range of 100 ℃–270 ℃, and the other is the weightlessness

308   between 270℃ and 340℃, which is caused by the removal of crystalline water on the

309   surface of FeOOH [40], and the total mass loss rate reaches 10.05%. Comparing the

310   decomposition of FeOOH, the weight loss of FePc is significantly faster between 350

311   ℃ and 400 ℃, and the maximum weight loss temperature is 373 ℃, which is mainly

312   due to the decomposition of CuPc. The TG curve of $FePc@SiO_2$ is similar to that of

313   FePc, and the mass loss rate of $FePc@SiO_2$ in the whole process decreases to 8.23%

314   and 10.21% respectively, implying that the mass loss rate of coated FePc decreases

315   owing to the outstanding heat resistance of coating layer of amorphous silica.

316   Moreover, The mass loss rate of $FePc@SiO_2$-M is 8.49% and 12.22% respectively.

317   This is because of the presence of KH602 on $FePc@SiO_2$ surface, the alkyl chain

318   structure of KH602 is susceptible to thermal decompose, as a result the mass loss rate

319   increases compared with $FePc@SiO_2$.

320   **Insert Fig. 7**

321   There is a mass loss peak in the range of 100-200 ℃, compared with DTG curves

322   (Fig.7b), implying that FeOOH gradually dehydrates in this range. The peak of mass

13

323 loss changs significantly between 250 °C and 350 °C. The mass loss peak position of

324 FePc, FePc@SiO$_2$ and FePc@SiO$_2$-M all moves to the high temperature, indicating

325 that their thermal decomposition temperature increases, compared with that of

326 FeOOH. The SiO$_2$ forms a dense coating layer on the surface of FePc, which hinders

327 heat transfer during heating. In addtion, after coating and surface treatment, the mass

328 loss peak of FePc is sharper than that of FePc@SiO$_2$ and FePc@SiO$_2$-M, that is the

329 decomposition of FePc is fastest within the same range.

330   Compared with the differential thermal analysis (DTA) curves of Fig.7c and Fig.7d,

331 the temperature of FeOOH endothermic peak is 306 °C, and that of FePc, FePc@SiO$_2$

332 and FePc@SiO$_2$-M are 309 °C, 310 °C and 314 °C, respectively. In particular, the

333 maximum thermal decomposition temperature of FePc@SiO$_2$-M is 435 °C (7c). The

334 results indicate that when FeOOH combines with CuPc to form FePC, its maximum

335 decomposition temperature and heat resistance are significantly improved. Combined

336 with the analysis of TEM, we believe that the function of SiO$_2$ coated on FePc surface

337 is to improve the heat resistance of FePc effectively. Moreover, the temperature of

338 endothermic peak about FePc@SiO$_2$-M in DTA curve is 314°C. Further more the

339 decomposition temperature increases slightly compared with that of FePc@SiO$_2$,

340 which is attributable to the presence of KH602 on the surface of FePc@SiO$_2$. During

341 the heating process, the KH602 is first heated and carbonized, and attached on

342 FePc@SiO$_2$ surface. In the subsequent heating process, the formed carbonization

343 layer blocks the heat transfer to FePc@SiO$_2$, so the thermal decomposition

344 temperature of FePc@SiO$_2$ increases. The above results strongly show that the

345 surface coated and modification successfully improves the heat resistance of FePc

346 pigment, the prepared green pigments are also expected to be used in the

347 high-temperature coating industry.

14

3.6 Hydrophobicity and dispersibility test

349   The water contact angle (WAC) test was used to evaluate the

350   hydrophilicity/hydrophobicity of the pigment surface, and the results are shown in

351   Fig.8A. The WAC of FeOOH is 7.79°, that is FeOOH has high hydrophilicity. This is

352   due to the presence of -OH groups on the surface of FeOOH, which makes the surface

353   of FeOOH hydrophilic. The WAC of CuPc is 84.19°, that is because the molecular

354   structure of CuPc is an organic macrocyclic structure composed of C, O and N

355   elements. The WAC of FePc is 86.38°, and the hydrophobic property is slightly

356   increased, compared with that of CuPc. The WAC of FePc@SiO$_2$ is reduced to 75.68°,

357   which is due to the existence of a lot of -OH groups on the surface of SiO$_2$ coating.

