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Functional pigments from chromium(III) oxide nanoparticles

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ABSTRACT

Pigments with properties such as weather stability, thermal resistance and having functional properties such as NIR reflectance are desirable. In this, the inorganic pigments serve better than the organic pigments. However, the release of metal ions such as Pb and Co on exposure to the environment is raising alarms. One of the approaches considered ideal is to use naturally occurring oxides or their synthetic analogs as pigments after suitable modifications. One such classic example is that of chromium(III) oxide. We report a predominant solid state route, wherein a chromium–urea complex prepared under solvent free conditions was calcined at high temperature to obtain chromium(III) oxide nanoparticles. Introducing rare earth metal ions such as La and Pr, which have in recent years been reported to be environmentally benign and available in sufficient quantities resulted in nano-oxides with enhanced near-infrared reflectance, thus qualifying them as cool colorants.

1. Introduction

Exponential growth of nanomaterials possessing unique and enhanced properties when compared to the bulk has been reported during the last decade. Nanotechnology seems to have penetrated into almost all fields of science, with major breakthroughs reported from time to time. Cr_2O_3 is known for its increased pigment opacity, high UV attenuation, poor deterioration and transparency to visible light. Several noteworthy applications in paints, plastic, construction materials, refractories, enamels, etc. have been possible with Cr_2O_3 [1,2]. Some of these applications are due to its high oxidative resistance and melting temperature [3]. A permanent green coloring in cement or lime-bonded construction material is reported to be achieved only by using Cr_2O_3 [2]. By employing nano-sized chromium(III) oxide, newer or enhanced applications in surface coatings have been possible [4].

Colorant researchers are recently focusing on the development of cool pigments which have high near-infrared (NIR) solar reflectance to control heat buildup. A high solar reflectance from roofs, automobiles, upholstery, etc. can reduce heat gain [5,6]. Higher NIR reflectance depends on factors such as particle size, particle size distribution and refractive index of the material. Electronic structure of several metal ions is ideal for obtaining the desired refractive index [7]. Mixed metal oxides of Cr_2O_3 with TiO_2, Al_2O_3 and V_2O_5 [8] as well as some nano-crystalline oxides have been reported as NIR reflective pigments. The doping with rare earths which have right electronic structure for reflective properties has been reported recently [9–13]. Coupling this information with the toxicity reports on vanadium compounds [14] and the environmentally benign characteristics of rare earth elements such as low cytotoxicity [18,19], it is possible to develop rare earth doped Cr_2O_3 nanoparticles for high NIR reflective coating.

Many research groups have reported the synthesis of Cr_2O_3 nanoparticles by complexing chromium(III) salts with urea under aqueous conditions [15–17]. Herein, we report a green synthesis protocol for nano-Cr_2O_3 utilizing a solvent free approach employing urea decomposition strategy. The nano-Cr_2O_3 thus obtained has been characterized using XRD and SEM and has been effectively modified to function as a NIR reflective cool green colorant by doping with rare earth elements for surface coating applications.

2. Materials and methods

2.1. Materials

Chromium nitrate nonahydrate and praseodymium nitrate hexahydrate were purchased from Sigma–Aldrich, urea was

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procured from Fischer Scientific, India and lanthanum nitrate hexahydrate from Central Drug House (P) Limited, India. All chemicals were employed as obtained without further purification.

2.2. Instrumentation

Milling was carried out using Fritsch, pulverisette. Thermogravimetric analysis was performed using Thermo-Gravimetric Analyzer (TGA) – Model Q50 of M/s TA Instruments. For TGA measurements a heating rate of 10 °C/min and temperature range of 20–800 °C/min were employed. The Powder X-ray diffraction studies was carried out on a Rigaku, Miniflex (II) Desktop X-ray diffractometer and the diffraction patterns were recorded using CuKα ($\lambda = 1.5406$ A°), 30 kV, 15 mA with a scan speed of 4°/min; step size of 0.05°. Morphology of products was analyzed by scanning electron microscopy (HITACHI, Japan, model no: SU6600). Elemental analysis was carried out by energy dispersive spectrometer (EDAX) which employed an INCA suite program. Reflectance measurements of the synthesized samples were recorded with Perkin–Elmer Lambda 35. NIR reflectance measurements were carried out on Cary 5E. CIE illuminant D65 was used for color measurements and color measurements were calculated using the software CIELAB (1976) color space. The difference between two colors (ΔE) was calculated using the formula,

