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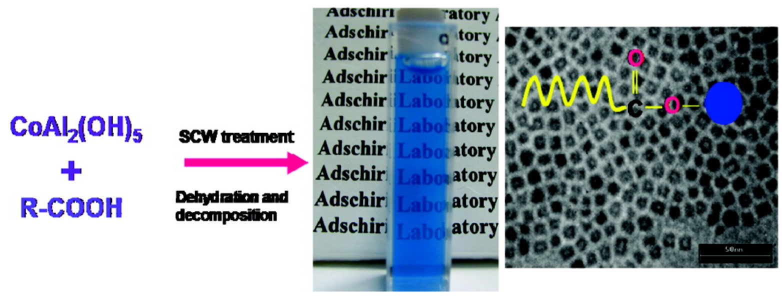

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# Transparent $CoAl_2O_4$ Hybrid Nano Pigment by Organic Ligand-Assisted Supercritical Water

Dinesh Rangappa,[†] Takashi Naka,[†] Akitsugu Kondo,[‡] Masahiko Ishii,[‡] Toshikatsu Kobayashi,[§] and Tadafumi Adschiri*,[†]

*Contribution from the Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8579, Japan, Material Engineering Division III Vehicle Engineering group, Toyota Motor Corporation, Higashifuji Technical Center, Shizuoka, Japan, and Innovative Technology Laboratory, R&D, Nippon Paint Co. Ltd., Osaka, Japan*

Received February 15, 2007; E-mail: ajiri@tagen.tohoku.ac.jp

***Abstract:*** Transparent types of inorganic pigments are important as they can be used in a variety of applications, such as metallic finishing, contrast enhancing luminescent pigments, high-end optical filters, and so on. Currently, the difficulty in producing monodisperse and stable binary metal oxide nano pigments at low temperature hampers the applicability and realization of transparent blue nano pigments. Here, for the first time, we report organic ligand capped $CoAl_2O_4$ hybrid transparent nano pigment, which has a particle size less than 8 nm with well-stabilized single nanocrystals, using organic ligand-assisted supercritical water as the reaction medium. The organic ligand capping could effectively inhibit the particle growth and also control the size of nanocrystals. This helps to diminish the scattering effect of the nano blue pigment, realizing a transparent cobalt blue nano pigment without any postheat treatment.

## 1. Introduction

Inorganic pigments have been extensively used by mankind since ancient times. There is no alternative for inorganic pigments in coloring building materials, glasses, glazes, plastics, and ceramics. Recently, there is a growing interest in nanoparticle pigments.[1] The optical property of a pigmented paint depends on the optical properties of pigment particles, their size, shape, and the volume concentration. The most important properties for colored pigments are tinctorial strength and the hiding power, which are determined by the scattering and absorption cross sections of the pigment particles.[2−4] To elevate the scattering effect, it is desirable to prepare pigment particles with size much smaller than their wavelength.[5] Further, one can realize transparent pigments by tuning the scattering and absorption cross sections where scattering reaches less than 5%. Transparent types of pigments are important as they can be widely used for metallic finishing, where their high level of transparency gives an attractive finishing and improves the weatherability resistance.

Recently, with the development of new synthetic technologies for various materials, different colored, monodisperse nano pigments can be obtained, which will probably lead to a new development in the pigment industry.[6,7] However, it has been a challenge to synthesize complex or mixed metal oxide blue pigments at low temperature without additional heat treatment, which have great potential in pigment industry.[7] Among the blue pigments, cobalt blue is well known as Thenards blue. It has been widely used in color TV tubes as contrast-enhancing luminescent pigments, high-end optical filters, magnetic recording media, and as a heat resistant ceramic.[2,8] This compound has been prepared by different methods, where a higher reaction temperature or postheat treatment was necessary to synthesize pure $CoAl_2O_4$ nanocrystals.[9] In fact, so far, researchers have not succeeded in preparing transparent blue pigments, as it is difficult to synthesize monodisperse and agglomerated free single nanocrystal $CoAl_2O_4$ particles at low temperature.[9] In addition, for the fabrication of transparent pigment, perfect dispersion of nanoparticles is necessary. For that purpose, surface modification of nanoparticles with organic ligand is

† Tohoku University.
‡ Toyota Motor Corp.
§ Nippon Paint Co. Ltd.

