

Fabrication of Two-Dimensional Structures of Metal Oxide Nanocrystals Using Si Substrate Modified with 3,4-Dihydroxyhydrocinnamic Acid

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Sufficiently high-coverage monolayer structures of cerium oxide nanocrystals modified with decanoic acid, with sizes of ~9 nm, were fabricated on the surface using a silicon substrate modified with 3,4-dihydroxyhydrocinnamic acid where catechol group lied at the top. By doing this, no further pretreatment for the modified nanocrystals is required to fix them chemically on the substrate. Selective adhesion between nanocrystals and the substrate for the two-dimensional assembly can be attributed to the chemical bonding formed by on-site ligand exchange on the catechol-terminated substrate. Catechol-carboxyl group ligand exchange results in high-efficient due to higher affinity of catechol to metal oxide surfaces. This affinity difference enabled to perform this on-site ligand exchange even at room temperature.

1. Introduction

Highly crystalline metal oxide nanoparticles have been extensively investigated in various fields such as electrochemistry and optics and used in catalysis. Characteristics of nanometer-sized materials, e.g., catalytic or magnetic effects, are expected to be different from those of bulk materials.¹ Recently, the assembling of a highly crystalline metal oxide nanoparticle layer at room temperature has attracted considerable attention.^{2,3} Highly crystalline metal oxide films have a high potential for use in active catalysts, high refractive index films, and even high-permittivity insulating materials. However, such high-quality films are fabricated by subjecting them to high-temperature treatments, which damage heat-sensitive substrates such as plastic polymers. If the process of fabricating a thin film can be divided into the processes—synthesis of highly crystalline nanoparticles at high temperature and assembly of the nanocrystals on substrates at room temperature, highly crystalline metal oxide thin films can be fabricated on such heat-sensitive substrates.

For the fabrication of two-dimensional structures or monolayer-controlled thin films of nanoparticles on the surface, the interactions between nanoparticles should be decreased, whereas the interactions between nanoparticles and the substrate should be carefully designed.² In order to reduce the interactions between nanoparticles or to increase the interactions between nanoparticles and the solvent, surfaces of metal oxide nanoparticles

are modified with organic molecules that have a high affinity to the solvent.^{4–12} Too strong interactions between nanoparticles result in aggregation of nanoparticles. The interactions between nanoparticles and the substrate can be controlled by the formation of some covalent bonds^{13–18} or electrostatic attraction;^{19,20} selective adhesion between nanoparticles and the substrate can be attributed to the chemical bonding or electrostatic forces. Cattaruzza et al. have used carboxyl-carboxyl group ligand exchange by using free 10-undecenoic acid

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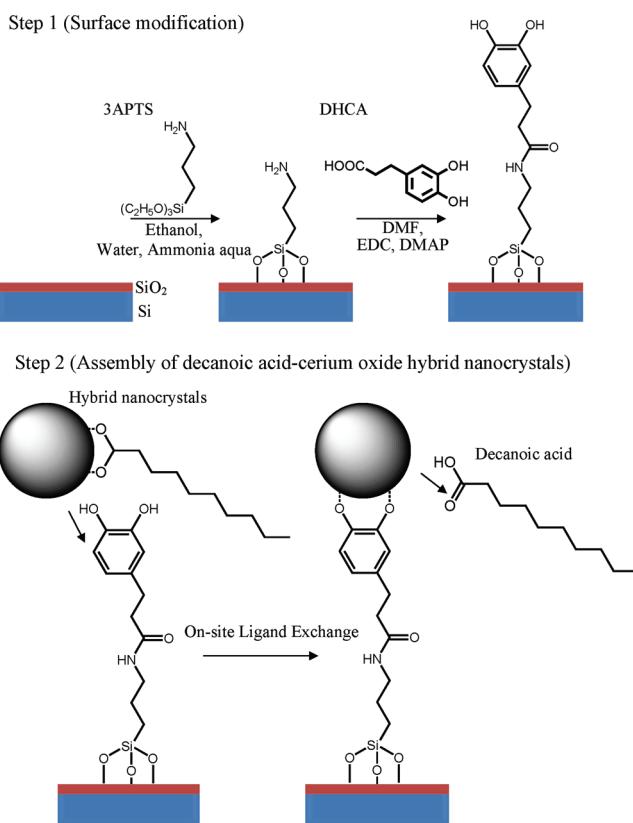
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(A) in order to produce linkers on Fe_3O_4 nanoparticles modified with carboxylic acid and then, (B) these linkers reacted with adsorption sites on the surface to establish the chemical bonding with the substrate.¹³ Other groups also took an (A)+(B) strategy to fix the nanoparticles on the substrate.^{14–18} However, the process (B) is generally harmful to dispersibility of nanoparticles in solvents. Besides, a modified nanoparticle system that consists of an inorganic core and organic molecules is governed by the chemical equilibrium in the solvent. It is impossible to remove all the free organic molecules, such as free modifiers or linkers, in the solvent with leaving them attached on the nanoparticles. Therefore, when the linkers on the nanoparticles react with adsorption sites on the substrate, the free linkers can be also reacted with those sites, thereby interfering with adsorption of nanoparticles. The efficient method to chemically fix high-dispersible nanoparticles to the substrate is anticipated for uniform two-dimensional assembly.