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}$$

2.3. Synthesis of Cr_2O_3 nanoparticles

A solvent free synthesis of chromium(III) oxide nanoparticles was adopted. $Cr(NO_3)_3 \cdot 9H_2O$ and urea were taken in the mole ratio of 1:9 and milled together for 60 min at the rate of 600 rpm. The mixture was treated in an autoclave for 20 min at a temperature of ca. 120 °C and pressure of 103 kPa. The resultant complex was characterized by UV–Vis spectroscopy and FTIR spectroscopy. The complex was dried in an air oven and calcined in furnace at 800 °C at the rate of 5 °C/min for 60 min, which resulted in Cr_2O_3 nanoparticles.

2.4. Synthesis of cool green pigments

Cr_2O_3 nanoparticles prepared were mixed along with lanthanum nitrate hexahydrate and praseodymium nitrate hexahydrate in various w/w ratios such as 1:0:0, 1:0.2:0.2, 1:0.5:0.5, 1:1.2:1.2 and 1:1.5:1.5, followed by milling at 600 rpm for 60 min. Homogenized mixture obtained was calcined in a furnace held at 1000 °C for 60 min with a rate of heating of 5 °C/min for the temperature range of 200–1000 °C. For surface coating applications, the pigment samples obtained were mixed in a vibratory shaker with linseed oil as the medium. The hiding power was then evaluated by coating on an opacity chart at a thickness of 100 μm using Control coater of RK print coater instrument, UK and the reflectance spectrum of the pigments was obtained from those charts.

3. Results and discussion

3.1. Studies on Cr–Urea complex

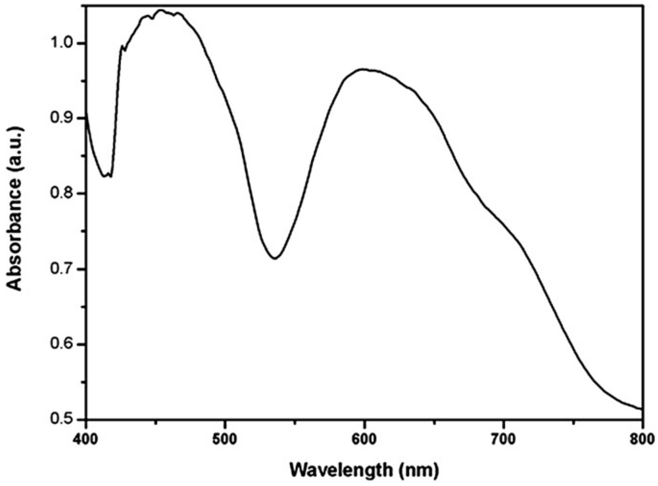

Fig. 1. UV–Vis absorbance spectrum of Cr–Urea complex before calcination.

The geometry of the Cr–urea complex and the coordination of urea through oxygen were confirmed using UV–Vis spectroscopy and FTIR. The UV-absorption spectra for the Cr_2O_3 nanoparticles prepared showed two broad peaks at 460 nm and 600 nm (Fig. 1). The possible transitions of the Cr(III) ion in the crystal fields are

$$^4A_{2g} \rightarrow {}^4T_{2g} \tag{1}$$

$$^2A_{2g} \rightarrow {}^2T_{1g}, {}^2E_{2g} \tag{2}$$

The transition stated in equation (1) shows absorption band around the region of 460 nm and it corresponds to the octahedral symmetry [1]. The transition in equation (2) shows the band in the region of 600 nm and it corresponds to the six-coordinate geometry.

FTIR spectrum of the complex (Fig. 2) was confirmed by absence of –CO– band attributable to urea at 1630 cm^{-1} with decrease in the wavenumber of –CO– (stretch) + $-NH_2$ (bend) observed at 1570 cm^{-1} of the complex.

TGA analysis of the complex (Fig. 3) illustrates the loss of water molecules in the region around 90–120 °C. Weight loss was also observed around the region of 150–450 °C. No major change in the weight of the residue was observed (<3%) in the temperature range of 700–800 °C, indicating that the Cr_2O_3 nanoparticles prepared by calcination at 800 °C could be thermally stable [20].