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essential, which is another challenge that has not been achieved until now due to the lack of suitable techniques that allows organic ligand molecules to tailor complex metal oxide surface such as $CoAl_2O_4$ at relatively higher temperature.

Recently, some researchers using organic-solution phase and liquid−solid solution-phase synthetic transfer routes with surfactants demonstrated a versatile pathway toward size- and shape-controlled metal oxide nanocrystals.[10,11] Combining this concept and the properties of supercritical water (SCW),[12,13] our group has succeeded in synthesizing the colloidal ceria nano crystals.[14] Using organic ligand molecules that are miscible with SCW, crystal growth can be limited and agglomeration can be inhibited in favor of small, well-dispersed particles.[15,16] Hereby, using organic ligand-assisted supercritical water as the reaction medium, for the first time, we are reporting complex metal oxide transparent $CoAl_2O_4$ hybrid nano pigment, which has a particle size less than 8 nm with well-stabilized single nanocrystals.

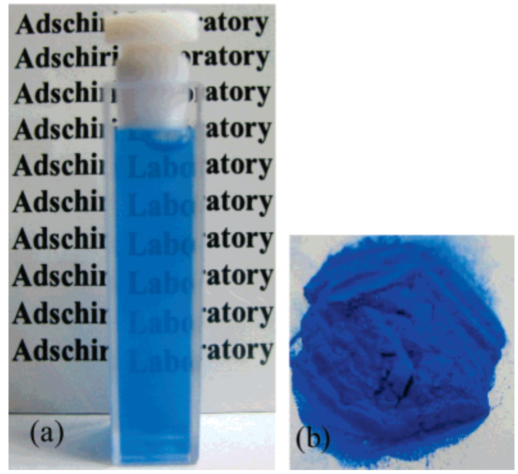


***Figure 1.*** (a) Dispersion of oleic acid capped cobalt blue nanocrystals pigment in hexane (1 wt %); (b) cobalt blue nano pigment powder.

## 2. Experimental Section

**Preparation of Cobalt Blue Nanocrystals.** The precursor solution was prepared by dissolution of metal sulfates in aqueous solution. In a typical synthesis, $CoAl_2(OH)_5$ was prepared with a solution of 0.1 M $CoSO_4$ to which 0.1 M $Al_2SO_4$ solution was slowly added by stirring at room temperature. To this mixture was added a 0.32 M NaOH solution carefully and slowly to obtain a pink color sol. The sol was thoroughly mixed using a magnetic stirrer for 2 h followed by centrifugation for 10 min and washed with distilled water. This procedure was repeated three times to remove sodium and sulfate ions from the mixture sol of $Co(OH)_2$ and $Al(OH)_3$. Later, 0.1 M precursor sol was made up by adding distilled water. Next, 2.5 mL of the 0.01 M precursor was transferred to a pressure-resistant SUS316 vessel (inner volume 5 mL). For surface modification of the nanocrystals, an appropriate amount of oleic acid or decanoic acid (0.5−1 g) was also loaded into the reactor vessel. The content of the reactor vessel was mixed well under ultrasonic bath for 1 h. The hydrothermal reaction was performed using a homogeneously mixed precursor in the reactor at 400 °C and 38 MPa pressure for 10 min and terminated by submerging the reactor in a cold-water bath at room temperature. The organic ligand-modified nanocrystals were extracted from the product mixtures with hexane. The final products were precipitated from the resulting hexane phase by the addition of ethanol as an anti-solvent reagent, and then separated by using centrifugation. The obtained nanocrystals could be redissolved in some organic solvents, such as hexane, toluene, and tetrahydrofuran.

