Nanostructures

Aminolysis Route to Monodisperse Titania Nanorods with Tunable Aspect Ratio**

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Nanocrystalline titanium dioxide (titania) has been investigated extensively, as it plays a prominent role in fundamental studies and has both potential and demonstrated applications in solar energy conversion,[1] photocatalysis,[2] photochromic devices,[3] and gas sensing.[4,5] Among the three natural crystalline forms of titanium dioxide (anatase, brookite, and rutile), rutile is the most stable phase, whereas anatase has superior optoelectronic and photochemical properties.[6] There have been a number of recent reports on the preparation of nanoscaled anatase titania in the form of nanoparticles, nanorods, nanowires, and nanotubes for significantly increasing its specific surface area and delocalization of carriers, which may enhance the performance of this material in highly efficient sensors, photocatalysts, and photovoltaic cells as compared with planar solids or powders.[5,7] To realize these promising high-performance applications, the various nanosized titanias and their derivatives must also fulfill a wide variety of requirements in terms of particle size, size distribution, shape and morphology, crystallinity, and phase purity. The current challenge is to control and tailor all these parameters and properties simultaneously in one synthetic approach or process.

Among the various synthetic routes developed in the last decades, the most general and versatile solution-phase synthetic strategy is based on the hydrolysis and condensation of titanium alkoxides to create nanosized titania with diameters that range from a few tens to several hundreds of nanometers.[8] Owing to extreme moisture or water sensitivity, in most cases, the very fast hydrolytic process at low temperature yields amorphous products with polydisperse size and mixed phases, and subsequent hydrothermal processing or calcination is necessary to induce crystallization. The high reactivity of tetrafunctional titanium alkoxides $Ti(OR)_4$ can be chemically modified by using carboxylic acids such as oleic acid as chelating ligands to decrease the number of TiOR groups available for violent hydrolysis by ligand substitution/exchange.[9] Chemical modification can decrease precursor reactivity and yield more controllable hydrolysis and condensation processes under mild reflux. Volatile water is maintained in a closed system at an elevated temperature of 80–100 °C, and long aging times of 6–12 h or more are required to promote further hydrolysis and improve crystallization of the final nanoproducts. Until now, an alternative high-temperature nonhydrolytic strategy was still preferred to make highly crystalline nanoparticles[10] because the amorphous form is usually inactive in various light-responsive properties such as photocatalysis.[11] The main conventional nonhydrolytic routes reported involve the elimination reaction between titanium tetrachloride and oxygen-donor molecules such as titanium alkoxides and organic ethers which yield environmentally unfavorable, volatile alkyl chlorides or hydrogen chloride. The fast formation of nanosized titania may also limit systematic morphological control in the presence of organic surfactants. Therefore, it is useful to explore and design new preparative reactions to avoid the existing specific problems encountered in conventional hydrolytic or nonhydrolytic routes.

Herein we present a novel high-temperature, nonhydrolytic synthetic approach to anatase titania nanocrystals. It was developed on the basis of a well-known ester aminolysis reaction that involves the nucleophilic attack of an amine group on the carbonyl carbon atom of titanium carboxylate derivatives[12] and the chemical modification of reactive molecular precursors with OLA as the chelating ligand. The high-temperature aminolysis of titanium carboxylate (titanium oleate) complexes can be well-controlled by using high-boiling long-chain oleylamine rather than volatile water. In addition to the preparation of size-tunable anatase TiO_2 nanodots, the "greener" aminolysis route can also provide much better control of the anisotropic growth and can be used

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to readily prepare monodisperse anatase TiO_2 nanorods with tunable length and diameter. An added benefit is that anatase TiO_2 nanorods can also be used as ideal host matrices for the preparation of transparent dilute magnetic oxides that have promising applications such as magneto-optical devices.[13]

