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Research Article

Environmentally Friendly Supramolecular Nanosheet Particles for Surface Coating

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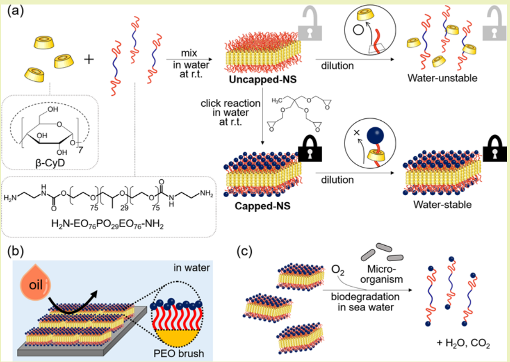
ABSTRACT: Global environmental problems have become increasingly severe in the recent years. Although inorganic nanoparticles and nanosheets (NSs) have been developed for their high functionality and stability, their toxicity and nonbiodegradability significantly impact the environment owing to their accumulation within ecosystems. This paper reports the fabrication of environmentally friendly supramolecular NS particles composed of cyclodextrin (CyD), a natural oligosaccharide, and highly biocompatible polyethers, and their stabilization, antifouling, and biodegradation properties. Supramolecules are typically unstable due to their noncovalent bonds; however, end-capped-pseudopolyrotaxane nanosheets (PPRNSs), featuring a bulky group at the axis end, is water-insoluble, maintaining stability even under extreme dilution. The capped-NSs possess polymer brushes, which, when coated on substrates, do not dissolve in water and exhibit repeatable antifouling properties. The crystalline CyDs in the capped-NSs are not water-soluble; however, biochemical oxygen demand (BOD) tests in seawater demonstrate their biodegradability. Thus, PPRNSs have the potential to be novel NS materials that can address environmental challenges. This study is expected to pave the way for advancements in nanosheet materials science and supramolecular chemistry.



KEYWORDS: *supramolecular self-assembly, nanosheet, polymer brush, cyclodextrin, oil-repellent property, biodegradable material, polyrotaxane*

INTRODUCTION

Global environmental issues have become increasingly severe in the recent years. Research has focused on developing materials with high functionality and stability, such as inorganic nanomaterials, heavy metals, plastics, rubber, and alkyl fluorides. Although these advancements have improved the convenience of human life, their release into the ecosystem, where they persist without degradation and accumulate over the long-term, creates environmental risks, thereby exacerbating the environmental burden.[1−4] The wastage of harmful organic solvents and energy in the synthetic methods for the preparation of chemical compounds and particle materials should also be considered.[5−7] The purification, use, and utilization of water have recently gained increasing interest.[8−11] The development of green chemistry is important for supporting a sustainable society.[7,9,12,13]

Low dimensional inorganic materials, such as clays and nanosheets (NSs), exhibit unique properties owing to their extremely large specific surface area and anisotropic structure, and are applied in various fundamental and application research fields such as coatings and fillers for surface improvement, gas barriers, mechanical property enhancement, and others.[14−19] However, the fabrication methods for synthetic inorganic materials require high energy and waste synthesis reagents. Furthermore, they are not biodegradable and accumulate in ecosystems, potentially exhibiting toxicity in the environment.

Supramolecular self-assembly of organic compounds exhibits advantages such as simple experimental operation, low production energy, and scalable production. The creation of nano- and microsized materials through the supramolecular self-assembly of molecular building units such as metal−organic frameworks (MOFs),[20] peptides and peptoids,[21,22] crystalline-coil block copolymers,[23−26] and cyclodextrins (CyDs)[27−31] has recently attracted the attention of researchers. In particular, CyDs are noteworthy because they are natural, safe, and abundant materials that have been studied for the construction of nano- and microstructured materials. Notably, the self-assembly of CyD proceeds mainly in water without any treatment.