**Analytical Characterization.** The XRD patterns were recorded on a RINT-2000 spectrometer (Rigaku, Tokyo, Japan) with Cu Kα radiation. The samples were ground to fine powders before being subjected to XRD. The TEM images were obtained using a transmission electron microscope (JEM-1200EX, Japan) operated at 120 kV. A Hitachi H-7100 electron microscope operating at 200 kV was used for HRTEM analysis. The samples for TEM and HRTEM measurements were dispersed in hexane before being transferred to the carbon-coated copper grids. UV−vis spectra were measured via a JASCO V-570 spectrophotometer. The light transmission spectra were detected via a Hitachi U3010 spectrophotometer. Spectra were recorded at room temperature. An FT-IR spectrum was measured via a JASCO FT/IR-680 spectrometer.

## 3. Results and Discussion

The nanocrystal formation under the organic ligand-assisted supercritical water involves three steps: (a) sub 10 nm single-crystal formation in a supercritical water hydrothermal condition;[13] (b) the miscibility of the organic ligand molecules with high-temperature water, which is due to the lower dielectric constant of the water at its supercritical condition;[17] and (c) controlled nanocrystal growth from the selective reaction of organic ligand molecules with the specific inorganic crystal surface.

The organic ligand-assisted SCW method resulted in colloidally stable cobalt blue nanocrystals pigment in a single step. The cobalt blue nanocrystals obtained can be dispersed well in hexane and remain non-agglomerated, even over several months. The dispersion of 1 wt % nanocrystal particles in hexane gives a transparent blue pigment solution as pictured in Figure 1. We can separate these nanocrystals by centrifugation and obtain pure powders (Figure 1b). The average particle size of decanoic acid capped cobalt blue dispersed particles measured by dynamic light scattering is about 10 nm as shown in Figure 2. This DLS size includes the size of the decanoic acid ligand. The DLS size excluding the organic ligand is more or less comparable to the particle size obtained from TEM and XRD data. DLS measurement shows that the majority of nanoparticles are non-agglomerated, resulting in a transparent pigment system in a nonpolar solvent.

The powder XRD patterns of the nanocrystals indicated that they form a spinel cubic (*Fd*3*m* with lattice size of 8.104 Å, JCPDS 44-0160) structure at SCW conditions (Figure 3). They are well crystalline directly after the preparation at 400 °C temperature. Broad diffraction patterns of the samples indicate that the particles are nanocrystals. The reaction temperature plays an important role in the formation of pure $CoAl_2O_4$

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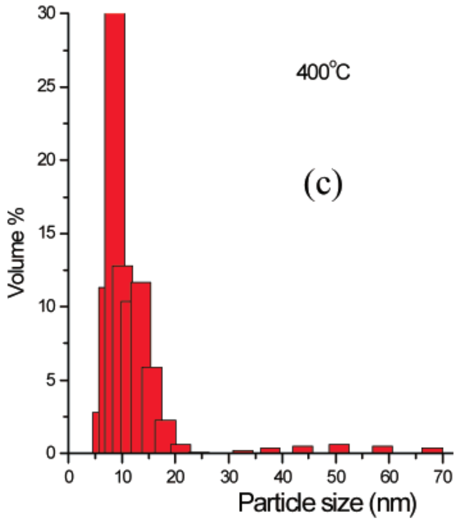


***Figure 2.*** Particle size distribution of decanoic acid ligand capped cobalt blue nanoparticles measured by dynamic light scattering.

