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Click Chemistry

Alternate Layered Nanostructures of Metal Oxides by a Click Reaction**

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The nanoconjugation of two metal oxides is expected to enhance and innovate their functionalities and properties. One of the best candidates for nanoconjugation is a photocatalyst consisting of titanium and tungsten oxides.[1–3] Conjugation between titanium oxide and tungsten oxide facilitates a charge separation, because excited electrons of titanium oxide will move to the conduction band of tungsten oxide.[4,5] Nanoconjugations precisely arranged on a nanometer scale are crucial for improved function and the development of new properties.

Nanostructural control using layered metal oxide is one of the most useful methods for arranging metal-oxide species on a nanometer scale. Layered metal oxide composed of various elemental species is expected to develop unique properties and applications. The interlayers of a layered metal oxide possess the cations for insertion of a bulky quaternary ammonium ion, thereby resulting in the formation of nanosheets by exfoliation of the layers.[6–8] Nanosheets are utilized in the formation of alternate-layer structures using self-organization[9] and the Langmuir–Blodgett method.[10,11] However, these methods require step-by-step operations, which takes a lot of time and labor for multilayer structures. On the other hand, a multilayer structure can also be created in one step. Sasaki et al. reported that an alternating layered structure can be synthesized by simply mixing a liquid dispersion of a double-hydroxide nanosheet with a positively charged surface and that of a metal-oxide nanosheet with a negatively charged surface.[12] However, in this case, cationic nanosheets must be combined, and there is no other choice than to choose layered double hydroxides as a cationic nanosheet. Therefore, the method of creating an alternating laminate structure using various metal-oxide nanosheets through a one-step process creates possibilities for varied chemical compositions.

To realize this new methodology of alternating nanoconjugation, we focused on click chemistry. Click chemistry is a reaction used to easily form stable connections between specific functional groups.[13] Sharpless suggested that the Huisgen reaction, which is a cycloaddition reaction of alkyne and azide groups, is the main reaction of click chemistry. Dinolfo et al. reported porphyrin multilayer films on inorganic substrates by the reaction of alkyne and azide groups, which indicated that click chemistry is suitable for the synthesis of multilayer structures.[14–16] However, explosive sodium azide is commonly used for introducing an azido group, and the experimental operation is not easy.[17,18] Therefore, the thiol–ene reaction of click chemistry was used. A thiol–ene reaction starts when a radical initiator reacts with a thiol group, and alkene and thiol groups react in good yields.[19–21] The thiol–ene reaction was also applied to ferrocene multilayer films.[22] Therefore, heterogeneous materials can be selectively connected.

Herein, we propose a new methodology to realize alternating multilayer powders by using a thiol–ene reaction (Figure 1). Two kinds of metal-oxide species were each modified with alkene and alkyl thiol groups, and dispersed into organic solvent to exfoliate the layers. A radical initiator was added to the dispersion to induce a thiol–ene reaction, then the powder of hundreds of layers of alternate stacks was synthesized in one step. Titanium oxide–tungsten oxide alternating laminate was used as a photocatalyst. Recently, heterojunctions between titanium oxide and tungsten oxide nanoparticles obtained by click chemistry showed enhancement of the photocatalytic reaction.[23] Alternate layers of metal oxides are a promising structure because of the large area of nanoconjugations.

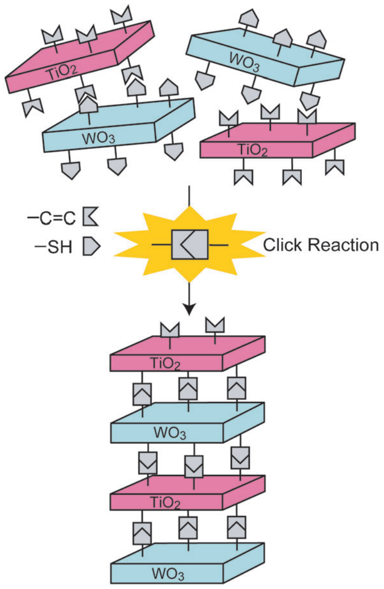

Figure 1. Alternating layers of metal oxide obtained by a click reaction.