Materials based on supramolecular self-assemblies exhibit some general problems, including instability. Because these materials are constructed through noncovalent bonds, they are

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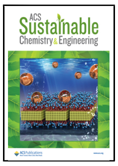

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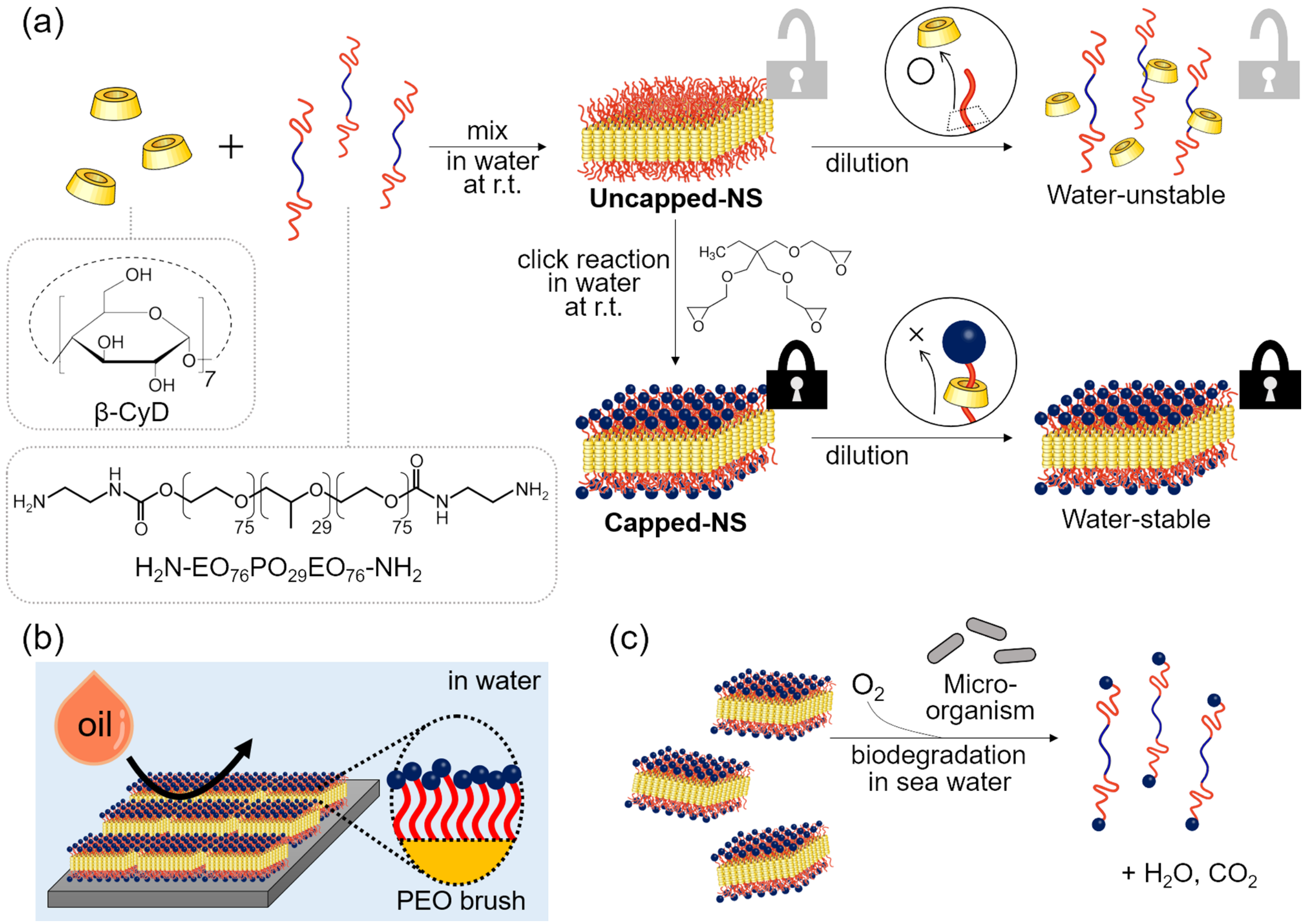

Figure 1. Schematic diagram summarizing this study. (a) Formation, preparation, and stability of uncapped- and capped-NSs. (b) Oil-repellent property of the capped-NS-coated PEO brushes on a material surface. (c) Biodegradation of capped-NSs in natural seawater investigated using the biochemical oxygen demand (BOD) test.