Here, we report a new, simple, and efficient method for assembling cerium oxide nanocrystals modified with decanoic acid two-dimensionally on the surface by modifying substrates with 3,4-dihydroxyhydrocinnamic acid (DHCA). By doing this, no further pretreatment, as process (B), for the modified nanocrystals is required to fix them chemically on the substrate. We have modified highly crystalline metal oxide nanoparticles with carboxylic acid during their synthesis in supercritical water (SCW).^{4–6} These modified nanocrystals can be mono-dispersed in organic solvents such as tetrahydrofuran (THF), toluene, or cyclohexane.^{4,6} In order to chemically anchor high-dispersible decanoic acid-cerium oxide hybrid nanocrystals, we used on-site ligand exchange between the carboxylic group of decanoic acid, a modifier of nanocrystals, and the catechol group of DHCA terminated on the Si substrate (see Scheme 1). The proposed method has at least four major advantages. (1) The catechol group coordinates with solid surfaces of nanocrystals in exchange with the carboxyl group of carboxylic acid even at room temperature due to a high affinity of catechol to various metal oxides, such as Fe_3O_4 , TiO_2 , or ZrO_2 , etc.^{21–27} (2) Nanocrystals with a high affinity for solvents can be prepared. No process of attaching free DHCA onto nanocrystals as linkers is included in this method. (3) A comparison with the process using free DHCA shows that it is favorable to use DHCA chemically bonded with a substrate in terms of chemical equilibrium. Decanoic acid attached to the hybrid

Scheme 1.^a



^a Step 1. The surface is modified with 3APTS, a type of silane coupling agent with an amino group at the top (amine-Si), and then the carboxyl group of DHCA is condensed with the amino group of the 3APTS-terminated surface (DHCA-Si). Step 2. When decanoic acid-cerium oxide hybrid nanocrystals are adsorbed on the DHCA-terminated surface, decanoic acid at the bottom of the nanocrystals is locally exchanged with DHCA, and the nanocrystals covalently bond with the substrate.

nanocrystals can be exchanged with DHCA chemically bonded with the substrate without any harmful effect of free decanoic acid in the solvent. (4) This method is highly versatile and can be divided into three steps—synthesis of highly dispersible nanocrystals at high temperature, modification of the substrates, and the assembly of the nanocrystals on these substrates at room temperature. Nanocrystals modified with carboxylic acid can be used in this method regardless of their cores since a high affinity of the catechol group to various metal oxide nanoparticles was used.

2. Experimental Section

Preparation of Decanoic Acid-Cerium Oxide Hybrid Nanocrystals. The hydroxylated cerium oxide precursor (0.05 M) with 2.5 mL of water was transferred to a pressure-resistant hastelloy vessel (inner volume 5 mL). The synthesis of the precursor was described elsewhere in detail.⁴ To synthesize cerium oxide nanocrystals modified with decanoic acid, 0.09 g of decanoic acid was also loaded into the vessel. The hydrothermal reaction was performed in the reactor at 400 °C for 10 min. The organic-ligand-modified nanocrystals were extracted from the product mixtures with hexane (3 mL). The final products were precipitated from the resulting hexane phase by an addition of ethanol (10 mL) as an antisolvent agent and then separated by using centrifugation. The products were

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centrifuged and washed with a mixture of toluene (10 mL) and ethanol (10 mL) twice. After having been dissolved in cyclohexane, those were freeze-dried to obtain the hybrid nanocrystals. The CeO₂ hybrid nanocrystals synthesized were characterized using transmission electron microscopy (TEM; HitachiH7650, Hitachi).

Modification of Silicon Substrates. Silicon (100) samples with dimensions of 1.5 cm × 0.8 cm were subjected to ozone treatment for 30 min to produce hydroxylated silicon oxide for surface modification. To create adsorption sites for the hybrid nanocrystals, first, 1.15 g of 3-aminopropyltriethoxysilane (3APTS) was introduced in a mixture of ethanol (45.6 mL), water (0.76 mL), and 28% ammonia aqua (1.26 mL), and the samples were immersed in that solution for 5–6 h to produce amine group termination. Then, the substrates were rinsed with ethanol. Then, the substrates were subjected to heat treatment at 130 °C for 3APTS to attach firmly to the substrates. Second, the samples were immersed in 5 mL of *N,N*-dimethylformamide (DMF) containing 0.2 M of 3,4-dihydroxyhydrocinnamic acid (DHCA), 0.2 M of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC), a condensation agent, and 0.02 M of *N,N*-dimethyl-4-aminopyridine (DMAP), a catalyst, for 15 h for the condensation of carboxyl group of DHCA with amine group. After the treatment with DHCA, the silicon substrates were washed with fresh ethanol to remove the remaining DMF. In some experiments, hexyltriethoxysilane was used for termination of hexyl group on the silicon substrate. Hexyltriethoxysilane (0.75 g) was introduced in a mixture of ethanol (47.3 mL), water (1 mL), and 28% ammonia aqua (1.8 mL), and the samples were immersed in that solution for 10 h to produce hexyl group termination. X-ray photoelectron spectroscopy (XPS; ESCA-3400, Shimadzu) was performed to characterize the surface modification of Si substrate.