358   When SiO$_2$ is coated on the surface of FePc, the hydroxyl number of the FePc@SiO$_2$

359   increases, so the WAC decreases slightly. After modification with KH602, the WAC

360   of FePc@SiO$_2$-M increases to 91.14°, showing hydrophobic performance. This is due

361   to the carbon chain structure of the KH602. Although there is no obvious absorption

362   peak of alkyl chain of KH602 in FT-IR spectrum, the change of WAC of

363   FePc@SiO$_2$-M also indirectly confirmed that the FePc is coated with SiO$_2$, and

364   modified with KH602, successfully.

365   **Insert Fig. 8**

366   In order to further analyze the dispersion effect of FePc@SiO$_2$-M, industrial grade

367   samples iron green pigment (835 type) were used for dispersion comparison

368   experiments. Weigh 50 mg of sample and place it in 20 mL of water or chloroform

369   solution. After ultrasonic dispersion for 1 min, let it stand for 24h, and compare the

370   dispersion in different solvents. The results are shown in Fig.8B. Samples (a) and (b)

371   show the dispersion of 835 type and FePc@SiO$_2$-M in water, and samples (c) and (d)

372   show the dispersion of 835 type and FePc@SiO$_2$-M in chloroform, respectively.

15

373 Comparing the photos, it is found that in aqueous solution and chloroform solvent, the

374 dispersity of FePc@SiO$_2$-M is better than that of industrial 835 type. This may be due

375 to the presence of a large number of hydroxyl groups on the surface of FePc@SiO$_2$-M

376 after coating , which is conducive to improving dispersion in aqueous solutions. After

377 modification with KH602, there are carbon chains on the surface of FePc@SiO$_2$-M,

378 which is conducive to dispersion in organic solvents. Unlike inorganic green pigments,

379 the prepared green pigments are expected to be used in fields such as plastics and

380 coatings.

381 *3.7 Color Difference Analysis*

382 The color difference parameters and CIE coordinate diagram of coated and

383 modified pigments are shown in the Table 1 and Fig.9. When the ratio of CuPc to

384 FeOOH is 1:5, the L^* value is 55.44, and the a^* value reaches -9.9 (negative).

385 Comparing the a^* values of pigments, it is found that although the a^* values of CuPc

386 and FeOOH are greater than 0, after the above pigments are compounded, the a^*

387 values of FePc is negative and the pigments are green. Furthermore, comparing the

388 value of b^* , it is found that the b^* value of FeOOH is greater than 0, indicating

389 FeOOH has yellow phase, while the b^* value of CuPc is less than 0, indicating CuPc

390 has blue phase. After the combination of two pigments, the color b^* value was still

391 greater than 0, and there is still an obvious yellow component. About FePc@SiO$_2$

392 pigment, the value of L^* and b^* decreased slightly, while the a^* value increased

393 slightly but remained negative (-8.5). The results show that the brightness of the

394 FePc@SiO$_2$ slightly decreased, the blue tone increased, and it is still green tone but

395 the green color faded. This is because the SiO$_2$ coating layer is white, and the

396 presence of the coating layer reduces the brightness and green tone of the pigment.

397 The value of L^* and b^* of FePc@SiO$_2$-M are similar to that of FePc@SiO$_2$, but the

16

398 value of $a*$ increases. The color coordinate Hab^0 of the pigment changed from 166.72

399 to 159.21, indicating that the hue angles of the FePc@SiO$_2$-M is also lie in the green

400 region of the cylindrical color space. This indicates that after surface modification

401 with KH602, the brightness and yellow-blue tone of the FePc@SiO$_2$-M unchanged,

402 while the green tone slightly fades. The experimental results show that the KH602 has

403 little effect on the color of the FePc@SiO$_2$ pigment.