A mixture of titanium isopropoxide (TIP; 1 mmol) and oleic acid (OLA; 5 mmol) was used to generate OLA complexes of titanium at 80 °C in 1-octadecene (ODE; 6 mL), followed by the injection of a predetermined amount of oleylamine (OA; 1–10 mmol) at 260 °C to give various nanosized TiO_2 preparations. TiO_2 nanorods were characterized by TEM (Figure 1 a–c); their length depends on the amount of OA used. When the OA content was increased from 1 to 2 to 3 mmol, monodisperse TiO_2 nanorods with lengths of 12, 30, and 16 nm were obtained, respectively, all with a diameter of about 2 nm. The use of OA at 4 mmol in the presence of the unchanged molar ratio of TIP (1 mmol) and OLA (5 mmol), spherical TiO_2 nanoparticles of ≈ 2.3 nm in diameter were obtained (Figure 1 d). Large excesses of OA only generate white titania precipitate. The high-resolution TEM image of a single nanorod (16 nm) shows the single-crystalline structure (Figure 1 c, inset). The lattice spacing of 0.35 nm corresponds to the *d* spacing between adjacent (101) crystallographic planes of anatase TiO_2 nanorods. The as-synthesized anatase nanorods were elongated along the [001] direction; the long axis of the nanorods is parallel to the [001] direction. These surface-capped nanorods can be well-spaced on the copper grid, and some of them are self-assembled with identical distance between them, as shown in Figure 1 a–c. The XRD patterns show a pure anatase phase without other titanium oxide polymorphs (Figure 2). The (004) diffraction peak becomes much stronger and sharper with an increase in length of the nanorods, whereas other peaks remain similar in shape and intensity. The strong peak intensity and narrow width of the ⟨004⟩ reflection and relatively lower intensity and broader width for the other reflections indicate preferred anisotropic growth along the *c* axis of the anatase lattice.

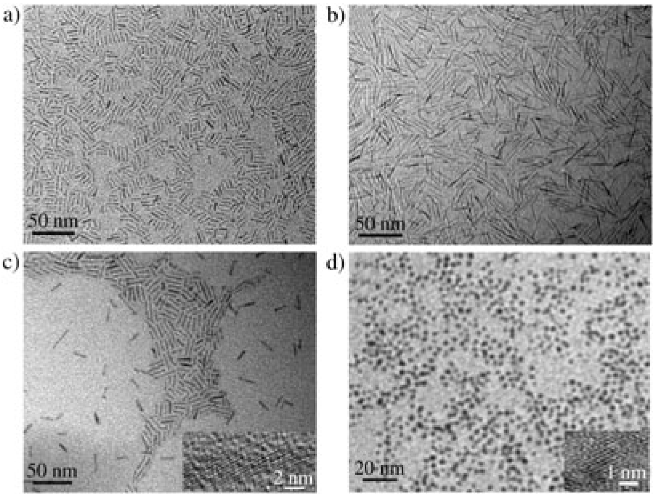


Figure 1. TEM images of length-tunable TiO_2 nanorods with lengths of a) 12, b) 30, and c) 16 nm, prepared at 260 °C with 1, 2, and 3 mmol of OA, respectively; the molar ratio of TIP (1 mmol) and OLA (5 mmol) was kept unchanged. d) TEM image of TiO_2 nanodots of 2.3 nm obtained at 260 °C with 4 mmol OA; the molar ratio of TIP and OLA was kept as described for parts a)–c). Inset in part c): HR-TEM image of a single titania nanorod (16 nm).

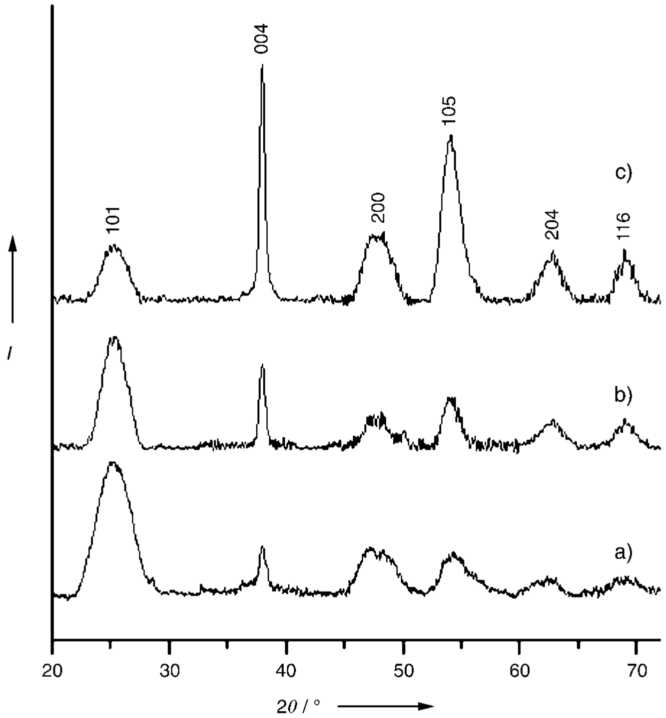


Figure 2. Powder XRD patterns of TiO_2 samples: a) spherical particles of diameter 2.3 nm (molar ratio TIP/OLA/OA = 1:5:4); b) 16-nm nanorods (molar ratio TIP/OLA/OA = 1:5:3); c) 30-nm nanorods (molar ratio TIP/OLA/OA = 1:5:2).