Assembly of Two-Dimensional Structures of Decanoic Acid-Cerium Oxide Hybrid Nanocrystals. For the adsorption of hybrid nanocrystals on the treated silicon substrate, the substrate was immersed in 0.2 mL of tetrahydrofuran (THF) or cyclohexane containing 1 mg of decanoic acid-cerium oxide hybrid nanocrystals and subjected to sonication for 1 h. After the adsorption, the sample was rinsed with the fresh solvent. For the characterization and high-resolution observation of the structures, field emission scanning electron microscopy (FE-SEM; HitachiS4800, Hitachi) was carried out. Quantitative analysis of nanocrystals adsorbed on the substrate was carried out using image analysis software (ImageJ, Wayne Rasband National Institutes of Health). To extract nanocrystals in images, contrast differences are used on the images. Atomic force microscopy (AFM; SPM3800, SII) was used for topography images of the structures. The thickness and refractive index of the layered structures were evaluated by spectroscopic ellipsometry (SE; FE-5000S, Otsuka Electronics). The incident angle of the light beam was 70°. The wavelength was varied from 300 to 800 nm during the investigation of the optical characteristics of the structures. SE was carried out at more than three macroscopically spaced points on the samples.

Synthesis of Composite Structure of DHCA-Silica Nanoparticles and Decanoic Acid-Cerium Oxide Hybrid Nanocrystals. Spherical silica nanoparticles (Polysciences, Inc.), with sizes of 0.01 μm, broad distribution, were used to confirm the occurrence of the on-site ligand exchange. First, 0.4 g of 3APTS was introduced in a mixture of ethanol (40 mL) and 28% ammonia aqua (0.4 mL), and the silica nanoparticles were immersed in that solution for 5–6 h to produce an amine group termination. The nanoparticles were centrifuged and washed with toluene (10 mL) twice to separate modified silica nanoparticles from the

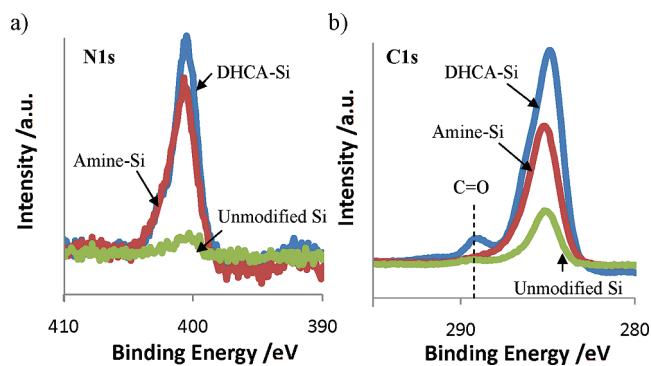


Figure 1. (a) N1s and (b) C1s XPS spectra of unmodified (unmodified Si), 3APTS-treated (amine-Si), and DHCA-treated silicon substrates (DHCA-Si).

solvent. After dissolving in water, the product was freeze-dried to obtain amine-silica nanoparticles. Then, amine-silica nanoparticles were subjected to heat treatment at 130 °C for 3APTS to attach firmly. Second, 0.025 M of amine-silica nanoparticles were immersed in DMF (10 mL) containing 0.025 M of DHCA, 0.025 M of EDC, and 0.01 M of DMAP for 20 h for the condensation of the carboxyl group of DHCA with the amine group. The final product was centrifuged and washed with toluene twice. After dissolving in water, the final products were freeze-dried to obtain DHCA-silica nanoparticles. Then, a composite structure of DHCA-silica nanoparticles and the hybrid nanoparticles was synthesized. Ten milligrams of decanoic acid-cerium oxide hybrid nanocrystals dispersed in cyclohexane (5 mL) and 2 mg of DHCA-silica nanoparticles dispersed in water (10 mL) were mixed, and the mixtures were sonicated for 10 min for the ligand exchange reaction to take place. After the reaction, the sediment between water and cyclohexane interface was extracted and centrifuged with cyclohexane (10 mL) twice to remove free hybrid nanocrystals. The final products were then centrifuged and washed with toluene (10 mL) twice. After dissolving in cyclohexane, they were freeze-dried to obtain the hybrid nanocrystal-DHCA-silica nanoparticle composite. Fourier transform infrared spectroscopy (FT/IR-680plus, Jasco) was used to investigate the surface modification of silica nanoparticles.