404   **Insert Table 1**

405   To quantify the differences in the color perceived by the human eye, color

406 coordinates were calculated for the pigments, as shown in Fig.9. In the CIE

407 chromaticity diagram (Fig. 9), point a (FeOOH) falls in the yellow area, while point b

408 (CuPc) appears blue. The pigments (c-e) fall into the yellow-green region in the CIE

409 coordinate, indicating that the color of the prepared green pigments is green tone. the

410 color coordinates of FePc and FePc@SiO$_2$ are coincide, the color coordinate of

411 FePc@SiO$_2$-M is biased towards the yellow-green region, but close to that of

412 FePc@SiO$_2$.

413   **Insert Fig. 9**

414 *3.8 Color stability*

415   In order to evaluate the heat resistance of FePc@SiO$_2$-M, the color stability of

416 samples before and after baking was measured. The results shown in Table 2. The

417 value of $L*$ slightly decreased, the $a*$ and $b*$ values slightly increased. According to

418 the color difference parameters of FePc@SiO$_2$-M before and after baking, the

419 calculated value of color difference ΔE is 1.623, and less than 5, which can meet the

420 industrial requirements for heat resistance of pigments. The experiment shows that

421 before and after baking, The color difference of FePc@SiO$_2$-M is not obvious, that is

422 FePc@SiO$_2$-M has excellent heat resistance and color stability.

17

423   **Insert Table 2**

424   The structure of the coating layer is closely related to the color change of the

425   pigment after being heated. The combination of FeOOH and CuPc reduces the $a*$

426   value and the pigment appears green. The presence of CuPc improves the heat

427   resistance of the pigments due to the initial decomposition temperature of CuPc being

428   430 $^{\circ}$C. When coated with SiO_2, the $a*$ value slightly increases, and the pigments

429   have a green tone. The coating layer SiO_2 inhibits dehydration, further improving the

430   heat resistance of the pigment. After surface modification with KH602, the $a*$ value

431   almost unchanged, and the pigment remains green tone. The coupling agent is

432   carbonized by heat during the high-temperature process, blocking heat transfer, and

433   effectively improving the heat resistance of the pigment. The prepared green pigment

434   overcomes the disadvantage of FeOOH being prone to color change at high

435   temperatures, and can maintain a green tone.

436   *3.9 Optical performance*

437   The minimum absorption peak of CuPc is 455 nm (blue light region) (Fig.10(a)),

438   the chromophore conjugation system of phthalocyanine is a polycyclic molecule

439   composed of four indoles, which contains a cyclic annulene with 18 electrons. In

440   addition, the minimum absorption peak of FeOOH is 583 nm (yellow light region),

441   but the minimum absorption peak of FePc is 537 nm. When these two pigments are

442   combined, according to the subtractive color-mixing principle [41], FeOOH absorbs

443   light near 350-450 nm that CuPc does not absorb; and CuPc absorbs light near

444   550-700 nm that the FeOOH does not absorb. The remaining light is only around 450

445   -550 nm, which is not completely absorbed by yellow and blue pigments. At the last,

446   this part of the light is reflected, and when we see it, it is a turquoise light. In addition,

447   the absorption peak position and intensity of the visible light absorption curve of the

18

448 composite pigment at about 667 nm have certain changes, compared to the visible

449 light absorption curve of CuPc. This indicates that the interaction between FeOOH

450 and CuPc occurs at the interface, which changes the coordination field splitting

451 energy.

452 **Insert Fig. 10**

453 The diffuse reflectance of prepared pigments at 300-2500 nm is depicted in

454 Fig.10(b). The reflectivity of FeOOH is high than that of CuPc, while the reflectivity

455 of composite pigments is between the above two pigments. After weighting treatment

456 by multiplying the experimental spectral reflectance with the normalized spectral

457 irradiance of the sun, the NIR reflectance (R) was obtained. The FeOOH exhibited a

458 NIR reflectance of 64.3%, while the NIR reflectance of CuPc is 53.9%. The

459 composite pigments FePc exhibited an enhanced NIR reflectance, which is ascribed to

460 the FeOOH. The high NIR reflectance (64.5%) of FePc@SiO$_2$ could be ascribed to

461 the multiple refection of lights on thin layers of SiO$_2$. However, the KH602 silght

462 decreased the NIR reflectance of pigment to 57.9%. Compared to the maximum NIR

463 reflectance of pure Cr$_2$O$_3$ (49.0%) [42], all the prepared green pigments show high

464 NIR reflectance. More importantly, all the prepared green pigments exhibit high NIR

465 reflectance, which lets them suitable for use as cooling pigments.