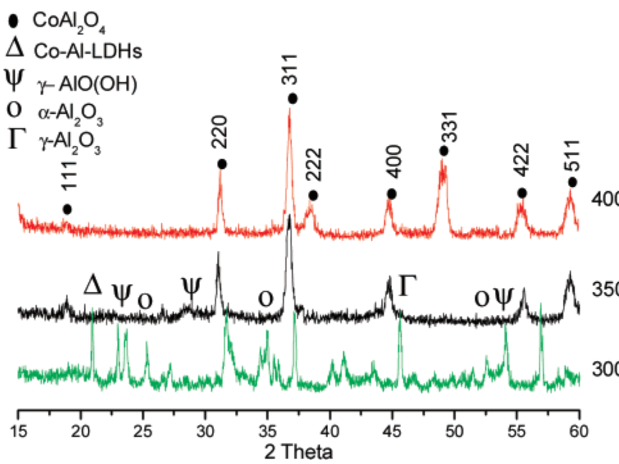


***Figure 3.*** XRD pattern of cobalt blue nano pigments obtained at different temperatures.

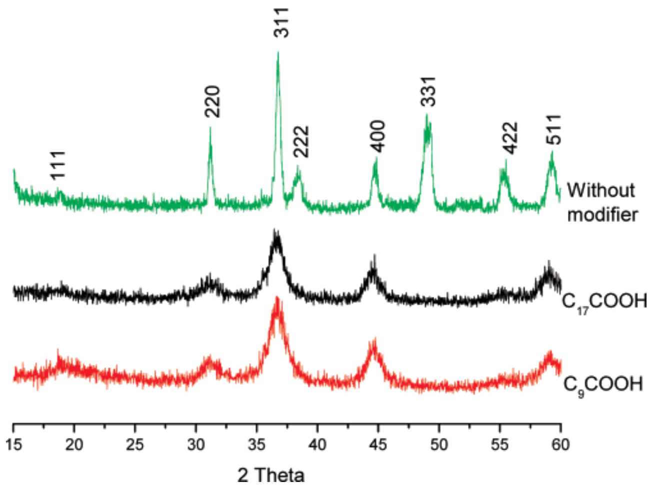


***Figure 4.*** The powder X-ray diffraction (XRD) patterns of cobalt blue nano pigments and hybrid nano crystal pigment capped with organic ligand molecules.

nanoparticles in the organic ligand-assisted SCW conditions. This is because of the rapid and homogeneous reaction atmosphere under SCW. Generally, a high reaction temperature or postheat treatment was necessary to synthesize pure $CoAl_2O_4$ crystalline particles. It is well known that $CoAl_2O_4$ particles prepared in the solution process without heat treatment generally possessed AlOOH or $\gamma$-$Al_2O_3$ as impurities. Chen et al. reported that $CoAl_2O_4$ nanoparticles were synthesized by a conventional hydrothermal method at 245 °C after a long 24 h reaction, but $\gamma$-AlOOH was included in the final product as impurity. In the present study, the pure $CoAl_2O_4$ nanocrystals were obtained at 400 °C temperature in 10 min reaction time without any postheat treatment. The effect of temperature (300, 350, and 400 °C) on the crystal phase and crystallinity of the product is shown in Figure 3. As evidenced from the XRD patterns, nanocrystals synthesized below 350 °C included traces of AlOOH phase. However, the impurity phase disappeared to show pure spinel $CoAl_2O_4$ as the temperature was increased above 380 °C. Therefore, we could obtain single nanocrystalline pure cobalt aluminate at the lowest temperature of 400 °C, exploiting the advantage of supercritical water.

The XRD pattern of the nanocrystals formed in the absence of organic molecules shows a relatively sharp peak with higher intensity. When organic molecules were introduced into the system, the organic ligand capped the nanocrystals surface, thereby inhibiting the growth of the particles. The XRD patterns of the nanocrystals modified with organic ligand indicate that the intensity of all of the peaks decreased with a peak broadening (Figure 4). This suggests that the size of the nanocrystals was decreased with organic ligand capping. The average crystallite size of the unmodified nanocrystals calculated by the XRD data using Scheerer's equation is 50 nm, while the average crystallite size of nanocrystals synthesized with organic modification is about 8 nm. These data support that each particle dispersed in a solvent is a single nano crystal without any aggregation. From the TEM and HRTEM images, we can further confirm that nearly monodisperse nanocrystals with cubic morphology were obtained by using the organic ligand-assisted SCW approach.