To elucidate the mechanism of titania nanorod formation, we investigated the respective roles of OA and OLA in the noncoordinating ODE system under the optimized conditions for preparing 30-nm titania nanorods with a TIP/OLA/OA molar ratio of 1:5:2. Interestingly, when either OLA or OA is used alone, TiO_2 cannot be obtained even at 260 °C. This observation indicates a synergistic effect of OA and OLA in generating titania nanorods. As reported in the literature, TIP ($Ti(OiPr)_4$) can readily react with OLA ($C_{17}H_{33}COOH$) to generate yellow OLA–titanium complexes $(C_{17}H_{33}COO)_xTi(OiPr)_{4-x}$ at 80 °C in which one or more isopropoxide groups is replaced with an oleate ligand with concomitant release of isopropyl alcohol.[9,14] Although heating the resulting titanium carboxylates at 260 °C does not produce TiO_2, the subsequent injection of a predetermined amount of OA ($C_{18}H_{35}NH_2$) can "decompose" it to form monodisperse anatase titania nanorods. We note that similar reaction systems were also used for the preparation of metal oxide or chalcogenide nanoparticles such as Fe_2O_3, Fe_3O_4, $MnFe_2O_4$, $CoFe_2O_4$, and ZnSe with fatty acid as a stabilization/coordination reagent, and primary amine as an efficient activation reagent to accelerate the formation of nanoparticles.[15]

The mechanism of formation of nanosized TiO_2 was further studied systematically by FTIR spectroscopy. Figures 3 a and b show the FTIR spectra of pure OLA and the mixture of TIP (1 mmol) and OLA (2 mmol) after 20 min at

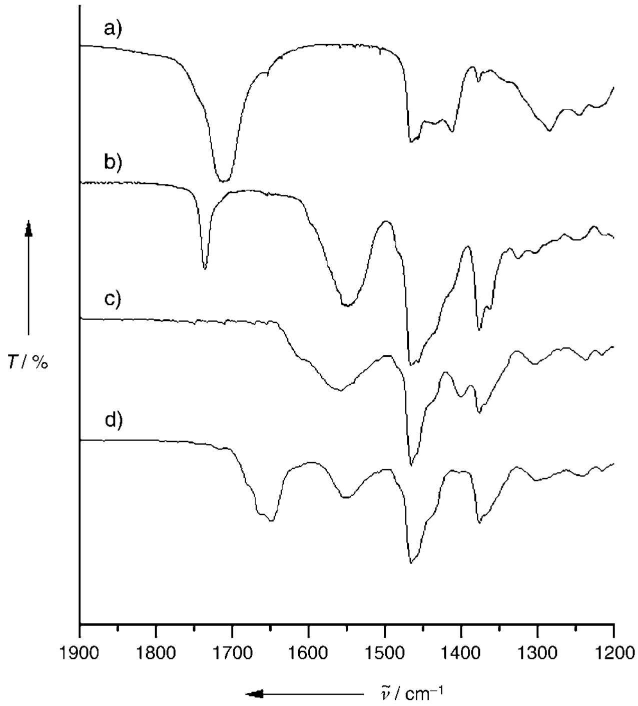
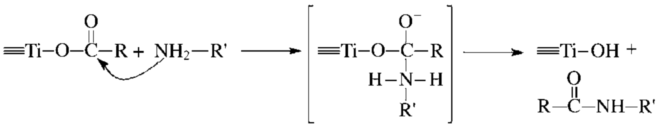


Figure 3. FTIR spectra of a) OLA; b) a mixture of OLA and TIP after treatment at 80 °C; c) the same mixture after washing with acetone and hexane; d) the mixture after further aminolysis to generate nanosized TiO_2.