466

467 **3 Conclusion**

468 Iron oxide green pigments, a composite green pigments of phthalocyanine blue and

469 FeOOH pigments, was prepared by intermittent stirring. The characterization results

470 shown that the aspect ratio of FePc decreased compared to FeOOH pigment. XPS

471 analysis shown that CuPc and FeOOH pigments were bound by hydrogen bonds. The

472 thermal decomposition temperature of the coated pigments increased from 266 ^{o}C to

19

473 314 °C, significantly improving its heat resistance. In addtion, the color difference ΔE

474 of pigment was 1.623 after baking at 240 °C for 30 min. The surface modification of

475 composite pigments improved their hydrophobicity and dispersibility in organic

476 media. After the combination of FeOOH and CuPc pigments, the a^* value of the

477 pigments changed from a positive value to a duplicate value, presenting the pigments

478 had green tone. The coating and surface modification had improved heat resistance to

479 some extent, but had little impact on the a^* value of the pigment, and the pigment

480 remains in a green tone. Particularly, all the newly designed green pigments displayed

481 high NIR reflectance. The prepared pigments have high heat resistance and dispersion

482 properties, and are expected to be used in fields such as plastics and high-temperature

483 coatings. More noteworthy is that the coated green pigments can also be used as cold

484 pigments.

485

490

491 **CRediT authorship contribution statement**

492 **Minhong Xu** designed experiments and wrote the main manuscript text, **Yuhua Guo**

493 analyzed sequencing data, **Guoxiang Pan** (Corresponding Author) wrote - review the

494 manuscripts, **Qiang Shen** analyzed sequencing data, **Mengyu Zhou** analyzed

495 experimental results, **Qiu Liang** carried out experiments. All authors reviewed the

496 manuscript.

497

20

498   **Declarations**

499   **Conflict of interest** The authors declare that they have no conflict of interest.

500

501   **References**

502   [1] S. Li ,B. Mu, Z. Meng, Y. Zhu, H.Zhang, A. Wang, Facile color regulation of

503   organic/inorganic hybrid pigments combining with palygorskite and CoNi

504   layered double hydroxides, Dyes Pigments. 213 (2023) 111162.

505   https://doi.org/10.1016/j.dyepig.2023.111162

506   [2] B. Tang, Q. Xiang, Z. Fang, X. Zhang, Z. Xiong, H. Li, C. Yuan, S. Zhang,

507   Influence of Cr^{3+} substitution for Mg^{2+} on the crystal structure and microwave

508   dielectric properties of $CaMg_{1-x}Cr_{2x/3}Si_2O_6$ ceramics, Ceram Int. 45 (2019)

509   11484-11490.

510   https://doi.org/10.1016/j.ceramint.2019.03.016

511   [3] C. Ding, A. Han, M. Ye, Y. Zhang, L. Yao, J. Yang, Synthesis and

512   characterization of a series of new green solar heat-reflective pigments: Cr-doped

513        $BiPO_4$ and its effect on the aging resistance of PMMA (Poly(methyl

514   methacrylate)), Sol Energ. Mat. Sol. C. 191 (2019) 427-436.

515   https://doi.org/10.1016/j.solmat.2018.12.007

516   [4] S. Ai, H. Zheng, J. Yu. Preparation and Reflectance Spectrum Modulation of

517   Cr_2O_3 Green Pigment by Solution Combustion Synthesis, Materials. 13 (2020)

518   1540. https://doi.org/10.3390/ma13071540

519   [5] T. Chen, J. Zha, X. Zhang, X. Hu, W. Jiang, Z. Xie, J. Wan, Synthesis and

520   characterization of $Pr_xZr_{1-x}SiO_4$ (x = 0–0.08) yellow pigments via non-hydrolytic

521   sol-gel method, J. Eur. Ceram. Soc. 38 (2018) 4568-4575.