3. Results and Discussion

3.1. Characterization of Modified Si Substrates. The surface treatment of silicon was carried out so that a covalent bond was formed between nanocrystals and the substrate (see Scheme 1, step 1). To create adsorption sites for decanoic acid-cerium oxide hybrid nanocrystals, first, 3APTS was attached on the surface to produce amine group termination. Second, the samples were immersed in DMF containing DHCA, EDC, a condensation agent, and DMAP, a catalyst, for the condensation of carboxyl group of DHCA with an amine group on the surface. The XPS of the sample immersed in 3APTS solution, amine-Si sample, shows that the surface was terminated with an amine group (Figure 1 (a)). The peak centered at 400.7 eV in the N1s spectrum of the amine-Si sample is associated with C–N from the amine group.²⁶ The small peak was also found on the Si sample due to some contamination. After the immersion in the DHCA solution, DHCA-Si sample, the surface was terminated with DHCA where

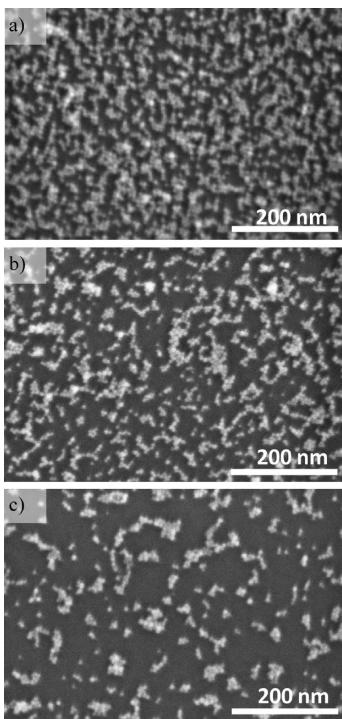


Figure 2. SEM images of decanoic acid-cerium oxide hybrid nanocrystals fabricated on (a) DHCA-Si, (b) unmodified Si, and (c) amine-Si.

the catechol group lied at the top. From the N1s spectrum of the DHCA-Si sample shown in Figure 1(a), the peak associated with C–N from amide groups was observed at 400.5 eV. The peak associated with C=O from an amid bond was clearly observed at \sim 288 eV in the C1s spectrum of the DHCA-Si sample (Figure 1 (b)).^{28,29} The broad peak centered at \sim 285 eV consists of the peaks associated with the sp^3 carbon and C–N from an amide group.²⁶ DHCA was chemically attached on the substrate by these processes.

3.2. Fabrication of Two-Dimensional Nanocrystal Structures Using Catechol-Terminated Substrates. Two-dimensional nanocrystal structures on the catechol-terminated silicon substrate mentioned above were fabricated by using on-site ligand exchange (see Scheme 1, step 2). For the adsorption of the hybrid nanocrystals, the substrate was just immersed in THF containing the hybrid nanocrystals and subjected to sonication. After the adsorption, the samples were rinsed with the fresh solvent. The average size of the nanocrystals used was found to be 8.56 ± 1.45 nm by TEM. FE-SEM images of the samples after the adsorption of hybrid nanocrystals on the DHCA-Si, unmodified Si, and amine-Si samples are shown in parts (a), (b), and (c), respectively, of Figure 2. Figure 2(a) clearly shows that decanoic acid-cerium oxide hybrid nanocrystals were dispersed two-dimensionally on the DHCA-Si sample. The coverage of nanocrystals adsorbed was $45.6 \pm 2.2\%$ from the SEM images. The hybrid nanocrystals were adsorbed through on-site

Table 1. Water Contact Angle of Hydroxylated Silicon (Unmodified Si) and Surfaces Terminated with DHCA (DHCA-Si), Amine Group (Amine-Si), and Hexyl Group (Hexyl-Si)

substrate	hydroxylated	DHCA-Si	amine-Si	hexyl-Si
water contact angle [°]	9	47	54	95

ligand exchange between nanocrystals and the modified substrate. Comparing to the method using carboxyl-carboxyl group ligand exchange,¹³ the catechol-carboxyl group ligand exchange results in high-efficient due to a higher affinity of catechol to metal oxide surfaces. This high affinity of catechol was reported for Fe_3O_4 , TiO_2 , ZrO_2 , SnO_2 , Al_2O_3 , and CuO .^{21–27} The nanocrystals seem to slightly aggregate on the substrates compared to Fe_3O_4 nanoparticles.¹³ Nanocrystals adsorbed were stuck to each other on the substrate. In contrast to highly hydrophobic hydrogen terminated surfaces,¹³ more hydrophilic surfaces were used in this research; adsorptive water on hydrophilic surfaces is likely to make hydrophobic nanocrystals aggregated on the surfaces. As shown in Figure 2(b), smaller numbers of hybrid nanocrystals were found even on unmodified Si. The coverage was $29.4 \pm 1.1\%$. The larger number of nanocrystals were stuck to each other on hydrophilic unmodified-Si although the coverage of nanocrystals was lower than on DHCA-Si. This supports that adsorptive water on hydrophilic surfaces causes aggregation of the hydrophobic nanocrystals. The water contact angles of surfaces of hydroxylated silicon and surfaces terminated with an amine group and DHCA are listed in Table 1.