3.2. Characterization of Cr_2O_3 nanoparticles

The crystallinity of the nanoparticles and their size was determined through powder XRD. Calcination to a higher temperature of

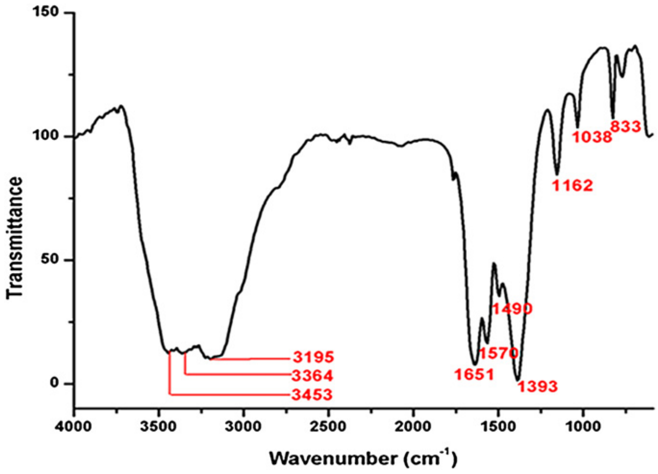

Fig. 2. FTIR spectrum of Cr–urea complex before calcination.

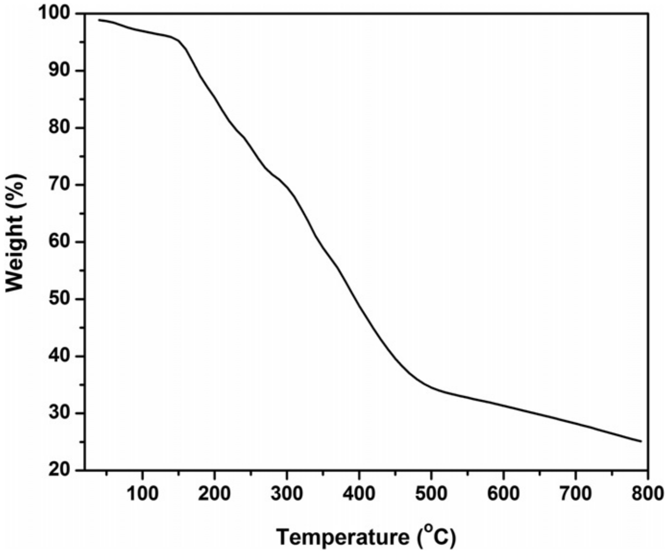

Fig. 3. TGA curve of Cr–urea complex before calcination.

about 800 °C resulted in a highly pure and crystalline Cr_2O_3 nanoparticles with a trigonal crystal system indexed to *R-3c* space group with lattice constants $a = 4.965$ Å, $c = 13.618$ Å, which is in close agreement with the standard database of bulk Cr_2O_3, ICDD PDF 38-1479. The crystal size of the synthesized nanoparticles was determined by line broadening method using Scherrer formula [21]. The crystal size determined along the planes perpendicular to the 104, 110 and 116 planes was found to be 30 ± 3 nm (Fig. 4). The morphology of nanoparticles were spherical with size ranging from 19 to 30 nm as obtained from the SEM image (Fig. 5).

3.3. *Rare earth doped Cr_2O_3 (Cr:La:Pr:O) nanoparticles*

Thermal decomposition of free urea is reported to be complete at temperatures below 500 °C. Our experiments on the thermal degradation profile of the complex at temperatures of up to 800 °C indicate below 6% weight loss at temperature above 600 °C, indirectly providing evidence for the absence of nitrogenous compounds in the final Cr_2O_3. Acid washing (10% H_2SO_4, 30 min stirring, 1000 rpm) confirmed the absence of Cr(VI) in the leachate. X-ray diffraction patterns of the pigment closely matched with that of Lanthanum praseodymium chromium oxide (ICDD PDF 74-2920) at higher concentration of rare earth elements whereas at lower concentration close matching was to that of Cr_2O_3 (ICDD PDF 38-1479). In Fig. 6, the peaks marked as asterisks correspond to the rare earth elements in the samples, indicating the homogeneous distribution of the rare earth ions in the Cr_2O_3 matrix. The morphology of these pigments was spherical with size ranging from 70 to 95 nm as observed from the SEM images (Fig. 7). The EDAX analysis of these composites revealed their purity and also the doping of the rare earth elements in it. The stability of the nanocomposite against metal ion leaching was confirmed through EDAX measurements of the acid and alkali washed samples [22]. For this, a known weight of the pigment was treated with 10% H_2SO_4/NaOH (30 min stirring, 1000 rpm). The treated sample was washed, dried in an air oven at 100 °C for 12 h and subjected to EDAX