522   https://doi.org/10.1016/j.jeurceramsoc.2018.05.021

21

[6] I. Mjejri, S. Mornet, M. Gaudon, From nano-structured polycrystalline spheres with Zn1-xCoxO composition to core-shell Zn1-xCoxO@SiO$_2$ as green pigments, J. Alloy Compound. 777 (2019) 1204-1210.

https://doi.org/10.1016/j.jallcom.2018.10.333

[7] T. Thongkanluang, T. Kittiauchawal, P. Limsuwan, Preparation and characterization of Cr$_2$O$_3$-TiO$_2$-Al$_2$O$_3$-V$_2$O$_5$ green pigment, Ceram Int. 37 (2011) 543-548.

https://doi.org/10.1016/j.ceramint.2010.09.044

[8] G. Germinario, I. Werf, L. Sabbatini. Pyrolysis gas chromatography mass spectrometry of two green phthalocyanine pigments and their identification in paint systems, J. Anal. Appl. Pyrol. 115 (2015) 175-183.

https://doi.org/10.1016/j.jaap.2015.07.016

[9] J. Choi, W. Lee, J.P. Kim, Broad-absorbing tetrabenzocorrolazine green photosensitizer for the enhanced conversion efficiency in dye-sensitized solar cells, J. Porphyr. Phthalocya. 20 (2016) 804-812.

https://doi.org/10.1142/S108842461650098X

[10] Z. Hu, Q. Wang, J. Liu, K. Liu, Q. Chang, Synthesis and chromatic properties of V-doped and V/Y-codoped ZrO$_2$ yellow pigments, J. Alloys Compd. 856 (2021) 157397-157408.

https://doi.org/10.1016/j.jallcom.2020.157397

[11] T. Masui, T. Honda, Wendusu, N. Imanaka, Novel and environmentally friendly (Bi,Ca,Zn)VO4 yellow pigments, Dyes Pigments. 99 (2013) 636-641.

https://doi.org/10.1016/j.dyepig.2013.06.030

[12] K.V.Raj Athira, P. Prabhakar Rao, K.Rajesh, Potential NIR reflecting yellow pigments powder in monoclinic scheelite type solid solutions: BiVO$_4$-GdPO$_4$ for

22

548   cool roof applications, Inorg. Chem. Commun. 149 (2023) 110416.

549   https://doi.org/10.1016/j.inoche.2023.110416

550 [13] V. Elakkiya, S. Sumathi, Low-temperature synthesis of environment-friendly

551   cool yellow pigment: Ce substituted $SrMoO_4$, Mater Lett. 263 (2020)

552   127246-127250. https://doi.org/10.1016/j.matlet.2019.127246

553 [14] A. Mrm, B. Lz, A. Es, Synthesis and characterization of goethite (α-FeOOH)

554   magnetic nanofluids, Int. J. Thermofluids. 15 (2022) 100169.

555   https://doi.org/10.1016/j.ijft.2022.100169

556 [15] F. Fang, Y. Jia, P.Y. Wu, Q.Y. Zhang, Y.P. Jiang, S.S. Zhou, D.Y. Peng, Facile

557   one-pot preparation of goethite/parabutlerite nanocomposites and their removal

558   properties and mechanism toward As(V) ions. Appl. Surf. Sci. 324 (2015)

559   355-362.

560   https://doi.org/10.1016/j.apsusc.2014.10.174

561 [16] X. Qian, M. Ren, Y. Zhu, D. Yue, Y. Han, J. Jia, Zhao Y., Visible Light Assisted

562   Heterogeneous Fenton-Like Degradation of Organic Pollutant via

563   α-FeOOH/Mesoporous Carbon Composites, Environ. Sci. Technol. 51 (2017)

564   3993-4000.

565   https://doi.org/10.1021/acs.est.6b06429

566 [17] M. cc. POMIS, M. Menu , C. Vignaud, Red Palaeolithic pigments: natural

567   hematite or heated goethite? Archaeometry, 41 (1999) 275-285.