80 °C. A characteristic C=O stretching band of OLA appears at 1710 cm^{-1} in Figure 3 a. The disappearance of the free C=O stretching band at 1710 cm^{-1} in Figure 3 b shows that OLA reacts completely with TIP (or excludes the presence of un-ionized OLA). The resulting oleate anion ($C_{17}H_{33}COO^-$) is expected to show asymmetric and symmetric COO^- stretching bands at $\approx$1565 and $\approx$1434 cm^{-1}, respectively, as were observed in titanium acetate.[16–18] The latter is normally more difficult to locate as a result of its overlap with C–H bending vibrations at 1467, 1450, and 1375 cm^{-1} (attributed to symmetric CH_2, asymmetric CH_3, and symmetric CH_3 in oleate (or OLA), respectively).[16] In our case, the new strong band at $\approx$1555 cm^{-1}, attributed to the asymmetric stretching vibration of carboxylate anions, indicates the coordination of OLA to titanium centers to form titanium oleate complexes by ligand exchange/substitution.[16]

The characteristic C=O stretching vibration of isopropyl oleate at 1736 cm^{-1} in Figure 3 b is clearly distinguished from that of titanium oleate complexes. The by-product, isopropyl oleate, was generated either by nonhydrolytic elimination/condensation of unstable carboxylatotitanium alkoxide $(C_{17}H_{33}COO)_x Ti(OiPr)_{4-x}$, which can remove some of the oleate and isopropoxide ligands together, or a slow esterification reaction between the reactant OLA and the released isopropyl alcohol. Figure 3 c shows the FTIR spectrum of the reaction mixture of OLA with TIP after washing with hexane/acetone (1:1) to remove isopropyl oleate for further reaction. As a result, only the asymmetric COO^- stretching frequency at $\approx$1560 cm^{-1} appeared after the complete removal of isopropyl oleate from the reaction system. Further reaction was carried out at 260 °C for 20 min after the injection of 2 mmol of OA into the reaction mixture. In comparison with Figure 3 c, the new stretching vibrations at 1651 and 1550 cm^{-1} in Figure 3 d are attributed to different carbonyl stretches in single-substituted amide, which is discussed further below. Almost the same evidence was also obtained when acetic acid was used to replace OLA to prepare titania particles (Supporting Information). The above results indicate that the carbonyl groups of titanium carboxylate precursors can undergo nucleophilic attack by OA to form amides, as opposed to water, which attacks the highly electron-deficient/electrophilic Ti^{IV} center and thus hydrolyzes titanium alkoxides. This process is similar to the conventional aminolysis reaction of organic esters.[12] The conventional aminolysis mechanism of esters may resemble an S_N2 reaction with a tetrahedral transition state or intermediate, which requires a nucleophile ($R'NH_2$) to collide with the electropositive carbonyl carbon in the ester to form an organic amide (RC(O)NHR′). In our case, the resulting tetrafunctional titanium carboxylate (titanium oleate) complexes $(C_{17}H_{33}COO)_x Ti(OiPr)_{4-x}$ were aminolyzed by OA to form unstable hydroxyalkoxides $(C_{17}H_{33}COO)_{x-1}Ti(OH)(OiPr)_{4-x}$ via a tetrahedral transition state through nucleophilic attack by OA on the carbonyl carbon atom of titanium oleate complexes (Scheme 1). Consequently, the subsequent polycondensation reaction of the resulting hydroxylated titanium precursors produces extensive Ti–O–Ti networks covalently capped with carboxylates.[19]



Scheme 1. Aminolysis reaction between titanium carboxylate complexes and primary amine.

During the growth of TiO_2 nanocrystals, as (001) planes have higher surface energy or are more chemically reactive than others,[20] carboxylate groups coordinated to (001) faces could be more easily aminolyzed under the attack of OA and form or extend the Ti–O–Ti network along the [001] direction. Less reactive titanium carboxylate precursors are also helpful in maintaining high monomer concentrations in the reaction solution for elongated growth of titania nanocrystals, as has been suggested.[21] Various amounts of OLA were used to optimize the preparation conditions of titania nanorods, and more than 4 mmol of OLA was necessary to prepare soluble TiO_2 nanocrystals in the noncoordinating ODE system. It was also observed that upon increasing the amount of OA from 1 to 2 mmol, the length of the resulting monodisperse titania nanorods increased from 12 to 30 nm. However, with the further increase of OA content to 3 mmol, nanorod length was decreased to 16 nm, which indicates suppression of anisotropic growth at higher OA contents. Finally, only spherical nanoparticles were formed when 4 mmol of OA was used, and aggregated particles were produced when $\geqslant$5 mmol of OA was used; this indicates the decreased stabilization that results from the consumption of surface-coordinated oleate ligands on particle surfaces. Moreover, the increased OA content can accelerate the aminolysis reaction to form nanoparticles.