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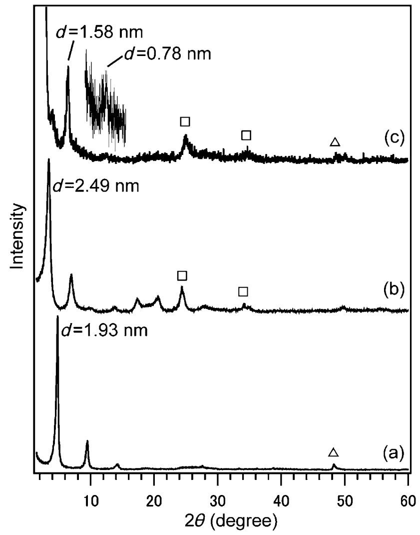

Figure 2. Powder XRD patterns of a) alkene-modified layered titanium oxide, b) thiol-modified layered tungsten oxide, and c) click-reacted sample.

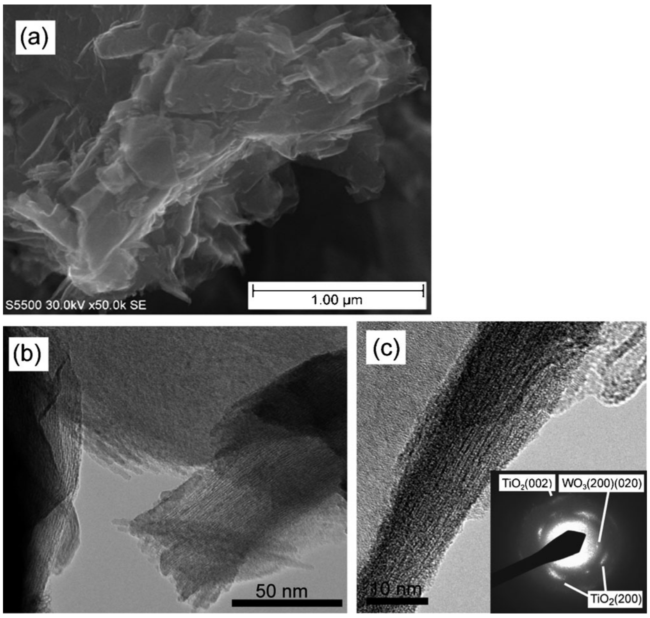

Figure 3. a) SEM and b,c) TEM images of click-reacted sample. Inset in (c): ED image.

XRD patterns of the organic-modified layered metal oxides and the click-reacted product are shown in Figure 2. The alkene-modified titanium oxide and thiol-modified tungsten oxide showed peaks in small-angle regions, thus indicating the preservation of their layered structures. Large *d* values (2.49 and 1.93 nm) were attributed to the residue of octylamine, as shown by CHN elemental analysis (see the Supporting Information). The pattern of the click-reacted sample showed new peaks at $d = 1.58$ and 0.78 nm, which were assigned to the (001) and (002) planes of a layered structure, respectively, thus strongly suggesting the formation of the alternating multilayer structure. A decrease in the *d* value from that of the starting materials was caused by the elimination of octylamine. The interlayer distance was estimated to be 0.72 nm, which indicated that the click-reacted organic groups were obliquely arranged. The (00*l*) peak intensity attributed to the alternating layered structures decreased after the click reaction, either because the nanosheets were highly flexible or because the interlayer distance was changeable due to the sheets being bounded in organic components.

Click-reacted samples varying in the carbon numbers of the alkyl thiol and alkene groups were used to evaluate the alternate layered structures (see the Supporting Information). The d_{001} values increased with increasing number of carbon atoms. This behavior strongly suggests the formation of the alternate layered structures. Besides, the peaks of the crystal plane that were independent of the layer plane direction were preserved for layered titanium oxide (△) and layered tungsten oxide (□, see Figure 2). Therefore, the crystalline structure of the original layered metal oxides was preserved.

SEM and TEM images of the alternating multilayer structures are shown in Figure 3. The SEM image shows the random stacking of numerous layers. The lateral size and thickness of the randomly stacked nanosheets are hundreds of nanometers and dozens of nanometers, respectively, which suggests that dozens of layers were alternately stacked. Black lines derived from a layered structure appeared in the TEM images (Figure 3 b and c). These were stripped edges of the nanosheets where the layers could be observed. The dozens of layers of the nanosheets were regularly stacked, which demonstrated that they were click-reacted through a one-step process. The random stacking observed in the SEM image occurred from the aggregation of the dozens of layers. Distances between the black lines were approximately 1.7 nm, thus supporting the formation of a layered structure as assigned by the XRD pattern.