prone to structural changes in response to slight changes in environmental conditions (such as concentration, pH, and temperature). The instability of supramolecular materials poses challenges in applied research. The durability of materials is crucial to ensure their practical use and safety. Efforts have been made to enhance the stability of supramolecular materials by changing their hydrophilicity and hydrophobicity and the covalent bonding of the compound (cross-linking).[32,33]

Our group reported the self-assembly of supramolecular NSs (pseudopolyrotaxane NSs (PPRNSs)) by simply mixing *β*-CyD and biocompatible linear polyether, poly(ethylene oxide)$_{76}$-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide)$_{76}$ ($EO_{76}PO_{29}EO_{76}$) in water at room temperature (r.t.).[34] *β*-CyD selectively covers the central PO segment and inclusion complexes assembled into the PPRNSs (Figure 1a) owing to the crystallization-driven self-assembly process. The crystallization of CyD bundles the axis polymer; therefore, the sided EO chains are densely assembled and form PEO brush layers that exhibit oil-repellent properties in water.[35] Furthermore, the reaction of two ethylene glycol diglycidyl ethers (EGDGEs) with one $-NH_2$ at the axis ends of the PPRNSs inhibits the dethreading of CyD from the axis (end-capping), leading to the suppression of PPRNS dissolution in water.[36] The ability to regulate solubility is a notable feature of PPRNSs owing to the lack of established methods to control the stability of supramolecular materials. PPRNSs can be easily prepared by mixing safe, abundant, and inexpensive components in water at r.t.

Because the components of PPRNSs are highly biocompatible, they are a promising candidate for a new class of environmentally friendly NS materials. This paper reports the water stabilization, oil-repellent properties, and biodegradability of PPRNSs to demonstrate the emergence of new types of NS materials. Totally water-insoluble PPRNSs were fabricated using an improved end-capping method by reacting a bulky epoxy reagent, trimethylolpropane triglycidyl ether (TMPTG), with the $-NH_2$ at the axis end in water at r.t. (Figure 1a). Subsequently, the PPRNSs were coated on a Si wafer to evaluate their stability and function on the surface (oil-repellent properties based on the PEO brush layer) (Figure 1b). Finally, the biodegradability of the PPRNSs in seawater were investigated by assuming a spillage in the environment (Figure 1c).

■ EXPERIMENTAL SECTION

Materials. CyD and hydroxyl-terminated $EO_{75}PO_{29}EO_{75}$ were purchased from Fujifilm Wako Pure Chemical Corporation. TMPTG was purchased from Sigma-Aldrich. Commercially available chili oil was used in the experiments. All the reagents were used as received. SpectraPor 2 standard RC single-layer membranes (Repligen) were used for the dialysis experiments. Seawater was collected from the Miyagawa Beach in Miura City, Kanagawa, Japan. The seawater was mixed with sediment collected from the same location. The mixture

