Electronic Supplementary Information (ESI)

Surface-functionalized hydrophilic monolayer of titanate and its application to dopamine detection

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Experimental method

Materials: All the reagents were used as purchased without purification.

Synthesis of the layered DEG-VE/VBA-TiO_2 and its exfoliation: The VBA-TiO_2 was synthesized from Cs-TiO_2 as the starting material through the formation of H-TiO_2. The Cs–TiO_2 was prepared by a solid-state synthesis.[S1] The mixture of titanium dioxide (TiO_2, Ishihara Sangyo, ST-01) and cesium carbonate (Cs_2CO_3, Junsei, 99%) was heated at 800 ˚C for 20 h. The molar ratio of TiO_2 and Cs_2CO_3 was set at 5.2:1.0. The interlayer cecium ion was exchanged to proton with immersion of Cs–TiO_2, typically 5 g, in 500 cm^3 of 1 mol dm^{-3} HCl at 25 ˚C for 3 days. The resultant H-TiO_2 was then immersed in aqueous solution containing 4-vinylbenzylamine (VBA, TCI, 92.0%) for 10 days. The molar ratio of the interlayer proton to VBA was set at 1.0. The chemical formula of the H-TiO_2 was assumed to be the same as that in the previous report,[4c] namely $H_{0.7}Ti_{1.825}\square_{0.175}O_4\cdot H_2O$. The VBA concentration was calculated on the basis of the chemical formula. The resultant VBA-TiO_2 powder was washed with purified water and ethanol and then dried. The powder of the VBA-TiO_2, typically 0.296 g, was mixed with 4 cm^3 of diethylene glycol monovinyl ether (DEG-VE, TCI, 96.0%). The molar ratio of DEG-VE to the intercalated VBA ($R_{\mathrm{DEG\text{-}VE/VBA}}$) was set at $R_{\mathrm{DEG\text{-}VE/VBA}} = 44$. The dispersion liquid was maintained at 75 °C under stirring. After 24 h, 1 wt% of 2,2’-azoisobisisobutyronitrile (AIBN, Wako, 98%) was added in the liquid phase of DEG-VE. The graft reaction was performed at 75 °C for the further 24 h without stirring. The resultant material was washed with excess amount of purified water. The collected DEG-VE/VBA-TiO_2 precipitates, namely 0.05 g, was dispersed in 20 cm^3 of purified water. The dispersion liquid was put in a sonic bath for 1 h and then maintained at 60 °C for 5 days. The precipitate was collected by centrifugation at 9000 rpm for 10 min. Then, the collected precipitate was dispersed in purified water and maintained at 60 °C for 5 days again. The resultant supernatant dispersion liquid of the DEG-VE/VBA-TiO_2 monolayers was obtained after centrifugation at 9000 rpm for 10 min.

Characterization: The crystal structure, namely the interlayer distance, was analyzed by X-ray diffraction (XRD, Rigaku, Mini Flex II and Bruker D8 Advance) with Cu-Kα radiation. The morphology of the precursor layered materials before exfoliation was observed by field-emission scanning electron microscopy (FESEM, FEI Sirion, Hitachi S-4700, and Jeol JSM-7600F) operated at 5.0 kV. The sheet-like morphology after the exfoliation was observed by field-emission transmission electron microscopy (FETEM, FEI Tecnai F20) operated at 200 kV and atomic force microscopy (AFM Shimadzu, SPM-9600). The aqueous dispersion liquid of DEG-VE/VBA-TiO_2 monolayer was dropped on a copper grid supported by a collodion membrane for FETEM observation. The aqueous dispersion liquid, approximately 10–40 mm^3, was dropped on a cleaned Si substrate heated at 100 ˚C by using a temperature-controlled stage. A silicon (Si) wafer was cleaned with immersion in a mixed solution of HCl/methanol (CH_3OH, Kanto, 99.8%) (1:1 by volume) for 30 min and then in a concentrated sulfuric acid (H_2SO_4, Kanto, 96.0%) solution for 30 min. The substrate was dried with blowing of nitrogen gas. The contents of organic molecules in the layered composites were estimated by thermogravimetry (TG) analysis (Seiko, TG-DTA 7000) in air atmosphere. The presence of the intercalated molecules in the interlayer space was analyzed by KBr method of Fourier-transform infrared (FT-IR) absorption spectroscopy (Jasco, FT/IR-4200). The UV-Vis absorption spectra were obtained by a spectrophotometer (Jasco, V-670). The solid-state samples, such as the layered DEG-VE/VBA-TiO_2, were measured by a diffuse-reflectance mode with an integrating sphere. The liquid sample, such as the DEG-VE/VBA-TiO_2 monolayers, was measured in a quartz glass cell by a transmittance mode.