Covalent bonding is not supposed to take place between hybrid nanocrystals and the substrates on unmodified Si and amine-Si. Thus, those nanocrystals observed were rather residual nanocrystals after rinse. This appeared stronger adhesion of nanocrystals on hydrophilic surfaces. Adsorptive water on hydrophilic surfaces affected rinse with nonpolar organic solvents. As compared to the surface terminated with an amine group, the hydroxylated silicon surface was highly hydrophilic; fewer nanocrystals were found on amine-Si, coverage of $17.2 \pm 1.0\%$, (Figure 2(c)) consistently. The coverage of nanocrystals on the DHCA-Si sample was found to be much higher; nevertheless, the surface terminated with DHCA was as hydrophobic as that with amine group indicating that the adsorbed nanocrystals were more than just residual.

Thermal stability of two-dimensional hybrid nanocrystal structures on DHCA-Si was tested to investigate bonding between nanocrystals and the substrates. Figure 3(a),(b) shows SEM images of two-dimensional hybrid nanocrystal structures on the DHCA-Si samples after having been heat treated for 1 h in argon flow (35 sccm) regulated at the pressure of 100 Pa at 200 and 300 °C, respectively. The coverage of nanocrystals on DHCA-Si after having been heat treated at 200 and 300 °C is plotted in Figure 3(c). After having been heat treated at 200 °C, the structures still remained intact on the DHCA-Si sample ($42.8 \pm 1.5\%$). After having been heat treated at 300 °C, nevertheless the structures started

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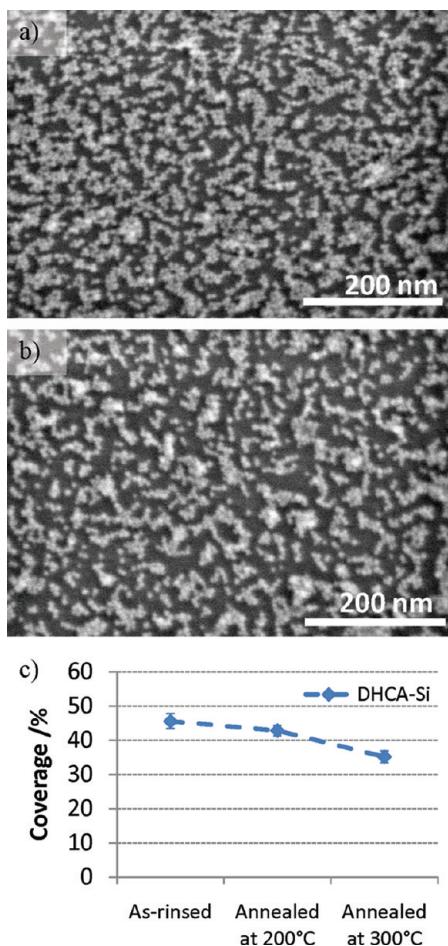


Figure 3. SEM images of nanocrystals fabricated on DHCA-Si samples after heat treated at (a) 200 °C and (b) 300 °C. (c) The plots of coverage of nanocrystals adsorbed on DHCA-Si for as-rinsed, after subsequent annealing at 200 and 300 °C.

to break up, and the structures were still preserved on the DHCA-Si surface ($35.1 \pm 1.7\%$). A higher temperature needs to detach the hybrid nanocrystals significantly. The temperature dependence of desorption of the hybrid nanocrystals that was adsorbed on the DHCA-Si substrate consistently shows chemical bonding of the catechol group onto the metal oxide surfaces. Detachment of the catechol group from the surface was observed at the temperature range of 200 to 400 °C from simultaneous gravimetric and differential thermo-analysis of catechol modified SnO_2 nanoparticles.²⁶

The decanoic acid-cerium oxide hybrid nanocrystals adsorbed have a heterogeneous ligand structure by ligand exchange taking place locally on the surface; one side of the hybrid nanocrystals is modified with the catechol group of DHCA, and the other sides are modified with the carboxyl group of decanoic acid. Generally, it is difficult to prove the ligand exchange locally taking place on the silicon substrate because of its limited surface area. However, we can assume silica nanoparticles to be a nanoscale silicon substrate. FTIR has revealed that on-site ligand exchange can take place on the surfaces of silica nanoparticles at room temperature. To confirm the occurrence of the ligand exchange, a composite structure of DHCA-silica nanoparticles and decanoic acid-cerium