568   https://doi.org/10.1111/j.1475-4754.1999.tb00983.x

569 [18] E. Sani, L. Mercatelli, M.R. Martina, S. Barison, F. Agresti, Magnetic-field

570   tunability of optical properties in colloidal suspensions of goethite (α-FeOOH)

571   nanorods, Opt. Mater. 96 (2019) 109303-109310.

572   https://doi.org/10.1016/j.optmat.2019.109303

573 [19] S.G. Menon, H.C. Swart, Microwave-assisted synthesis of blue-green NiAl$_2$O$_4$

574 nanoparticle pigments with high near-infrared reflectance for indoor cooling, J.

575 Alloy Compd. 81 (2020) 152991-152998.

576 https://doi.org/10.1016/j.jallcom.2019.152991

577 [20] S.G. Menon, D.N. Hebbar, S.D. Kulkarni, K.S. Choudhari, C. Santhosh, Facile

578 synthesis and luminescence studies of nanocrystalline red emitting Cr: ZnAl$_2$O$_4$

579 phosphor, Mater. Res. Bull. 86 (2017) 63-71.

580 https://doi.org/10.1016/j.materresbull.2016.10.009

581 [21] J.M. Rynkowski, T. Paryjczak, M. Lenik, On the nature of oxidic nickel phases

582 in NiO/γ-Al$_2$O$_3$ catalysts, Appl. Catal. Gen. 106 (1993) 73-82.

583 https://doi.org/10.1016/0926-860X(93)80156-K

584 [22] X. Wang, F. Yu, X. Duan, D. Yuan, Effects of Annealing Temperature and SiO$_2$

585 Matrix on the Structure and Optical Properties of Co-Doped ZnAl$_2$O$_4$/SiO$_2$

586 Nanoglass–Ceramic Composites, J. Phys. Chem. C. 116 (2012) 2313-2321.

587 https://doi.org/10.1021/jp209837q

588 [23] H. Huang, Z. Lan, W. Li, W. Mo, J. Zhang, A novel and low-cost CuPc@C

589 catalyst derived from the compounds of sunflower straw and copper

590 phthalocyanine pigment for oxygen reduction reaction, RSC Advances. 11 (2021)

591 15590-15597.

592 https://doi.org/10.1039/D1RA01775F

593 [24] T. Zhang, C. Zhou, Properties of copper phthalocyanine blue (C.I. Pigment Blue

594 15:3) treated with poly(ethylene glycol)s, Dyes Pigments. 35 (1997) 123-130.

595 https://doi.org/10.1016/S0143-7208(97)84839-5

596 [25] I. Arčon, A. Kodre, M. Mozetič, XAS study of oxygen plasma-treated

597 micronized iron oxide pigments, Vacuum. 80 (2005) 178-183.

24

598   https://doi.org/10.1016/j.vacuum.2005.08.012

599 [26] R. Snovski, J. Grinblat, M.T. Sougrati, J.C. Jumas, S. Margel, Synthesis and

600   characterization of iron, iron oxide and iron carbide nanostructures, J. Magn.

601   Magn. Mater. 349 (2013) 35-44.

602   https://doi.org/10.1016/j.jmmm.2013.08.043

603 [27] R. Levinson, H. Akbari, P. Berdahl, Measuring solar reflectance—Part I:

604   Defining a metric that accurately predicts solar heat gain, Sol. Energy. 84 (2010)

605   1717-1744.

606   https://doi.org/10.1016/j.solener.2010.04.018

607 [28] R. Levinson, H. Akbari, P. Berdahl, Measuring solar reflectance—Part II: Review

608   of practical methods, Sol. Energy. 84 (2010) 1745-1759.

609   https://doi.org/10.1016/j.solener.2010.04.017

610 [29] L. Yuan, X. Weng, M. Zhou, Q. Zhang, L. Deng, Structural and

611   VisibleNearInfrared Optical Properties of Cr-Doped TiO_2 for Colored Cool

612   Pigments, Nanoscale Res. Lett. 12 (2017) 597.

613   https://doi.org/10.1186/s11671-017-2365-5

614 [30] Y. Li, S. Le, Z. Wang, Y. Hong, Q. Pu, Preparation and characterization of the

615   Sr^{2+}-doped γ-Ce_2S_3@c-SiO_2 red pigments exhibiting improved temperature and

616   acid stability, Appl. Surf. Sci. 508 (2020) 145266.