The TEM image of the nanocrystals synthesized without organic ligand molecules showed spherical shape particles with an average diameter of 50 nm and nanocrystals are aggregated (Figure 5c). When oleic acid and decanoic acid (molar ratio to $CoAl_2(OH)_5$ precursor 50:1) were added to the reaction system, as a result the particle growth was limited to an average diameter size of 7.5 and 8 nm, respectively. These nanocrystals exhibit a self-assembled 2D array on the surface of carbon coated copper grid with a nearest-neighbor spacing of ca. 4 and 3 nm maintained by oleic acid and decanoic acid capping groups, respectively, as shown in Figure 5a and b. This inter particular distance corresponds to that of the two organic ligands existing between two particles. The size of oleic acid and decanoic acid is 2 and 1.5 nm, respectively. The histograms of the particle size distribution analyzed by using transmission electron micrographs data are plotted as shown in Figure S1 (see Supporting Information). These data are consistent with DLS and XRD data that were mentioned before. The single-crystallinity and structure of the synthesized sample were further confirmed by HRTEM. Distinct lattice planes in the HRTEM image in Figure 5d further suggest that the particles obtained are single crystals. The HRTEM image of a selected individual particle shows a well-resolved lattice plane with an interplanar spacing of 0.24 nm corresponding to [311] plane of the cubic *Fd*3*m* space group, which was identified on the basis of data from the standard cobalt blue database JCPDS file, no. 44-0160.

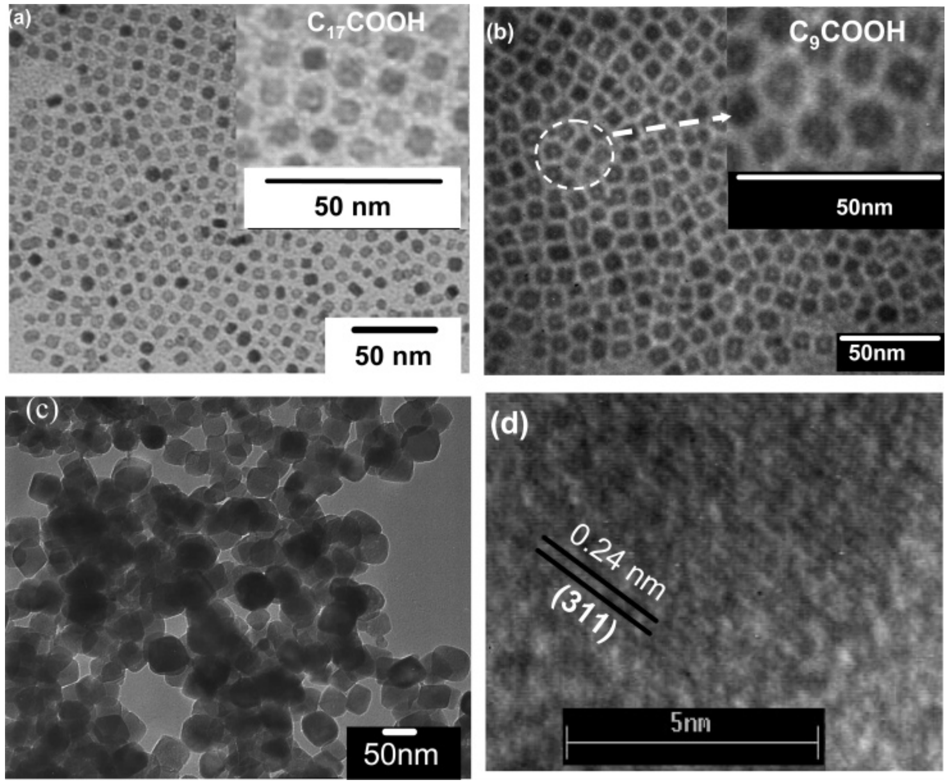


***Figure 5.*** TEM (a, c) and HRTEM (b, d) images of colloidal cobalt blue nanocrystals: (a) nanocrystals capped with oleic acid, (b) nanocrystals capped with decanoic acid, (c) nanocrystals without modifier, and (d) well-resolved lattice plane of a selected particle in (b).