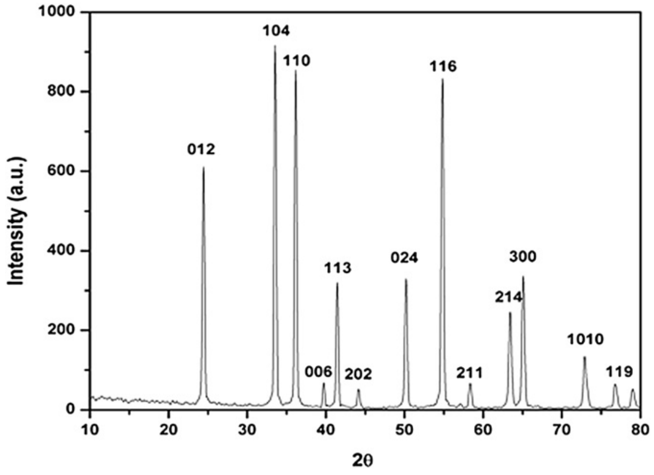

Fig. 4. Powder X-ray diffraction pattern of Cr_2O_3 nanoparticles. The average crystal size of these nanoparticles was calculated to be 30 nm using Debye–Scherrer equation.

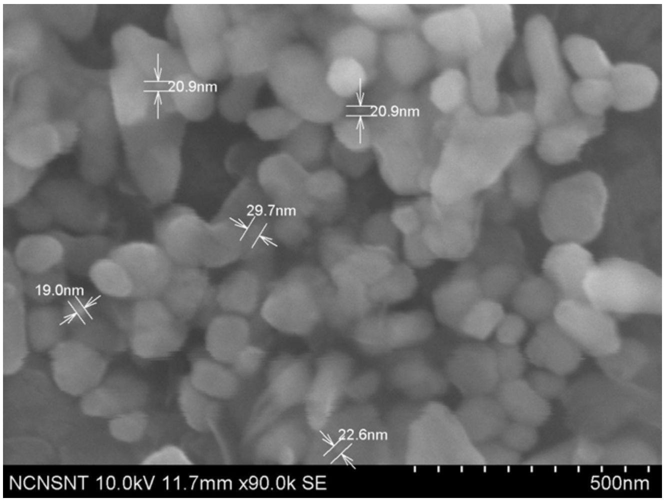

Fig. 5. SEM image of Cr_2O_3 nanoparticles with size ranging from 19 to 30 nm.

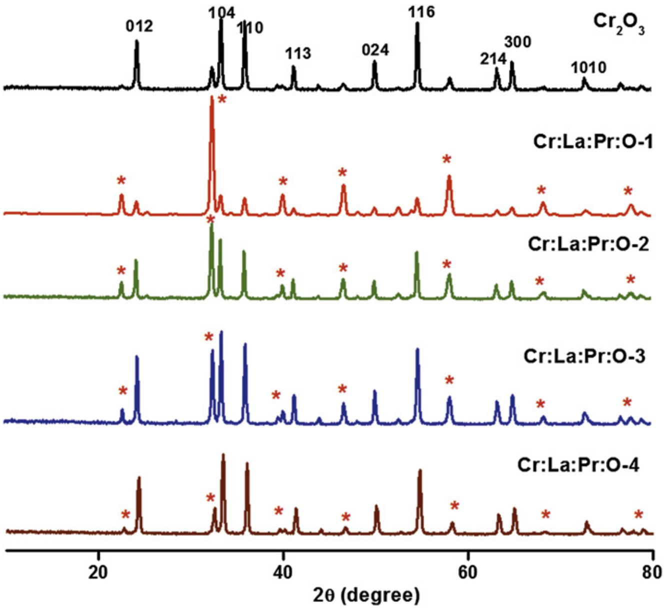

Fig. 6. Powder X-ray diffraction pattern of Cr:La:Pr:O nanoparticles compared with the pattern of Cr_2O_3 nanoparticles. The average crystal size of these nanoparticles was calculated to be 33.5 nm using Debye–Scherrer equation.