Energy-dispersive X-ray spectroscopy (EDS) analysis in this selected area showed a $Ti/W = 1.04$ molar ratio. The ratio approached $Ti/W = 1.19$ under reaction conditions. The electron diffraction (ED) pattern of the selected area is shown in the inset of Figure 3 c. The arced spots in the ED pattern were observed in the regions at 0.24, 0.17, and 0.12 nm, after calibration was attempted according to the spots on the (111) plane of gold nanoparticles. These spots were identified as (200) and (020) layered tungsten oxides and (200) and (002) layered titanium oxides, which indicated that the intralayer molecular orderings of layered titanium oxide and layered tungsten oxide remained after the click reaction. These results strongly demonstrated that alternating layered metal oxides were synthesized by the reaction between layered titanium oxide modified with alkene groups and layered tungsten oxide modified with thiol groups.

Cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectra of the organic-modified layered metal oxides and the click-reacted product are shown in Figure 4 for confirmation of the thiol–ene reaction. The layered titanium oxides modified with alkene (Figure 4 a) showed peaks of $\delta = 114$ and 135 ppm derived from the double bond of the alkene groups. In the alternating multilayer structure of Figure 4 c, however, the peaks derived from the alkene group

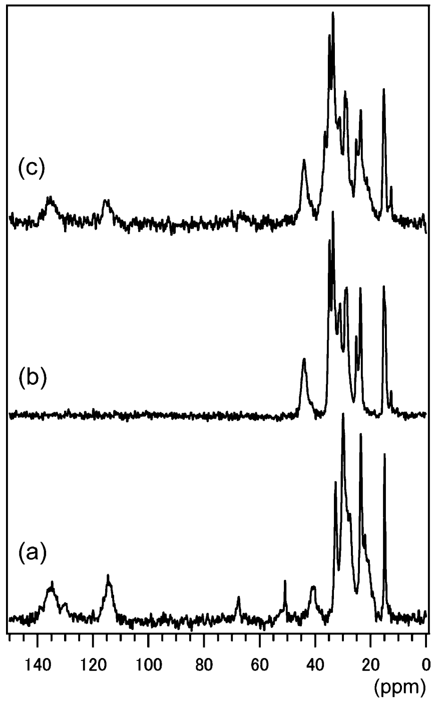

Figure 4. CP/MAS ^{13}C NMR spectra of a) alkene-modified layered titanium oxide, b) thiol-modified tungsten oxide, and c) click-reacted sample.

substantially decreased. The decrease in peak intensities attributed to the alkene groups suggested a partial click reaction on the interlayer surface. The partial reaction of the alkene groups probably occurred through both the number of the functional groups (see the Supporting Information) and the difficulty in the reaction of radicals with the thiol groups on the nanosheet. The radicals usually react with thiol groups in the thiol–ene reaction, because of the difference in the kinetics between thiol and alkene groups. Actually, the alkene groups remained after thermal radical reaction in the presence of azobisisobutyronitrile (AIBN). The click reaction between interlayers was improved by changing the reactive groups between the titanium oxide and the tungsten oxide, which means that layered titanates were reacted with thiol groups. Layered titanium oxides were more easily exfoliated into the nanosheets than the layered tungsten oxides. Therefore, the thiol groups immobilized on the layered titanium oxide easily reacted with the radical initiator. Actually, the alkene groups on the layered tungsten oxide almost completely disappeared after the click reaction with thiol-grafted layered titanates (see the Supporting Information). The alkene groups on the layered metal oxides appropriately reacted with the thiol groups on the other material.

Nanosheets produced by the exfoliation of layered metal oxides are often applied as photocatalysts.[24–27] The electronic structure of the click-reacted sample was different from that of the starting materials, as indicated by the UV/Vis spectrum of the click-reacted sample being different from the simple summation of those for titanate and tungstate (see the Supporting Information). Therefore, this clicked sample was expected to be a novel photocatalyst.