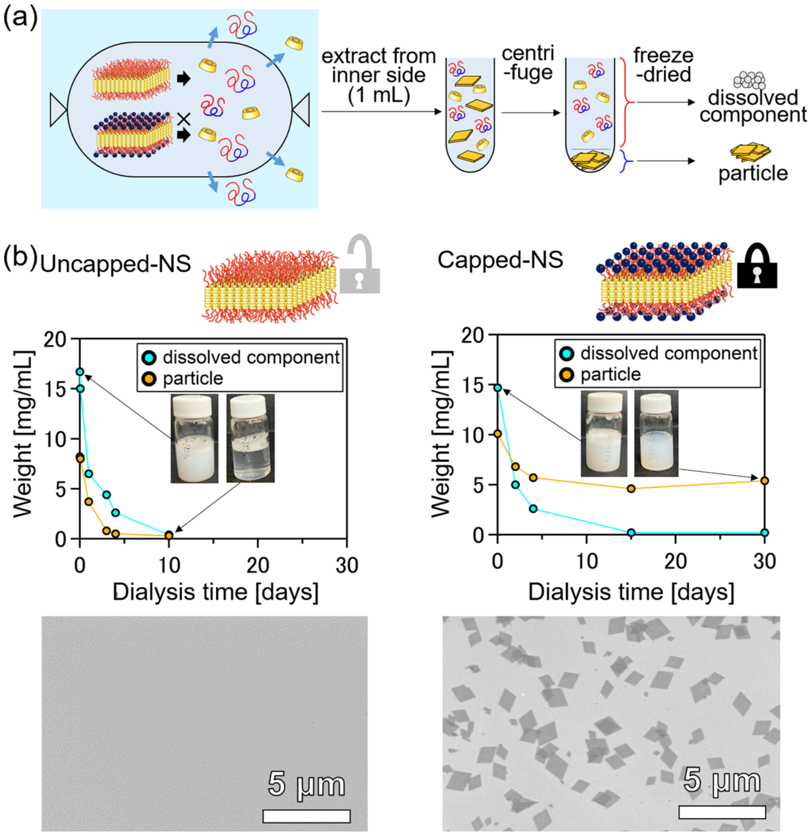

Figure 2. (a) Schematic diagram of the dialysis experiment on the uncapped- and capped-NSs. (b) Plots of the weights of the dissolved components and particles in the dialysis membrane as a function of the dialysis time and SEM images of the particles at the terminus of dialysis.

was then filtered to obtain seawater containing bacteria extracted from the sediment (extracted seawater).

Instrumentation. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-7800-F SEM. The contact angle of the water droplets in air was measured using a Kyowa Interface Science Co., Ltd. CA-V. The BOD was measured using an OxiTop intelligent digital sensor (IDS) (WTW, Germany).

Sample Preparation. *Synthesis of H_2N-$EO_{76}PO_{29}EO_{76}$−NH_2.* The procedure followed that reported previously.[37]

Preparation of Uncapped NSs. The procedure followed that reported previously with minor modifications.[37] Briefly, β-CyD (180.0 mg) was dissolved in 10 mL water. Thereafter, 80.0 mg H_2N-$EO_{76}PO_{29}EO_{76}$−NH_2 was added to the solution, which was stirred for over a month.

Preparation of Capped NSs. TMPTG (1−200 equiv vs axis [mol/mol]) was added to a water dispersion of uncapped-NSs and reacted for 1 week at 25 °C.

Sample Preparation for SEM Observations. Uncapped- and capped-NS water dispersions were drop-cast on an untreated Si wafer. The cast samples were immersed in water to ensure that the Si wafer was coated with NSs under dilute conditions. The Si wafers retrieved from the water were dried in air and then under vacuum for 1 day for SEM observation.

Sample Preparation for the BOD Test. A capped-NS water dispersion was centrifuged, and the collected precipitate was freeze-dried. The obtained white powder was used for the BOD test.

Dialysis Test. The uncapped- and capped-NSs were dialyzed to determine their water insolubility. The uncapped-NS water dispersion (20 mL) immediately after formation and 20 mL of the capped-NS water dispersion immediately after the end of the reaction were placed in dialysis bags. The dialysis bags containing the NS samples were dialyzed in 1 L water for 1 month. One milliliter of the sample in the dialysis bag was extracted at specific intervals. Each aliquot was centrifuged to separate the supernatant from the precipitate. The white powder obtained after freeze-drying was weighed.

Oil-Repellent Property Test. Uncapped- and capped-NS-coated Si wafers were prepared by dropping water or ethanol dispersions of them with different concentrations onto the wafers. These coated samples were then immersed in water, where the uncapped NS dissolved and desorbed from the substrate, while the capped NS remained on the substrate. After drying them, the chili oil was dropped on the uncapped-NS-coated, capped-NS-coated, and untreated Si wafers, which were then immersed in water.

BOD Test. The BOD test was used to assess the biodegradability of the samples. The procedure was as follows. Samples of the prepared extracted seawater (50 mg and 150 mL) were placed in a 250 mL medium bottle and stirred using an attached stirrer at 25 °C. The test was conducted in a Heratherm incubator with a cooling function (Thermo Fisher Scientific) at 25 °C. The biodegradation rate was calculated from the BOD over 120 days using the following formula

$$\text{biodegradability}(\%) = \frac{\text{BODs} - \text{BODb}}{\text{ThOD}} \times 100$$

where BODs and BODb represent the BOD of the sample and blank, respectively, and ThOD represents the theoretical BOD.