Dopamine detection: The dispersion liquid of the DEG-VE/VBA-TiO_2 monolayer, namely 1 cm^3, was mixed with 1 cm^3 of aqueous solution containing 2–2000 μmol dm^{-3} of dopamine. The concentration of the DEG-VE/VBA-TiO_2 monolayer was 1.79 ± 1.00 mg cm^{-3} in aqueous media. Purified water for dissolution of dopamine was degassed with bubbling of nitrogen gas prior to preparation of the aqueous solution. The UV-Vis spectra of the dispersion liquids were measured after several minutes of the mixing.

Reference

S1. T. Sasaki, Y. Komatsu and Y. Fujiki, *J. Chem. Soc., Chem. Commun.*, **1991**, 817.

FT-IR and TG analyses of the layered VBA-TiO_2 and DEG-VE/VBA-TiO_2

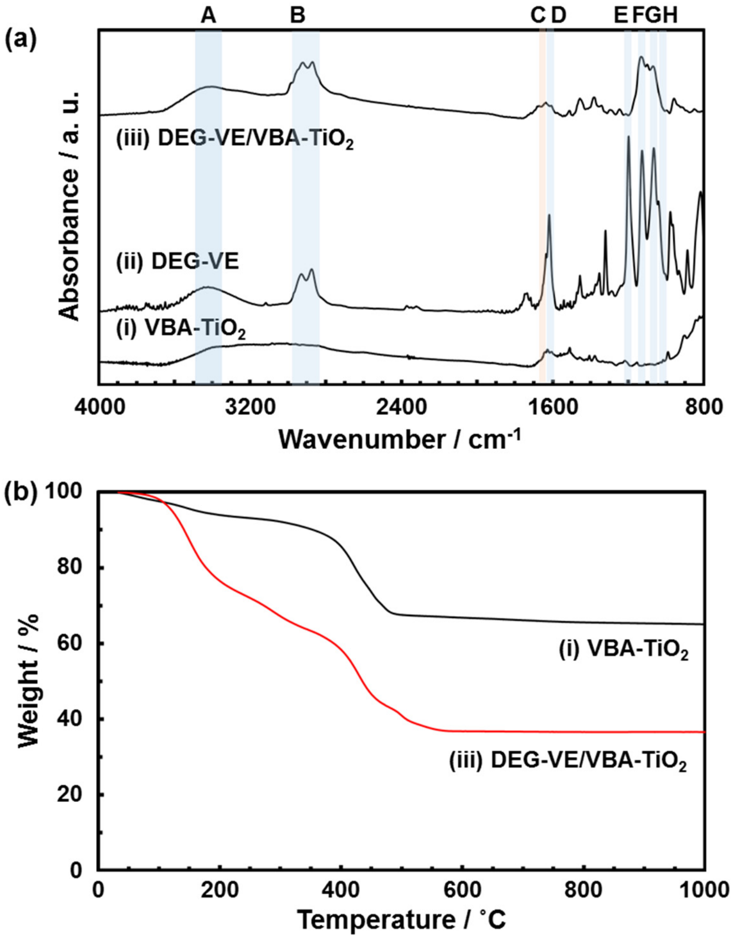

Fig. S1. FT-IR spectra (a) and TG curves (b) of the layered VBA-TiO_2 (i), DEG-VE (ii), and DEG-VE/VBA-TiO_2 (iii).The absorption in the FT-IR spectra is ascribed to the following functional groups: the stretching vibration of O–H group (A), the stretching vibration of C–H group (B), the stretching vibration of C=C group (C), the stretching vibration of the C=C group in vinylether (D), the asymmetric stretching vibration of C–O–C group in vinylether (E), the asymmetric stretching vibration of C–O–C group in aliphatic ether (F), the stretching vibration of C–O group in alcohol (G), and the symmetric stretching vibration of C–O–C group in vinylether (H).

The grafting of the DEG-VE induces the appearance of the absorption bands A, B, F, G (Fig. S1a). The results indicate the presence of O–H, C–H, and C–O–C groups. In contrast, the remaining absorption band C, corresponding to vinyl group, indicates the presence of the unreacted VBA molecule on the layer surface. The absorption bands of D, E, and H characteristic to vinylether were not observed on the resultant DEG-VE/VBA-TiO_2. Therefore, the unreacted DEG-VE was not contained on the resultant DEG-VE/VBA-TiO_2. The graft reaction partially proceeds on the surface VBA groups, even though a small amount of unreacted VBA remains on the surface.