The growth mechanism for the 2D cobalt blue hybrid nano pigments can be attributed to kinetic growth, which determines the final morphology of the nanocrystals. Here, organic ligand molecules had a pronounced effect on the morphology of the nanocrystals formed in the supercritical hydrothermal process, as reported for ceria nanocrystals.[14] The particle size of the cobalt blue nano crystal obtained in the absence of organic ligand is about 50 nm. When organic ligand is introduced to the reaction system, the organic ligand capped nanocrystals are formed. The organic ligands are miscible with water under supercritical hydrothermal condition due to the lower dielectric constant of water under supercritical conditions; thus, the resulting homogeneous phase provided a suitable environment for the interaction of organic ligand molecules with the surface of cobalt blue nanocrystals. Consequently, we were able to synthesize monodisperse nanocrystals by controlling the growth processes, which tend to take place at long reaction time. Because the growth process is time-dependent, the precursor with organic ligand, aged under ultrasonic bath for 1 h, promoted the surface modification under higher reaction temperature. In contrast to this result, the samples prepared without precursor aging time resulted in polydisperse nanoparticles with the size of 8−20 nm. In addition, the absence of organic ligand molecules led to the large spherical like particles with no control over the size and the morphology (Figure 5c). The reason for the aging effect is not clear; a detailed study to understand the interaction of precursor and organic ligand aged under ultrasonic bath is in progress. However, these results imply that the current successful synthesis of monodisperse nanocrystals can be attributed to the effective control of the growth processes under the organic ligand-assisted SCW conditions. Park et al.[18] reported the synthesis of monodisperse metal oxide nanocrystals from the separation of nucleation and growth process. Zhang et al.[14] reported the shape transformation of ceria nanocrystals from truncated octahedral to cubic caused by the suppression of the crystal growth on the [001] surface under similar organic ligand-assisted SCW conditions. These reports support our discussion that the effective control of the growth process is a key factor in obtaining size- and shape-controlled nanocrystals. In the present study, cobalt blue nanocubes were not formed at molar ratio less than 50:1; instead, relatively spherical and tetrahedral like particles were observed. These results suggest that, at suitable organic ligand concentration, the organic ligand molecules could effectively inhibit the growth of the nanocrystal in the entire crystallographic plane, which thus blocks crystal growth in all directions leading to the nanocube formation.

To examine the surface nature and interaction between the cobalt blue nanocrystals and organic ligand, we have analyzed the Fourier transform infrared (FTIR) spectrum of cobalt blue nanocrystals obtained from oleic acid and decanoic acid-assisted SCW synthesis. Bands observed in the 2800−2960 $cm^{-1}$ region were attributed to the C−H stretching mode of methyl and methylene groups (Figure 6). The bands at 1532 and 1445 $cm^{-1}$ correspond to the stretching frequency of the carboxylate group, which suggests that the carboxylate group from oleic acid and decanoic acid was chemically bonded to the surface of the cobalt blue nanocrystals and the other hydrocarbon groups were oriented outward.[19] This result is an evidence for the chemical

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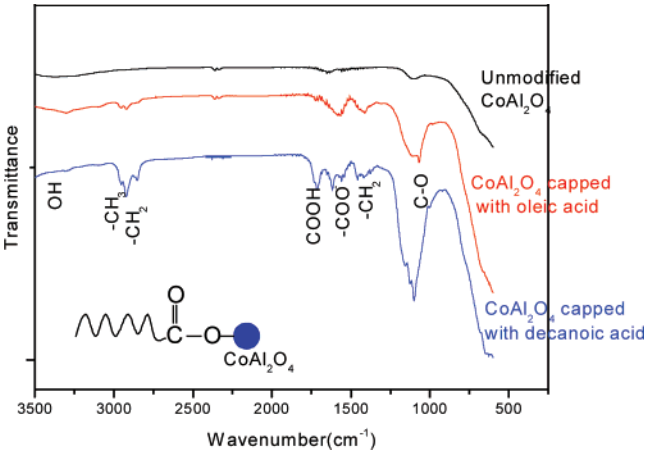


***Figure 6.*** FTIR spectrum of cobalt blue nanocrystals formed by oleic acid and decanoic acid-assisted SCW hydrothermal synthesis.