RESULTS AND DISCUSSION

Water-Insoluble PPRNSs by End-Capping. The reaction between the $-NH_2$ and epoxy groups is click chemistry that proceeds in water at r.t. under atmospheric pressure and neutral pH conditions, producing only water as a by-product.[38,39] TMPTG, which is bulkier than EGDGE (used in our previous study[36]), was used in this study to create end-capped PPRNSs (capped-NSs) using conventional amine-terminated PPRNSs (uncapped-NSs). EGDGE is not a bulky moiety; therefore, two EGDGE molecules are required to react

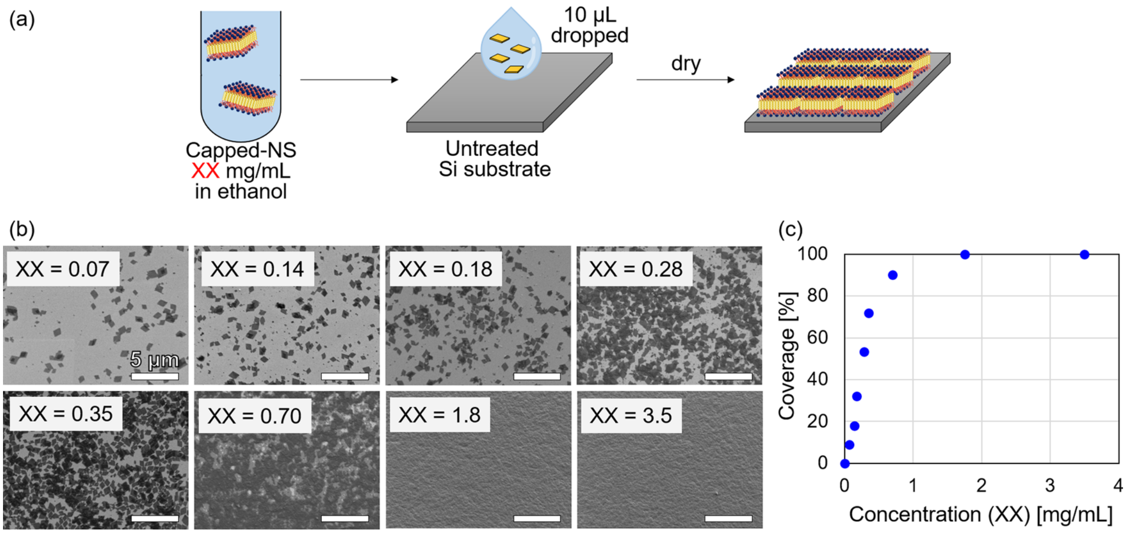

Figure 3. (a) Schematic diagram of the surface coating of the capped-NSs on the Si substrate. (b) SEM images of the Si substrate coated with capped-NS ethanol dispersions of various concentrations. (c) Plot of the coverage (obtained using image analysis of the SEM images) as a function of the capped-NS concentration in the ethanol dispersions.