The VBA molecule was intercalated in the $H_{0.7}Ti_{1.825}\square_{0.175}O_4\cdot xH_2O$ (□: vacancy). Therefore, the chemical formula is assumed to be $VBA_yH_{0.7-y}Ti_{1.825}\square_{0.175}O_4\cdot xH_2O$. The molar content of VBA in the VBA-TiO_2 was estimated from the TG curve (Fig. S1b). The weight loss lower than 200 °C is ascribed to the water molecule. The final product after the heating at 1000 °C is assumed to be $Ti_{1.825}\square_{0.175}O_4$. The remaining weight corresponds to VBA. Therefore, the weight ratio of the each content in the $VBA_yH_{0.7-y}Ti_{1.825}\square_{0.175}O_4\cdot xH_2O$ can be summarized as shown in Table S1. Based on the molar ratio, the chemical formula is estimated to be $VBA_{0.45}H_{0.25}Ti_{1.825}\square_{0.175}O_4\cdot xH_2O$ ($x<0.83$), as shown in the main text.

Table S1. Contents of the VBA-TiO_2 estimated from the TG curve.

Content	Formula weight / g mol^{-1}	Weight fraction / wt %	Amount in the each content in 100 g / mol
VBA	133.19	26.4	0.1982
$Ti_{1.825}\square_{0.175}O_4$	151.36	67.0	0.4427
H_2O	18.01	6.5	0.3367

The TG curves showed an increase in the weight loss after the grafting of DEG-VE (Fig. S1b). If the chemical formula of the VBA-TiO_2 is assumed to be constant, an increase in the weight loss can correspond to the grafted DEG-VE. The final product after the heating at 1000 °C is assumed to be $Ti_{1.825}\square_{0.175}O_4$ (Fig. S1b). The contents of VBA and H_2O is estimated from the molar ratio of the $VBA_{0.45}H_{0.25}Ti_{1.825}\square_{0.175}O_4\cdot xH_2O$ ($x<0.83$). Therefore, the molar ratio of the grafted DEG-VE to the surface VBA is estimated to be 3.10 (Table S2). Based on the FT-IR and TG analyses, the oligomeric DEG-VE was grafted on the surface VBA molecules. In addition, a small amount of the unreacted VBA molecule remained on the surface. Therefore, the uneven graft state lowers the periodicity of the layered structure (the pattern (iii) in Fig. 2a).

Table S2. Contents of the DEG-VE/VBA-TiO_2 estimated from the TG curve.