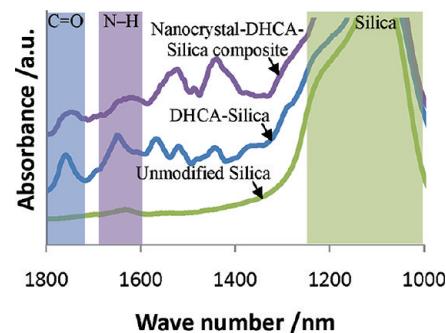


Figure 4. FTIR spectra of unmodified silica nanoparticles (unmodified silica), DHCA-treated silica nanoparticles (DHCA-silica), and decanoic acid-cerium oxide hybrid nanocrystals adsorbed on DHCA-treated silica nanoparticles (nanocrystal-DHCA-silica composite).

oxide hybrid nanocrystals was synthesized. As shown in Figure 4, the band ranging from 1000 to 1300 cm^{-1} is assigned with silica in the spectrum of the silica sample before modification. After silica nanoparticles modified with 3APTS and DHCA successively, DHCA-silica sample, the bands associated with the C–C stretching mode of aromatic rings were clearly observed at 1511 and 1557 cm^{-1} .^{24,26,27,30,31} The bands at 1430 cm^{-1} and shoulder at 1270 cm^{-1} are assigned respectively to the O–H bending and C–O stretching modes from the catechol group.^{26,27} The bands corresponding to the N–H bending and C=O stretching modes from an amide group were observed at 1639 and 1749 cm^{-1} , respectively.²⁶ The small band associated with the N–C stretching mode from an amide was observed at $\sim 1360 \text{ cm}^{-1}$.²⁶ These results show that DHCA is chemically attached to the surfaces of silica nanoparticles. The spectrum of the hybrid nanocrystal-DHCA-silica composite sample presented in Figure 4 shows that the bands corresponding to the stretching mode of the carboxylate anion groups of the hybrid nanocrystals at 1429 and 1514 cm^{-1} was simultaneously observed with the bands associated with silica.^{4,7} Furthermore, the bands at ~ 1610 and 1733 cm^{-1} associated with N–H and C=O were slightly shifted toward lower wavenumbers and broadened as compared to those bands from free DHCA-silica nanoparticles. The shoulder from the C–O stretching mode was shifted to 1240 cm^{-1} . The band at $\sim 1470 \text{ cm}^{-1}$, which corresponds to one of the C–C stretching modes of aromatic rings, was also slightly shifted; another band from aromatic rings overlapped with the band corresponding to the stretching mode of carboxylate anion groups. These results indicate that the hybrid nanocrystals covalently bond with DHCA-silica nanoparticles through the on-site ligand exchange on the surfaces.

3.3. Fabrication and Characterization of Monolayer-Control Nanocrystal Films through on-Site Ligand Exchange. Monolayer-controlled CeO_2 nanocrystal films were fabricated from solution in which large amounts of

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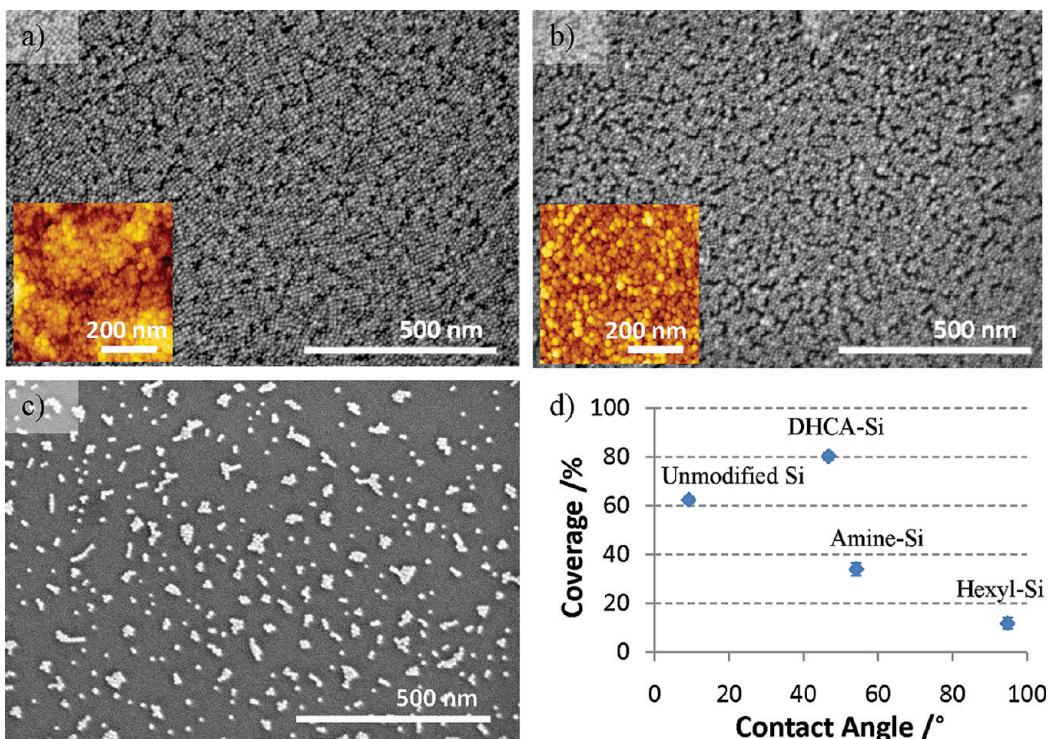