Although monodisperse TiO_2 nanocrystals with a tunable aspect ratio ranging from 1 to 13 (nanodots to nanorods) have been prepared, the resulting length-tunable TiO_2 nanocrystals have only a very small diameter of ≈ 2.0 nm, a result of the tight binding of OLA on the titania surface, which restrains its growth.[9,10c] To prepare diameter-tunable TiO_2 nanorods, a weaker capping agent, cetyltrimethylammonium bromide (CTAB), was used to decrease/balance the strong binding affinity of OLA on the anatase surface. With 1 mmol of TIP, 1 mmol of OA, and 5 mmol of OLA, only very narrow TiO_2 nanorods of diameter ≈ 2.0 nm were obtained (Figure 1 a). By introducing larger amounts of CTAB and maintaining a similar TIP/OA/OLA molar ratio, larger, diameter-tunable TiO_2 nanorods of 2.9, 3.8, and 4.6 nm (Figure 4 a–c) were produced under optimized conditions. From the above results, it is now known that higher OA content is required to prepare TiO_2 nanodots (Figure 1 d). Hence, to prepare larger TiO_2 nanodots, an larger amount of CTAB and a smaller amount of OLA were used to balance the stabilization of nanoparticles while retaining the TIP/OA molar ratio of 1:3. Thus, size-tunable TiO_2 nanodots of 2.3, 3.0, 4.2, and 6.0 nm were prepared under various reaction conditions (Figure 1 d and Figure 4 c–d). In comparison with bulk anatase titania (3.2 eV), a blue-shift of the absorption onset of anatase titania nanodots was observed. The blue-shift increased with decreasing size of the particles, which exhibit size-dependent optical properties (Supporting Information).

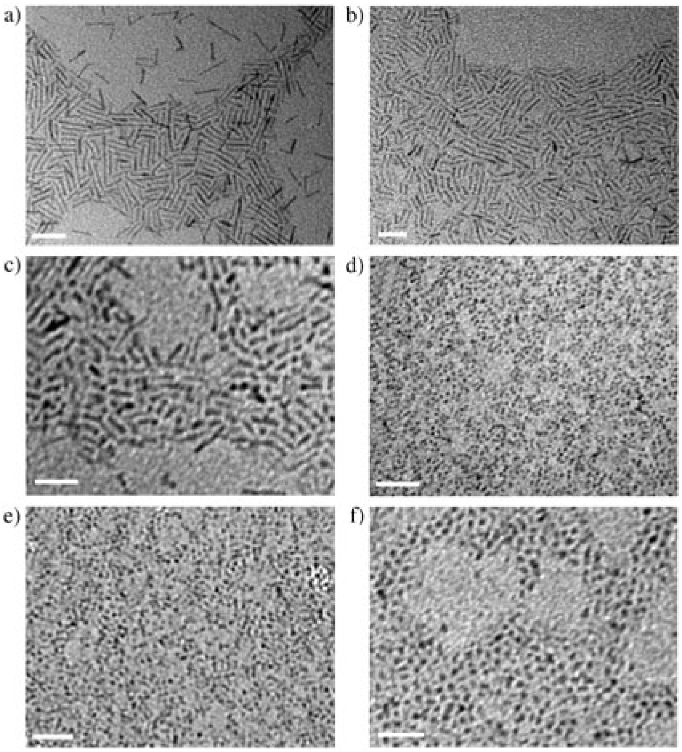


Figure 4. TEM images of diameter-tunable TiO_2 nanorods of length a) 2.9, b) 3.8, and c) 4.6 nm and size-tunable TiO_2 nanodots of size d) 3.0, e) 4.2, and f) 6.0 nm, prepared at different TIP/OA/OLA/CTAB molar ratios and temperatures (1 mmol of TIP was used for all the preparations): a) 1:1:5:3, 260 °C; b) 1:1:5:6, 260 °C; c) 1:1:4:6, 280 °C; d) 1:3:5:3, 260 °C; e) 1:3:4:5, 260 °C; f) 1:3:3:5, 300 °C. Scale bar: 50 nm.