Nanosheets also are known to absorb organic substances such as pigments between layers.[28–30] In alternating multilayers, methylene blue (MB) was absorbed between the layers by ion exchange with octylamine. Samples with MB between the layers were used to check the photocatalytic activity of the alternating multilayers in the degradation reaction with MB as a model compound. Light with a wavelength of 290 nm, or longer, was used to irradiate the click-reacted sample and the organic-modified layered metal oxides, and the degradation was evaluated by the diffuse reflection of the absorption spectrum from a decrease in the peak at 670 nm derived from MB. The results are shown in Figure 5. The alternating multilayer sample showed photocatalytic activity higher than that of layered titanium oxide and layered tungsten oxide. Additionally, the alternating multilayer sample showed photocatalytic activity higher than that of the clicked multilayers of only titanate and tungstate (see Figure S4 in the Supporting Information). It is conceivable that the charge isolation due to the close arrangement of titanium and tungsten oxides happens in dozens of layers at an interval of about 1 nm.

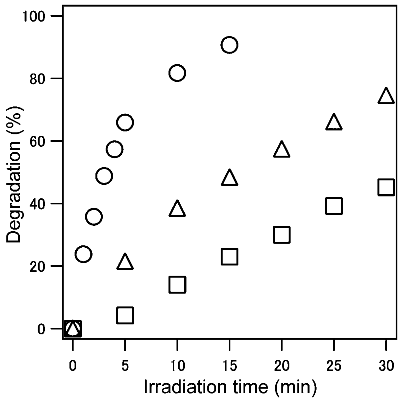

Figure 5. Photocatalytic activities of alkene-modified layered titanium oxide (△), thiol-modified layered tungsten oxide (□), and their click-reacted sample (○).

In summary, an alternating multilayer of titanium and tungsten oxides was synthesized by modifying layered titanium oxide with an alkene group and layered tungsten oxide with a thiol group and causing a thiol–ene reaction. The alternating multilayer showed superior photocatalytic activity when it was used for the decomposition reaction of MB. It should be possible to create similar alternating multilayers by using other layered metal oxides such as MnO_2 and SnO_2. A new lamination method that can create alternating multilayer structures in one step using a thiol–ene reaction has been realized. This method enables the synthesis of both alternating multilayers of various oxides of two types of metal, and a new type of material by the combination of other nanomaterials, such as nanotubes and nanoparticles, which also enables the design of novel functions.

Experimental Section

Starting materials of layered titanates ($H_xTi_{2-x/4}\square_{x/4}O_4$; $\square$: vacancy, $x \approx 0.7$)[31–33] and layered tungstates ($H_2W_2O_7$)[8,34,35] were synthesized according to previous reports. These starting materials were reacted with octylamine in heptane to insert octylamine molecules between the layers for expansion of the interlayer spaces.[36] Organic modifications with silane coupling agents were carried out in toluene under nitrogen.[37] Layered titanates were reacted with allyltrimethoxysilanes to immobilize the alkene groups onto the titanate interlayer surfaces at 90 °C for 2 days. Layered tungstates were reacted with 3-mercaptopropyltrimethoxysilane to immobilize thiol groups. Organically modified layered metal oxides were ultrasonicated in *N*,*N*-dimethylformamide (DMF) until no precipitate developed. After ultrasonication, the layered metal oxides were stripped into their thinnest layers. Titanium oxides modified with alkene groups were mixed with tungsten oxides modified with thiol groups. For the mixture, a ratio was used that would allow the summation of the areas of each sheet to be equal. Azobisisobutyronitrile (AIBN), as a radical reaction initiator, was added to this mixture as half of the equivalent amount of the thiol groups. The solution was reacted for 24 h at 80 °C,[38] then samples were collected by centrifugation. The centrifuged samples were washed with acetone and dried under vacuum, and the click-reacted sample was obtained as a yellow powder.

XRD was carried out with a Philips X'Pert MPD-OEC diffractometer with bent crystal monochromated $Cu_{K\alpha}$ radiation. CP/MAS ^{13}C NMR spectra were recorded on a Bruker CMX-300 spectrometer at a resonance frequency of 75.47 MHz.

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