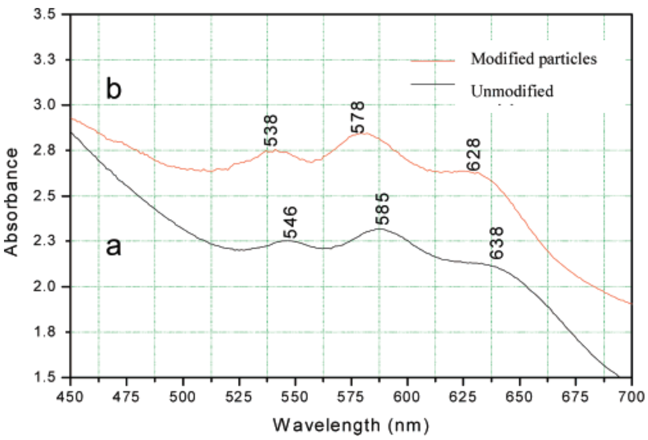


***Figure 7.*** UV−visible spectra of cobalt blue nano pigments synthesized with and without organic ligand capping.

bonds formation between the nanocrystal surface and organic ligand molecule in unique supercritical water reaction conditions similarly to that reported by Zhang et al., which are essential for the nanocrystals perfect dispersion in organic solvents and for the self-assembled type arrangement of individual nanocrystals. There is a band corresponding to free COOH acid, which might be due to the presence of some unreacted organic reagent in the samples. Because an excess of organic ligand (1:50) was used with starting precursor for surface modification, some of the solvated free acid was observed in the final product, which can be removed with washing.

***Table 1.*** Transparency, Scattering, and Color Parameters of the Decanoic Acid Capped Cobalt Blue Nano Pigment

| total transparency | direct transmission | scattering | absorption |
|---|---|---|---|
| 76% | 71% | 5% | 24% |
| Color Parameters | | | |
| $L^*$ | $a^*$ | $b^*$ | $C^*$ |
| 81.99 | −3.90 | −15.62 | 16.10 |

Optical properties of the as-prepared cobalt blue nanocrystals pigment were studied more quantitatively by measuring UV−vis spectra and the light transmission spectra. The energy level for $Co^{2+}$ ($3d^7$ configuration) in both octahedral and tetrahedral ligand fields presents three spin-allowed transitions. Regarding $Co^{2+}$ in a tetrahedral ligand field, which is responsible for blue color, the UV−vis spectra of the cobalt aluminate nanocrystals synthesized without organic ligand capping (Figure 7a) showed a three triple band ascribed to the $[^4A_2(F) \rightarrow {}^4T_1(P)]$ transition at around $\upsilon_1 = 638$ nm, $\upsilon_2 = 585$ nm, and $\upsilon_3 = 546$ nm. This triple band can be attributed to a Jahn−Teller distortion of the tetrahedral structure, according to Bambord. This spectrum is also consistent with those blue pigments reported elsewhere in the literature.[3,7] The samples that are prepared with organic ligand capping showed absorption bands around 628, 578, and 538 nm, with a slight shift to lower wavelength as shown in Figure 7b. This result is in contrast to results reported in the literature for cobalt aluminate particles with particle size above 50 nm. This blue shift indicates that the particle size reduction by the organic capping resulted in improved blue color when compared to that of uncapped large particles. However, further detailed study is necessary to confirm whether the blue shift is because of reduction in particle size. Further, we confirmed this hybrid nano pigment's optical property by measuring the light transmission spectra. In Figure 8, it can be seen that the absorption edge of the sample is somewhat steep, indicating very pure and brilliant color of the pigment. The color parameters ($L^*$, $a^*$, $b^*$), transparency, and scattering measurement of the synthesized cobalt blue nanocrystals are summarized in Table 1. The yield of blue color is mainly governed by the parameter $b^*$: the more negative is the $b^*$ value, the bluer is the color hue. The obtained cobalt blue nanocrystals produced