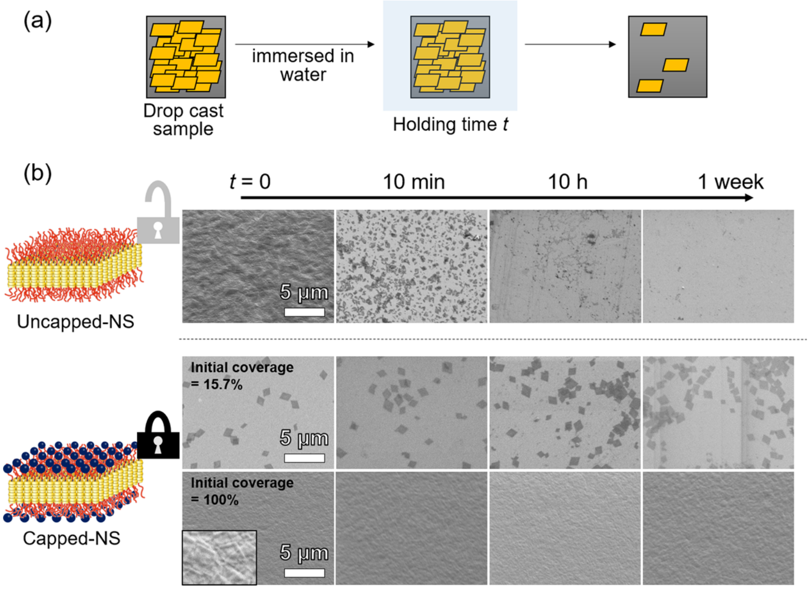

Figure 4. (a) Protocol for the coating and analysis of the stability of the capped- and uncapped-NSs on Si substrates. (b) SEM images of the uncapped- and capped-NS-coated Si substrate after immersion in water for different durations. The inset is a magnified image of the surface with a 100% coverage.

with each − NH_2 end for capping.[36] While, the addition of 1 equiv of TMPTG against axis ends achieved this in this study, indicating that one TMPTG has sufficient bulkiness to block the dethreading of CyD. TMPTG is more efficient for end-capping than EGDGE (details in Supporting Information).

The uncapped- and capped-NSs were dialyzed, and the dissolved and solid components inside the dialysis membrane were respectively weighed at different dialysis times to evaluate their stability (Figure 2). The dissolved components of the uncapped-NSs inside the dialysis membrane gradually diffused, leading to the dissolution of uncapped-NSs. Almost all the uncapped-NSs dissolved and diffused out of the membrane within 4 days of dialysis. In contrast, although both the solution and solid components of the capped-NSs inside the dialysis membrane gradually decreased during the initial phase of dialysis, the solid components remained consistent after 4 days of dialysis. The weight of the dissolved components on the 15th day was zero; however, the solid components remained. The SEM image of the remaining solid components after 30 days of dialysis exhibited a rhombus shape without any lacks (Figure 2b). These results indicate that the capped-NSs do not completely dissolve, even when they are infinitely diluted in water. The initial weight reduction during dialysis is attributed to the removal of unreacted materials, which corresponds to the purification process.

The PPRNSs became completely water-insoluble, even under diluted conditions, after the reaction with bulky TMPTG to cap the PPRNSs axis ends. The exposure of coated materials to water results in extremely low concentrations. Maintaining the assembled structure of noncovalent bond-based materials under these rigorous conditions is challenging. This study demonstrates that capped-NSs do

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not dissolve even under extreme dilution, indicating their potential for coating applications.

Coating and Stability of Capped-NSs on the Surface. The capped-NSs were dispersed in ethanol and coated on an untreated Si substrate using drop casting (Figure 3a). Figure 3b shows SEM images of the surface of the Si substrate after coating with capped-NS ethanol dispersions of different concentrations. The coverage was quantitatively analyzed by image analysis of three SEM images for each samples (Figure 3c and the details is described in Supporting Information). Capped-NS concentrations exceeding 1.75 mg/mL in the dispersion yielded coverages exceeding 100%, indicating the formation of multiple layers.

The stability of the uncapped- and capped-NSs on the surface against water was then investigated. The samples were prepared by coating Si substrates with uncapped- and capped-NSs, followed by immersion in water for a specified time and SEM observation (Figure 4a). Most of the uncapped-NSs with a coverage of 100% (uncapped-NSθ100) dissolved and desorbed within 10 min of immersion in water (Figure 4b). The coverage was approximately 0% after 10 h. Capped-NS samples with initial coverage rates of 15 and 100% were subsequently prepared (capped-NSθ15 and capped-NSθ100, respectively), and the same experiments were conducted (Figure 4b). The coverage rate of capped-NSθ15 did not change even after 1 week of immersion in water, indicating that capped-NSθ15 did not dissolve or desorb even after being immersed in water for 1 week. Similarly, capped-NSθ100 maintained a coverage rate of 100% after 1 week in water. This adhesion was possibly caused by the van der Waals and hydrophobic interaction between PEO chains and substrate.

The contact angles of the capped-NS-coated samples with varying coverages were measured and plotted as a function of the coverage (Figure 5a). The surface of the untreated Si substrate was hydrophobic with a contact angle of 61°. The contact angle of the coating containing capped-NSs decreased continuously with an increasing coverage. When the coverage reached 100%, the contact angle saturated at 15°. The PPRNSs (uncapped-NSs) used in previous studies were water-soluble and measuring the water contact angle was difficult. The water contact angle was successfully measured in air in this study using the completely water-insoluble capped-NSs.