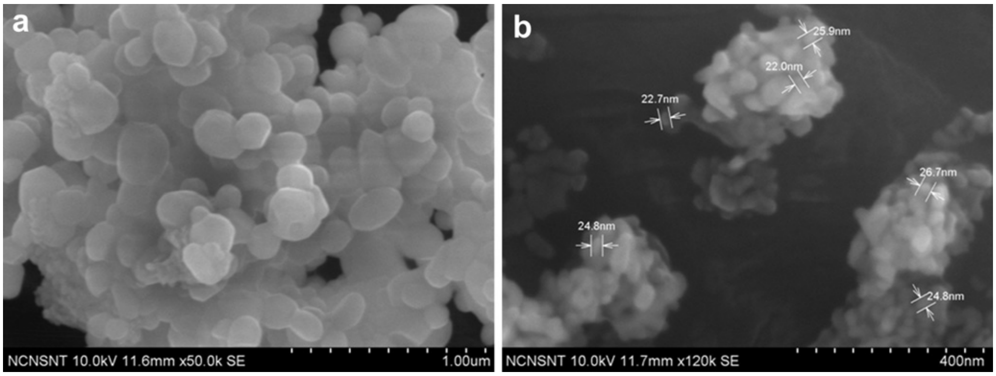

Fig. 7. SEM images of Cr:La:Pr:O nanoparticles with size ranging from 25 to 50 nm for different ratios of dopant concentration, (a) Cr:La:Pr:O-1 and (b) Cr:La:Pr:O-4.

Table 1
$L^*a^*b^*$ values of nano-sized pigments.

Samples	Atomic weight (%)			
	O (K)	Cr (L)	La (L)	Pr (L)
Cr:La:Pr:O-1	43.26	55.59	0.38	0.77
Cr:La:Pr:O-1 After acid wash	45.69	53.20	0.32	0.69
Cr:La:Pr:O-1 After alkali wash	46.01	52.93	0.41	0.65
Cr:La:Pr:O-4	46.26	52.92	0.46	0.36
Cr:La:Pr:O-4 After acid wash	47.34	51.85	0.42	0.39
Cr:La:Pr:O-4 After alkali wash	48.70	50.50	0.45	0.35

measurements. The atomic weight% distribution of Cr, La, Pr and O in the samples before and after washing presented in Table 1, indicates good stability of the composites to environmental conditions.

3.4. Cr:La:Pr:O nanoparticles as cool pigments

The rare earth doped nano-oxides prepared in this study were evaluated for their performance as a pigment for surface coating applications. The smaller size helps in attaining better coverage area due to their high surface area. The UV–Vis reflectance spectrum of these samples showed a marginal increase in their reflectance while moving toward the visible region (Fig. 8).

Table 2
$L^*a^*b^*$ values of nano-sized pigments.

Samples	L^*	a^*	b^*	H°	ΔE^a
Cr_2O_3	42.00	−15.39	16.75	132.57	2.3
Cr:La:Pr:O-1	47.34	−12.44	9.33	143.13	8.02
Cr:La:Pr:O-2	45.07	−10.88	6.72	148.29	10.44
Cr:La:Pr:O-3	47.61	−10.74	8.5	141.64	11.19
Cr:La:Pr:O-4	44.57	−10.18	6.15	148.86	11.24

[a] Standard chromium oxide – Color Index Name: PG 17, Color Index Number: 77299.