Content	Formula weight / g mol^{-1}	Weight fraction / wt %	Amount in the each content in 100 g / mol
DEG-VE	132.16	44.8	0.3390
VBA	133.19	14.6	0.1095
$Ti_{1.825}\square_{0.175}O_4$	151.36	37.0	0.2445
H_2O	18.01	3.65	0.2025

Morphologies of Cs-TiO_2, H-TiO_2, and VBA-TiO_2

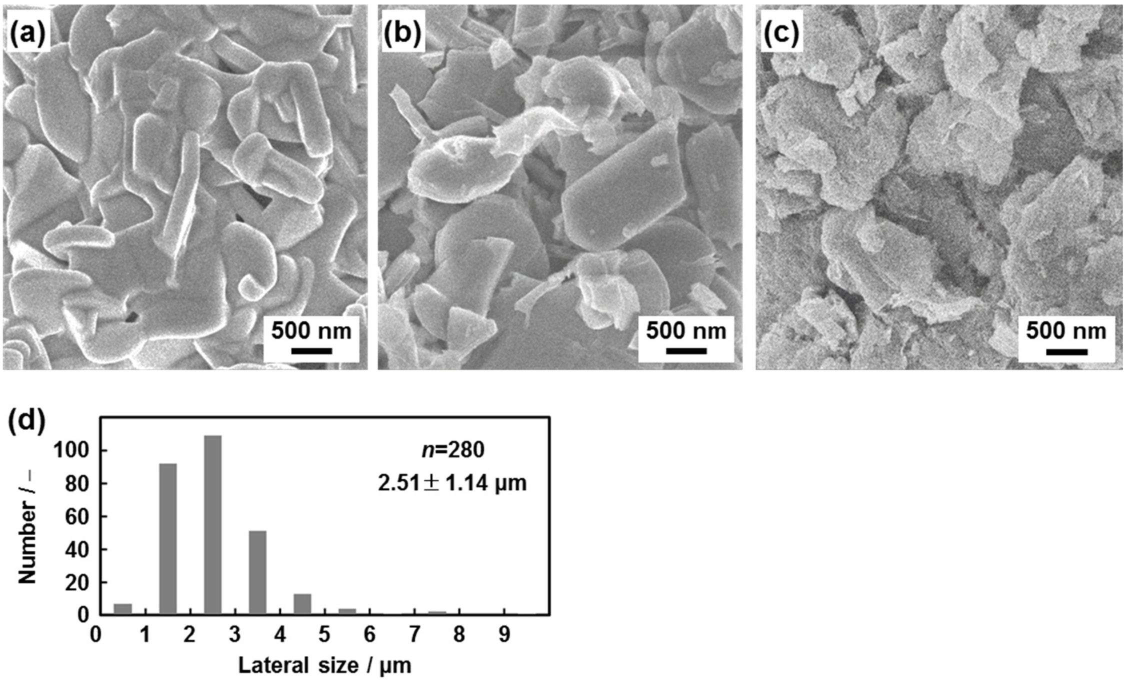

Fig. S2. SEM images of the Cs-TiO_2 (a), H-TiO_2 (b), and VBA-TiO_2 (c) and the lateral-size distribution of the layered DEG-VE/VBA-TiO_2 (d).

The precursor layered composite of VBA-TiO_2 was prepared from Cs-TiO_2 as the starting material through H-TiO_2 via the ion-exchange reactions. The platy morphologies, approximately 2 μm in size, were not changed in these ion-exchange processes. The average lateral size of the DEG-VE/VBA-TiO_2 was 2.51 ± 1.14 μm before the exfoliation. In contrast, the average lateral size of the DEG-VE/VBA-TiO_2 monolayer was slightly decreased to 1.02 μm ± 0.29 μm. The lateral size slightly decreases with the fracture during exfoliation.