Figure 5. SEM image of (a) as-adsorbed multilayer hybrid nanocrystal film deposited on DHCA-Si and (b) monolayer-controlled nanocrystal film fabricated on DHCA-Si by subsequent rinse with cyclohexane. In insets of (a) and (b), topographic images of as-adsorbed multilayer and monolayer-controlled nanocrystal films obtained by AFM were also displayed. (c) SEM image of hybrid nanocrystals remained on hexyl-Si after rinse with cyclohexane. (d) The plots of coverage of nanocrystals fabricated on unmodified Si, DHCA-Si, amine-Si, and hexyl-Si as a function of water contact angles of those terminations.

the hybrid nanocrystals were dissolved and subsequent rinse with cyclohexane using a silicon substrate modified with DHCA. Desorption of nanocrystals in a solvent was rather investigated in this section; meanwhile the adsorption was rather discussed in the 3.2 section. To obtain dense hybrid nanocrystals in cyclohexane, the solvent was gradually evaporated at a pressure of 500 hPa, regulated by an evaporator (Vacuum controller V-850, BUCHI). The SEM image presented in Figure 5(a) shows as-adsorbed multilayers of hybrid nanocrystals on the substrate. Three-dimensional self-assemble structures of hybrid nanocrystals were fabricated on the modified substrate. Monolayer-controlled structures of nanocrystals could not be obtained by mere self-assembly of nanocrystals in solution unless the density of nanocrystals in the solvent was carefully regulated. The top layer of this self-assemble structure was not fully covered with nanocrystals. Island structures from incomplete coverage of the top layer were clearly seen in a topographic image obtained by AFM as in inset of Figure 5(a). The SEM image presented in Figure 5(b) shows that a sufficiently high-coverage monolayer-controlled hybrid nanocrystal film was fabricated by subsequent rinse (coverage of $80.3 \pm 1.5\%$). Hybrid nanocrystals on the hybrid nanocrystals were washed away leaving monolayer structures of hybrid nanocrystals on the modified surface. Selective adhesion between nanocrystals and the substrate arises from uniform modification of the substrate with DHCA and the on-site ligand exchange. In the inset of Figure 5(b), the topographic image obtained by AFM is presented. From

topographic analysis performed by AFM, the residual nanocrystals remained on the nanocrystal monolayer were sufficiently low ($\sim 10\%$ from the image). Those nanocrystals appear as bright spots in the AFM image. The heights of those nanocrystals were evaluated to be ~ 8 nm in the image. Hybrid nanocrystals synthesized have a high affinity to the solvent. Thus, an adsorption coefficient between nanocrystals and the substrate can be defined in the solvent. The adsorption coefficient between nanocrystals and the substrate is much larger than that between nanocrystals because of the chemical bonding. Meanwhile, as presented in Figure 5(c), only a small number of nanocrystals remained after rinse ($11.9 \pm 2.2\%$) on the hexyl group terminated silicon substrate (hexyl-Si), where surface termination was similar to that of hybrid nanocrystals. This value is comparable to the coverage of nanocrystals remaining on the nanocrystal monolayer on DHCA-Si. The selectivity can be increased if the surfaces terminated with DHCA and the hexyl group are simultaneously used for such as a patterning process.

Dependence of hydrophobicity of the surfaces to the coverage of nanocrystals remaining was also observed, which was discussed in the 3.2 section. The phenomenon that more nanocrystals remained on hydrophilic surfaces after rinse more explicitly appeared when the substrate was rinsed in cyclohexane than in THF. This also supports the hypothesis that adsorptive water on hydrophilic surfaces affects rinse with nonpolar organic solvents; THF can somewhat remove adsorptive water on the

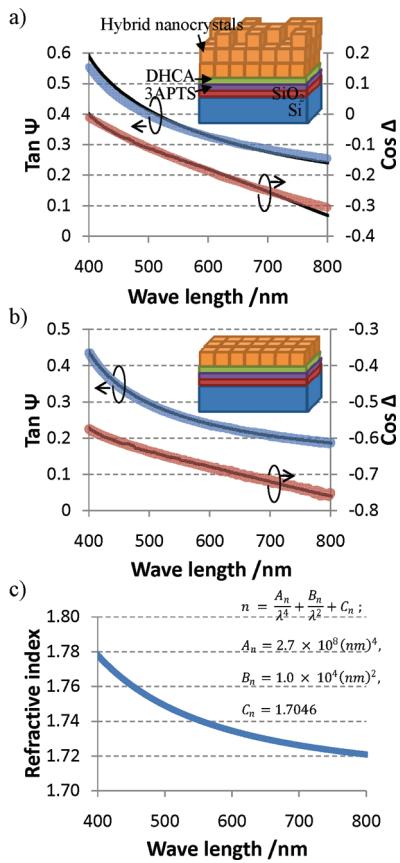


Figure 6. $\text{Tan}\Psi$ and $\text{Cos}\Delta$ of (a) as-adsorbed multilayer and (b) monolayer-controlled nanocrystal film measured by SE are plotted as a function of wavelength. Solid lines are the fitting curves, which were calculated by the optical model. In inset, a simple optical model of those structures is given. (c) The refractive index of the monolayer-controlled hybrid nanocrystal film is fitted by Cauchy model. The Cauchy formula and parameters are given in the legend.