Representative PEO brush fabrication methods, grafting-to and grafting-from, are generally challenging; the former has difficulty achieving a high density, whereas the latter requires synthetic methods. The construction of high-density PEO brushes on material surfaces is challenging. Using the PPRNSs, the material surface can be coated with PEG brushes by simply spraying the dispersion. Samples coated with capped- or uncapped-NSs (as controls) were prepared using the spray method. After drying, the samples were immersed in water for 1 h. When the uncapped-NSs were removed from the surface, the capped-NSs remained intact (Figure 5b). After removing the samples from water, chili oil was dropped onto the samples, and the oil-repellent properties were evaluated by immersing them in water (Figure 5c). The chili oil strongly adhered to the surfaces of the untreated Si substrates and uncapped-NS samples (low contact angle). In contrast, the capped-NS samples exhibited oil-repellent properties (high contact angles). Shaking the substrates in water removed the oil droplets from the capped-NS-coated samples but not from the uncapped-NS-coated samples (Movies S1 and S2). The capped-NS-coated samples repeatedly exhibited oil-repellent properties for more than ten cycles. Furthermore, the oil repellent properties could be exhibited not only for Si substrates but also for a variety of material surfaces such as rubber, aluminum foil, and plastic film. These results demonstrate that the spray coating of capped-NSs is a versatile PEO brush formation method (Supporting Information).

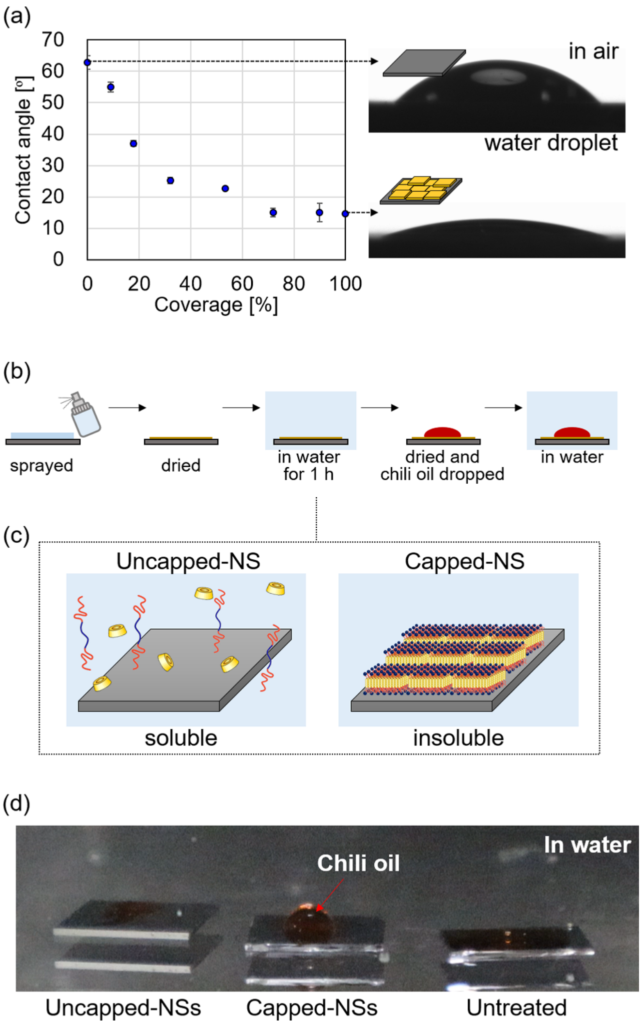

Figure 5. (a) Water contact angle of the capped-NS-coated Si substrate under air as a function of the coverage. (b) Schematic diagram illustrating the spray coating and oil-repellent experiment. (c) Illustration of the behaviors of the uncapped- and capped-NSs on the surface after immersion in water. (d) Photographs of chili oil on the samples in water.