Additional AFM images of the DEG-VE/VBA-TiO_2 monolayers

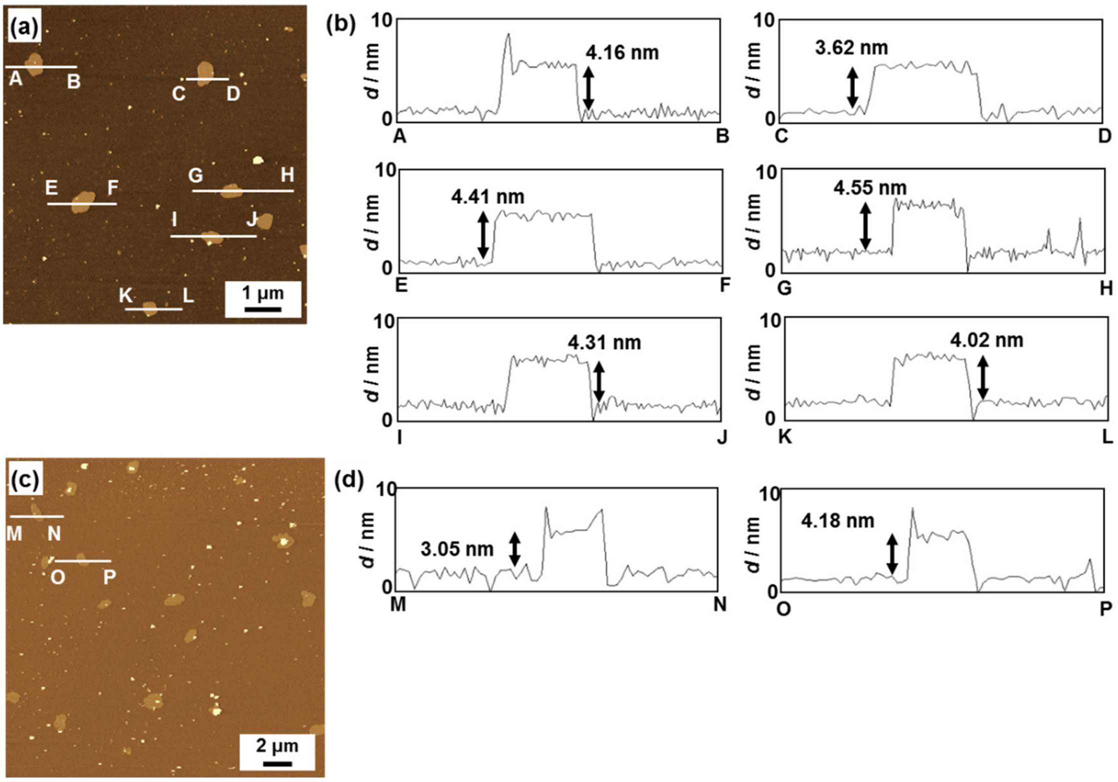

Fig. S3. Additional AFM images of the DEG-VE/VBA-TiO_2 monolayers and their height profiles.

Based on these images and the others, the histograms of the lateral size and thickness were prepared (Fig. 3c,d). In these AFM images, some thicker objects with the smaller lateral size were contained in the images. Those are assumed to be contaminant during preparation process of the AFM samples.

Yield of the DEG-VE/VBA-TiO_2 monolayers

The VBA-TiO_2 was synthesized through the ion-exchange processes starting from the Cs-TiO_2 via the H-TiO_2. Then, the DEG-VE was grafted to the layered precursor VBA-TiO_2. Since all the precipitates were collected in the successive processes, the yield can be regarded as approximately 100 %. The yield was lowered to 71.6 % after the exfoliation of the layered DEG-VE/VBA-TiO_2 into the monolayers because the unexfoliated precipitates were removed by centrifugation.

The yield was calculated from the initial concentration (C_i) of the layered DEG-VE/VBA-TiO_2 in an aqueous medium and the final average concentration (C_f) of the exfoliated DEG-VE/VBA-TiO_2 monolayers. The C_i was set at 2.5 mg g^{-1}. The average C_f was calculated to be 1.79 ± 1.00 mg g^{-1} on the basis of the density measurement of the three dispersion liquids, namely 0.990 mg g^{-1}, 1.18 mg g^{-1}, and 3.21 mg g^{-1}. Since the weight measurement included experimental errors, the average value was used for the calculation of C_f. Therefore, the yield as estimated to be 71.6 % on the basis of the concentration.