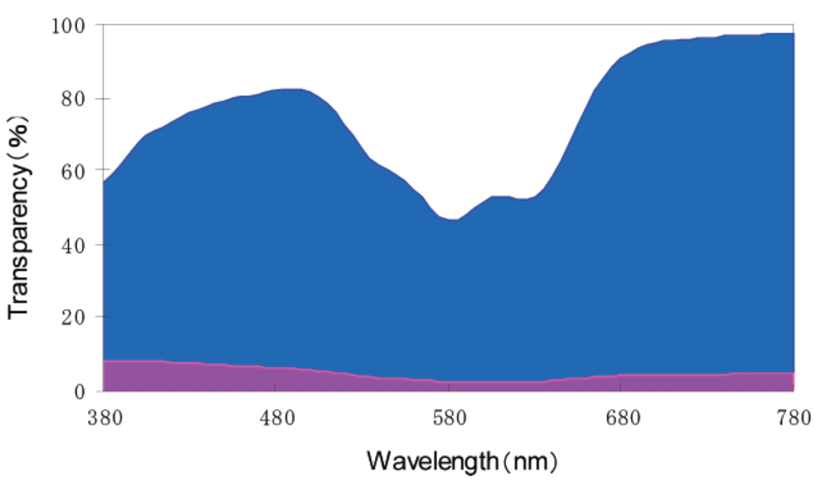


***Figure 8.*** Light transmission spectra of the hybrid cobalt blue nano pigment measured with 0.1 wt % nanoparticles dispersed in hexane.

much bluer color hues ($b^*$ values around −16). On the other hand, the coordinate $L^*$ obtained is about 82, which gives us the lightness of the pigment (the higher is $L^*$, the lighter is the color), also being an indirect measurement of the brightness or intensity of the pigment. The color parameter $a^*$ is about −4, which represents the difference between the green and red colors in the color coordinates. These color parameters are comparable to those cobalt-based blue pigments prepared by the traditional high-temperature ceramic synthesis procedure.[20] However, the organic ligand capped nanocrystal pigment shows excellent transparency, which has not been reported for complex metal oxide nanocrystal pigments. The transparency and scattering in Table 1 were determined by the light transmission spectra. The chromaticity and color matching parameters were calculated employing CIELAB procedure. The details of the measurement and calculations are provided in the Supporting Information. These data reveal that out of the total light passed, 76% of light corresponds to total transmittance (the blue area in the Figure 8) and 24% of light corresponds to absorption. The scattering was calculated by considering the total transmittance, in which 5% of light was scattered (maroon blue area in the Figure 8) and the remaining 71% of light was directly transmitted. In contrast to this, the cobalt blue nanoparticles synthesized without organic ligand capping showed only 37% transparency with a large amount of scattering of about 23%, which was due to the agglomerated particles. The brilliant transparency of the hybrid nano pigment is attributed to the typical small particle size of the pigment with particle surface capped with the organic ligand, which in turn resulted in a stable dispersion. This leads to a fine-tuning of the scattering of nanoparticle pigment. It was reported that, for colored inorganic pigments, there are particle size regions in which scattering has disappeared and the wavelength-dependent absorption constant reaches a finite value that means the pigment becomes transparent.[5] These results suggested that the nano size effect on the optical property of the cobalt blue nanocrystal pigment particles can be seen in terms of decreased scattering, less than 5% against 24% absorption, resulting in the transparent pigment system.

## 4. Conclusions

In conclusion, we report a simple and rapid synthetic method for the high-quality transparent cobalt blue nano pigment by the organic ligand-assisted supercritical water hydrothermal method. This method, in general, applies to a large variety of complex metal oxides and provides a scalable and flexible approach for the advanced material fabrication. The organic ligand capping could effectively inhibit the particle growth and also control the size of nanocrystals. The unusual small particle size of the pigment with particle surface capped with organic ligand resulted in a stable dispersion. This helps to diminish the scattering effect of the nano blue pigment, realizing a transparent complex oxide cobalt blue nano pigment without any postheat treatment.

**Supporting Information Available:** Histograms of the particle size distribution analyzed by using transmission electron micrographs data plotted (Figure S1). Details of the light transmission measurement and CIELAB color parameter calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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