surface. As presented in Figure 5(d), the coverage of nanocrystals on unmodified Si, DHCA-Si, amine-Si, and hexyl-Si is plotted as a function of a water contact angle of those terminations. The water contact angle of the surface terminated with the hexyl group is also listed in Table 1. As the water contact angle on surfaces was higher, the coverage of nanocrystals became smaller except for the coverage on DHCA-Si. The result proves selective adhesion of nanocrystals on the catechol-modified substrate due to on-site ligand exchange.

The structures presented in Figure 5(a),(b) were regarded as a continuous thin film from SE; the defects appeared as black dots in the images, with a size of ~ 10 nm, were sufficiently smaller than the wavelength of probe light. SE analysis was performed onto these nanocrystal films fabricated macroscopically on the substrate. The simple optical model, where thin transparent film layers of SiO_2 , 3APTS, and DHCA were stacked at the interface, was used to determine the complex dielectric function of the nanocrystal films (see the inset of Figure 6(a),(b)). The thicknesses of the interfacial layers, SiO_2 , 3APTS, and DHCA, were measured separately in advance to investigate the optical characteristics of the hybrid nanocrystal structures. The thicknesses of the SiO_2 , 3APTS, and DHCA layers were evaluated to be

1.35, 1.27, and 2.78 nm, respectively. The thickness of as-adsorbed multilayer structures of hybrid nanocrystals fabricated on the modified substrate was estimated to be ~ 26 nm; however, the simple optical model mentioned above could not regenerate $\text{Tan}\Psi$ and $\text{Cos}\Delta$ of the as-adsorbed film very well, as in Figure 6(a). This is presumably due to a very rough surface from incomplete coverage of the top layer of this film as observed in the AFM image in inset of Figure 5(a). Although it is not accurate, two or three nanocrystal monolayers are likely to have been adsorbed on the substrate before rinse. As presented in Figure 6(b), $\text{Tan}\Psi$ and $\text{Cos}\Delta$ of the monolayer-controlled film measured by SE were well regenerated by the simple optical model. The thickness of the monolayer-controlled film was estimated to be 10.6 nm; this value is almost the same as the size of the nanocrystals. This result clearly proves that the nanocrystal structures are monolayer-controlled macroscopically. The dispersion of the refractive index obtained from the complex dielectric function, which is calculated from the optical model as in the inset of Figure 6(b), is well fitted by the Cauchy model, where it is often used for transparent films,³² as shown in Figure 6(c). The film was transparent in the wavelength range of 400 to 800 nm. The Cauchy formula and parameters used for fitting are given in the legend of Figure 6(c). The refractive index of this film was 1.73 at a wavelength of 633 nm. Comparing to the refractive index of cerium oxide thin films obtained by other techniques such as electron beam evaporation at room temperature, this value was found to be sufficiently high.³³ Since the coverage of hybrid nanocrystals was estimated to be $\sim 80\%$ from the SEM image, if the surface was completely covered by them, the refractive index could increase to ~ 1.9 theoretically.³³

4. Conclusions

Two-dimensional structures or monolayer-controlled thin films of hybrid nanocrystals were fabricated on the surface by modifying substrates with DHCA; a chemical bond was formed between the nanocrystals and the substrate through the uniform modification of the substrate and the on-site ligand exchange. Dependence of hydrophobicity of the surfaces to the coverage of residual nanocrystals after rinse with solvents was observed. As the water contact angle on surfaces was higher, the coverage of nanocrystals became smaller except for the coverage on DHCA-Si. The result also proved selective adhesion of nanocrystals on the catechol-modified substrate due to on-site ligand exchange. From the analysis of FTIR onto the composite structures of DHCA-silica nanoparticles and hybrid nanocrystals, it was found out that the chemically adsorbed hybrid nanocrystals had a heterogeneous ligand structure; one side of the cubic nanocrystals was modified with the catechol group of DHCA and other sides were

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modified with the carboxyl group of decanoic acid. The results demonstrate that highly crystalline metal oxide nanocrystal films with a sufficiently high refractive index can be fabricated macroscopically at room temperature by using the proposed method, which involves three steps—synthesis of highly dispersible hybrid nanocrystals at high

temperature, modification of the substrates, and assembly of the nanocrystals at room temperature.

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