In conclusion, a high-temperature nonhydrolytic aminolysis approach has been developed, and its capability to produce highly crystalline, monodisperse anatase nanocrystals with controlled size and shape in a reasonable size range was demonstrated. By combining the advantage of chemical modification of reactive titanium isopropoxide by oleic acid, the high-temperature aminolysis reaction of titanium oleate complexes with decreased reactivity can be controlled very well for the anisotropic growth of titania nanorods with high-boiling-point oleylamine rather than volatile water. Weaker CTAB ligands were further used to balance the strong binding affinity of OLA ligands for producing larger titania nanodots and thicker titania nanorods. The aminolysis route is much greener because, unlike conventional nonhydrolytic routes, it does not form environmentally unfavorable, volatile alkyl chlorides or hydrogen chloride. In addition to the preparation of size-tunable anatase titania nanodots ranging from 2.3 to 6.0 nm, the "greener" aminolysis route can also provide much better control of anisotropic growth and allows ready preparation of monodisperse titania nanorods with tunable lengths and diameters that range between 2.3–30 nm and 2.0–4.6 nm, respectively. Meanwhile, our synthetic method has been extended further for the preparation of various oxide nanocrystals (e.g., ZrO_2) from different carboxylate precursors.

Experimental Section

Titanium isopropoxide (98 %, Acros), oleic acid (90 %, Aldrich), oleylamine (70 %, Aldrich), octylamine (99 %, Aldrich), 1-octadecene (90 %, Aldrich), cetyltrimethylammonium bromide (99 %, Acros), hexane (99 %, Tedia), and acetone (HPLC grade, Tedia) were used as received. All experiments were carried out by standard oxygen-free techniques under nitrogen flow.

In a typical preparation of length-tunable TiO_2 nanorods with a diameter of ≈ 2.0 nm, OLA (1.6 mL, 5 mmol) in 1-ODE (6 mL) was dried and degassed at 80 °C in a 50-mL three-neck flask for 1 h. Then TIP (0.3 mL, 1 mmol) was injected into the mixed solution and heated for 20 min. The solution gradually turned from colorless to a pale yellow, indicating the formation of titanium carboxylate complexes. Gaseous isopropyl alcohol was rapidly released while the mixture was heated at 260 °C for 10 min. The aminolysis reaction was then initiated by rapid injection of a predetermined amount of OA ranging from 1 to 4 mmol (0.32–1.28 mL) with vigorous stirring. After 1 h, the resulting solution was allowed to cool to room temperature. The resulting crude solution of TiO_2 nanorods was diluted with hexane (10 mL) followed by precipitation with acetone (20 mL). The crude product was recovered by centrifugation, dispersed in hexane (20 mL), and subjected to a second round of purification. The white powders obtained can be redispersed easily in nonpolar solvents such as hexane, toluene, and chloroform for further characterization. For the preparation of diameter-tunable TiO_2 nanorods and size-tunable TiO_2 nanodots, a certain amount of CTAB was mixed with OLA in 1-ODE, and the mixture was dried and degassed for 1 h. Then TIP (0.3 mL, 1 mmol) was injected into the mixed solution, which was heated for 20 min. The remaining procedure is identical to that described above, but with different experimental parameters as appropriate. TIP (0.3 mL, 1 mmol) was used for all the above preparations.

Powder XRD was performed with a Siemens D5005 X-ray powder diffractometer. XRD samples were prepared by dropping the a TiO_2 nanocrystal solution onto a silicon (100) wafer and drying at room temperature. TEM and HR TEM images were obtained with a JEOL 1010 and a Philips 3010 operating at accelerating voltages of 100 and 300 kV, respectively. TEM samples were prepared by placing a drop of a nanorod solution in hexane onto Formvar carbon-coated copper grids and drying in a desiccator. FTIR spectra were recorded with a FTS165 Bio-Rad FTIR spectrophotometer in the range of 4000–400 cm^{-1} with KBr plates.

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