The $L^*a^*b^*$ values calculated using CIELAB 1976 is presented in Table 2. The hue angle of all the samples was in the range of 130–150° which is ascribed to the green color. There is a constant decrease in the a^* value as the concentration of the Cr_2O_3 decreases, thus indicating the lessening of the green color intensity. The b^* values also decrease and move toward the blue region with the increase in concentration of the rare earth dopants. ΔE, a common method of quantifying color difference between two samples was determined. For this, the Cr_2O_3 synthesized in this work as well as the pigments prepared using rare earth were analyzed against the $L^*a^*b^*$ values of a standard green colored pigment (CAS No 1309-38-9). ΔE values of below 12 were observed, indicating a reasonable

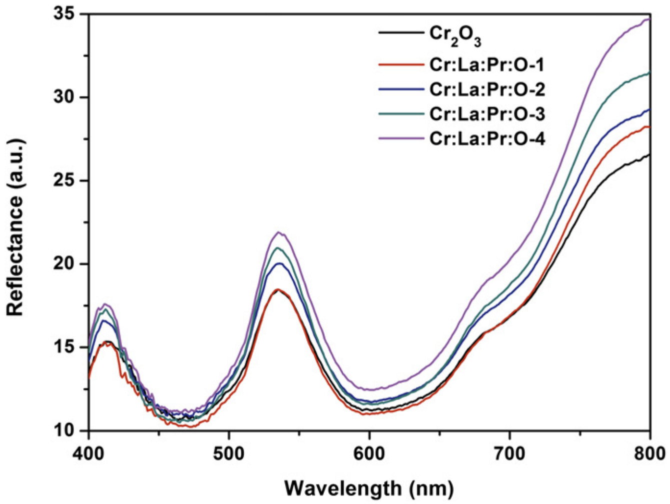

Fig. 8. UV–Vis reflectance spectrum of Cr_2O_3, Cr:La:Pr:O-1, Cr:La:Pr:O-2, Cr:La:Pr:O-3 and Cr:La:Pr:O-4.

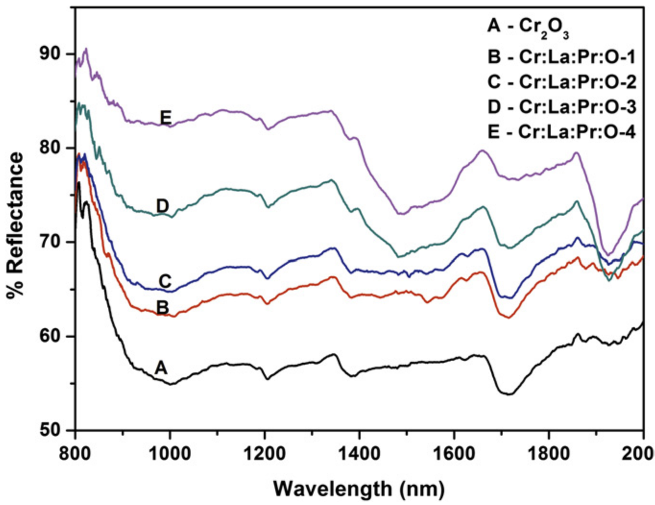

Fig. 9. Diffuse reflectance spectrum of Cr_2O_3, Cr:La:Pr:O-1, Cr:La:Pr:O-2, Cr:La:Pr:O-3 and Cr:La:Pr:O-4 with average reflectance of 55%, 63%, 68%, 75% and 85%, respectively.

matching of the color to the standard pigment, in spite of rare earth doping.

The presence of rare earth elements is expected to enhance the NIR reflectance of these pigments. The diffuse reflectance of the samples in the NIR region has been investigated (Fig. 9). It can be seen that the percentage reflectance increases with the increase in concentration of the rare earth dopants in it. Chromium(III) oxide nanoparticles had reflectance of around 55% in the NIR region, which increased as the rare earth dopant increased with the maximum of 85% reflectance in the concentration range investigated. Such an increasing trend in the reflectance is indicative of the ability of the pigments to reflect heat radiations to a greater extent than the conventional pigments.

4. Conclusion

In summary, Cr_2O_3 nano green pigments with high NIR have been successfully synthesized by doping with the rare earth salts. Rare earth dopants and the nano-size of pigments jointly result in a higher number of reflectance points when coated on a surface. Increasing concentration of the rare earth dopants increased the reflectance without affecting the green color of the pigment. This paper thus provides a classical possibility of combining material chemistry and knowledge on elements with right electronic structure to achieve NIR reflectance.

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