UV-Vis spectra of the dopamine detection experiments

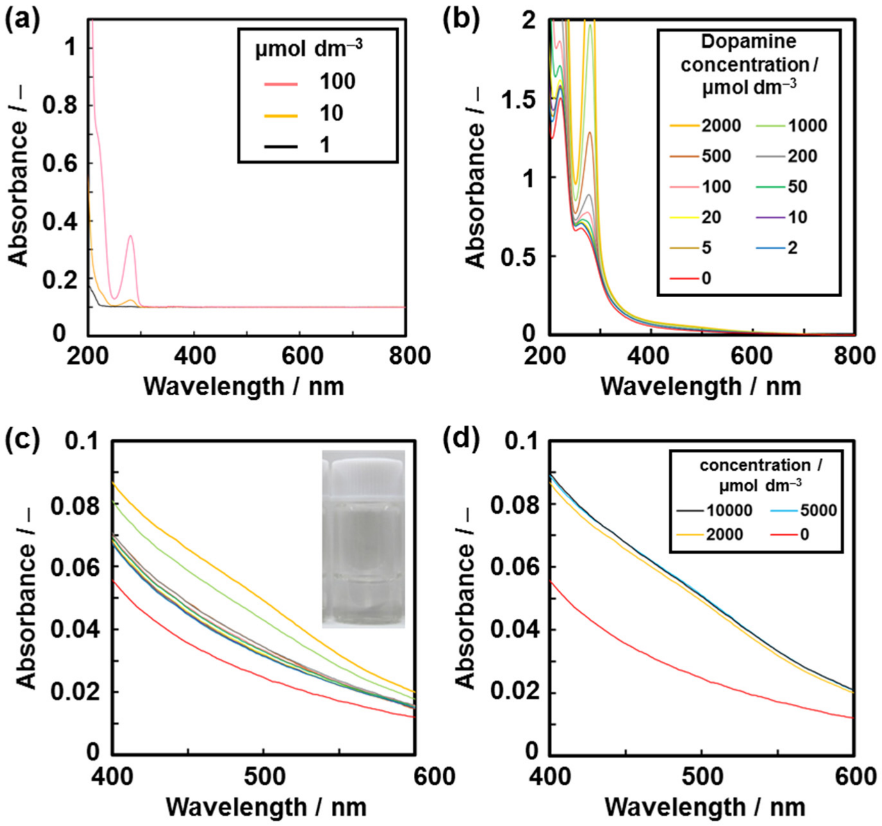

Fig. S4. UV-Vis absorption spectra of the dopamine aqueous solution (a) and the monolayer dispersion liquid with addition of dopamine aqueous solution within 2–2000 μmol dm^{-3} (b,c) and 2000–10000 μmol dm^{-3} (d). The inset of Fig. S4c shows the photograph of the DEG-VE/VBA-TiO_2 monolayer dispersion liquid containing 10 μmol dm^{-3} of dopamine.

Dopamine aqueous solution itself has no absorption in visible light region (Fig. S4a). When the dopamine aqueous solution was mixed with the dispersion liquid of the DEG-VE/VBA-TiO_2 monolayer, the absorption appeared in the visible-light region (Fig. 4b). The absorption is ascribed to the charge-transfer excitation from the adsorbed dopamine to titanate, as illustrated in Fig. 1c. The visible light absorption was increased with an increase in the dopamine concentration within 2–2000 μmol dm^{-3} (Fig. S4b,c). Therefore, the dopamine concentration can be estimated from the absorbance. However, the coloration was not recognized by the naked eye (the inset of Fig. S4c). In the present work, the absorbance at 500 nm was used for the colorimetric detection of dopamine. The absorbance was not increased in the dopamine concentration higher than 2000 μmol dm^{-3} (Fig. S4d). The result imply that the adsorption sites on the DEG-VE/VBA-TiO_2 monolayer is occupied by the saturated adsorption of dopamine.