617   https://doi.org/10.1016/j.apsusc.2020.145266

618 [31] B. Becerir, Assessment of the results of different color difference formulae under

619   different illuminants by wash fastness tests, Fiber Polym. 12 (2011) 946-956.

620   https://doi.org/10.1007/s12221-011-0946-y

621 [32] M. Ohmori, E. Matijevi, Preparation and properties of uniform coated colloidal

622   particles: 8. Silica on Iron, J. Colloid Interf. Sci. 160 (1993) 288-292.

623   https://doi.org/10.1006/jcis.1993.1398

624   [33] C. Yao, F. Wu, X. Lin, X. Yang, D. Lu, X. Wang, Study on Nanosized TiO_2

625   coated by silica in ultrasonic field, Chin. J.. Inorg Chem. 21 (2005) 59-64.

626   https://doi.org/10.3321/j.issn:1001-4861.2005.01.010

627   [34] X. Miao, H. Dai, J. Chen, J. Zhu, The enhanced method of hydroxyl radical

628   generation in the heterogeneous UV-Fenton system with α-FeOOH as catalyst,

629   Sep. Purif. Technol. 200 (2018) 36-43.

630   https://doi.org/10.1016/j.seppur.2018.02.012

631   [35] O. Gorduk, M. Gencten, S. Gorduk, M. Sahin, Y. Sahin, Electrochemical

632   fabrication and supercapacitor performances of metallo

633   phthalocyanine/functionalized-multiwalled carbon nanotube/polyaniline

634   modified hybrid electrode materials, J. Energy. Storage. 33 (2020)

635   102049-102061.

636   https://doi.org/10.1016/j.est.2020.102049

637   [36] H. Liu, Y. Jiang, D. Liu, S. Li, X. Yang, Y. Ji, Y. Cui, Thermal effect on

638   microstructure vibration of SiO_2 thin films, Vib. Spectrosc. 96 (2018) 101-105.

639   https://doi.org/10.1016/j.vibspec.2018.03.005

640   [37] G.M. Rignanese, A. Pasquarello, J.C. Charlier, X. Gonze, R. Car, Nitrogen

641   incorporation at Si(001)-SiO_2 interfaces: Relation between N 1s core-level shifts

642   and microscopic structure, Phys. Rev. Lett. 79 (1997) 5174-5177.

643   https://doi.org/10.1103/PhysRevLett.79.5174

644   [38] M. Xu, G. Pan, Y. Guo, S. Yang, Z. Fang, Surface modification and structure

645   analysis of coated iron oxide yellow pigments to improve dispersion in organic

646   solvents, Surf. Interface Anal. 53 (2021) 933-945.

647   https://doi.org/10.1002/sia.6995

648 [39] D. Dai, X. Lan, L. Wu, Z. Wang, Designed fabrication of lightweight SiC/Si$_3$N$_4$

649 aerogels for enhanced electromagnetic wave absorption and thermal insulation, J.

650 Alloy. Compd. 901 (2022) 163651.

651 https://doi.org/10.1016/j.jallcom.2022.163651

652 [40] A.N. Mansour, A. Brizzolara Robert, Characterization of the surface of α-FeOOH

653 powder by XPS, Surf. Sci. Spectra. 4 (1996) 357-357.

654 https://doi.org/10.1116/1.1247825

655 [41] Y. Chae, J.H. Xin, T. Hua, Color prediction models for digital Jacquard woven

656 fabrics, Color. Res. Appl. 41 (2016) 64-71.

657 https://doi.org/10.1002/col.21945

658 [42] T. Thongkanluang, T. Kittiauchawal, P. Limsuwan, Preparation and

659 characterization of Cr$_2$O$_3$–TiO$_2$–Al$_2$O$_3$–V$_2$O$_5$ green pigment, Thin. Solid Films.

660 37 (2011) 543-548.

661 https://doi.org/10.1016/j.ceramint.2010.09.044