Biodegradability of Capped-NSs. SEM observation of the capped-NSθ15 sample after 1 week of water immersion revealed the presence of bacteria (Figure 6a), which may have contaminated from the air. These bacteria were predominantly found on the capped-NS particles, implying that the bacteria recognized the capped-NSs. Finally, the biodegradabilities of the capped-NSs, CyD, and the axis PEO in the extracted seawater (the abundance ratio of bacteria is shown in Supporting Information) were investigated using the BOD test (Figure 6b). CyD alone biodegraded well. In contrast, the $EO_{76}PO_{29}EO_{76}$ triblock copolymer alone did not biodegrade, which is consistent with the fact that high-molecular-weight polyethers are less prone to marine biodegradation.[40] The biodegradation rate of the capped-PPRNSs after 120 days was 58%. Because the weight fraction of CyD in the capped-NSs

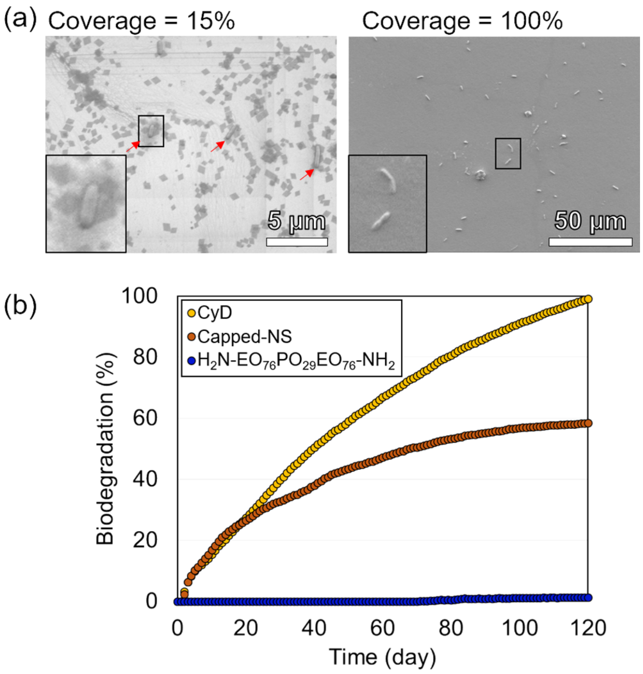

Figure 6. (a) SEM images of capped-NSθ15 and capped-NSθ100 after 1 week of immersion in water, where the bacteria preferably positioned on the capped-NSs. (b) Biodegradability of the CyD, capped-NSs, and axis PEO as a function of time.

was approximately 66 wt %, it was considered that the CyDs biodegraded, whereas the axis PEO did not. Although the axis PEO ($H_2N-EO_{76}PO_{29}EO_{76}-NH_2$) did not degrade, it is highly biocompatible; therefore, PPRNSs can be considered a new class of environmentally friendly NS particles.

CONCLUSIONS

This paper reports the fabrication and coating applications of environmentally friendly supramolecular NS particles, that is, PPRNSs with capping. An efficient capping method using a bulky epoxy reagent was used to enhance the water insolubility of the PPRNS. The capped-NSs were water-insoluble even under extremely diluted conditions, making it suitable as a surface-coating agent. The capped-NSs remained stable on the material surfaces for over 1 week of immersion in water and neither dissolved nor desorbed. The capped-NSs exhibited a biodegradation rate of 58 wt % after 120 days in seawater, where biodegradation is generally considered difficult. Although the PPRNSs did not dissolve in water, they biodegraded in seawater, indicating on-demand degradability when released into the environment. Notably, capped-NSs can be formed under mild conditions, that is in water and without any pH and temperature changes. This study is expected to open new avenues not only for nanosheet materials science but also for supramolecular chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.4c06972.

Uncapped_light (Movie S1) (MP4)
Capped_light (Movie S2) (MP4)
The water stability and ^1H NMR spectrum of capped-NSs reacted with different amounts of TMPTG, SEM image analysis, Oil-repellent property, and Abundance ratio of bacteria in the extracted seawater (PDF)

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Author Contributions

S.U. and K.I. designed the study and wrote the paper. S.U., H.Y. and K.I. supervised the research. S.U. and D.L. carried out the experiment except for the marine biodegradable test. S.A. and C.L. designed and carried out the marine biodegradable test.

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Notes

The authors declare no competing financial interest.

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