Supplementary Material (ESI) for New Journal of Chemistry

Supplementary Information

Enantioselective anion exchange on a positively charged poly(L-lysine) layer assembled on thin TiO_2-gel films

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1. TiO_2-gel films prepared by surface sol-gel process

The preparation procedure of ultrathin metal oxide gel films by means of surface sol-gel process has been described in our previous reports (*Chem. Lett.* 1996, 831; *Chem. Mater.* 1997, **9**, 1296, and in *Supramolecular Organization and Materials Design*, ed. W. Jones and C. N. R. Rao, Cambridge Press, Cambridge, 2002). This process takes advantage of surface hydroxyl groups for adsorption of metal alkoxides. After rinsing the surfaces of the substrate, the chemisorbed alkoxides are hydrolyzed in water to form ultrathin metal oxide gel layer. Then, hydroxyl groups are reproduced on the surface of the oxide gel layer and they are available for the next adsorption cycle of metal alkoxides. The metal oxide gel films can be prepared on any surfaces with hydroxide group, for example, on the surfaces of glass, quartz, silicon wafer, and polymer films.

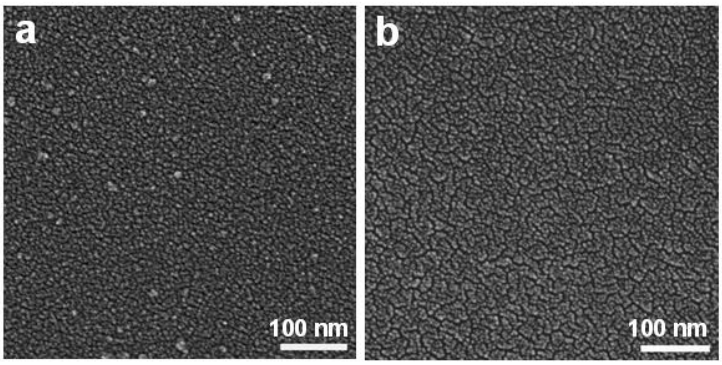

Figure S1. SEM images of (a) 5-layer titania film deposited on quartz substrate, and (b) bare mica plate.

Figure S1 shows SEM images of a quartz substrate with an ultrathin TiO_2-gel film (a) and a bare mica plate (b). To prevent the electric charge up, the samples were deposited by 2-nm thick platinum layer. The morphology on the latter surface is due to the aggregation of about 0.8-nm platinum particles. Except for a few particular aggregates, the surface of titania-coated quartz substrate (a) was extremely smooth. This indicates that TiO_2-gel film uniformly grew during five cycles of the surface sol-gel process. The film

density was estimated to be 1.7 g/cm^3 from quartz crystal microbalance (QCM) technique and cross-sectional SEM observation. This value was about two-fifths of crystalline TiO_2 and was very close to that of bulk TiO_2-gel. The metal oxide gel films prepared by the surface sol-gel process contain some unhydrolyzed alkoxide groups.

2. Adsorption and anion exchange of BCECF on PLL layer

Adsorption of BCECF on PLL layer. Fluorescent dye, BCECF, was adsorbed on a PLL layer in a similar manner to SRB. Figure S2 shows UV-vis absorption changes due to the growth of TiO_2-gel layers, the adsorption of PLL layer, and the following adsorption of BCECF. The concentration of BCECF was 0.36 mM, and the solution was adjusted to be pH 7.0. The inset shows UV-vis absorption spectra of BCECF adsorbed on a PLL layer at different pH.

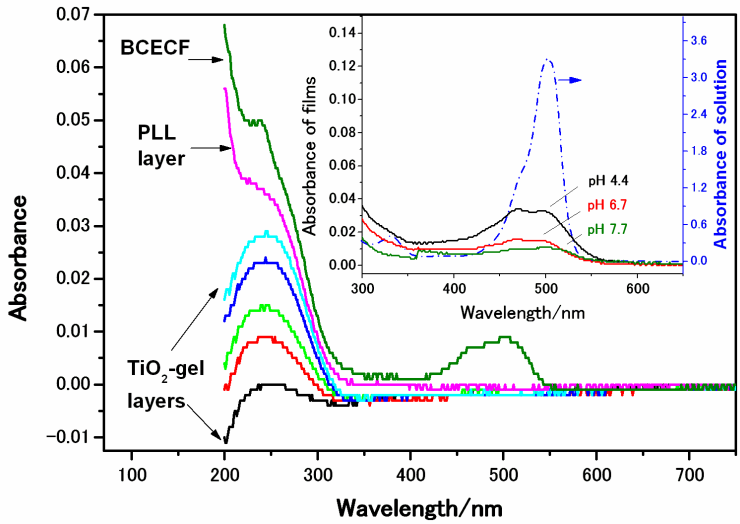

Figure S2. UV-vis absorption changes during stepwise deposition of TiO_2-layers, PLL layer, and BCECF. Inset shows absorption spectra of BCECF deposited on PLL layer at different pH. Dashed line shows absorption spectrum of 3.7×10^{-5} M aqueous solution of BCECF (pH 11).

As shown by the dashed line in the inset, BCECF gave a monomer peak at 506 nm and a shoulder at 466 nm probably due to the vibronic satellite of the main peak. When this fluorescent dye was adsorbed on a PLL layer from the solution at pH 4.4, the monomer peak was blue-shifted by 11 nm and the absorbance near 466 nm increased as compared to the main peak. The blue shift of 11 nm suggests that this dye was in a higher dielectric environment than water, in sharp contrast to SRB that showed 8-nm red shift. The increase of the absorbance near 466 nm indicates that the dye aggregated on the surface of PLL layer. When the pH of BCECF solutions increased to 6.7, the amount of adsorbed dye molecules significantly decreased. Furthermore, the absorbance near 466 nm decreased at pH 7.0 (shown in Figure S2) and pH 7.7 (shown in the inset) in comparison to the peak intensity at 495 nm. From these reasons, we concluded that the monomeric adsorption of BCECF on PLL layer becomes dominant at the pH more than 7.0.

Anion exchange between BECEF and D-glutamic acid. Figure S3 shows fluorescence spectra of BCECF released in *D*-glutamic acid solutions. As shown in the inset, the dye was quickly released within the first three minutes and then slowly released. The anion exchange was a little faster than the case of *L*-glutamic acid. However, the enantioselectivity was not as high as that of SRB.

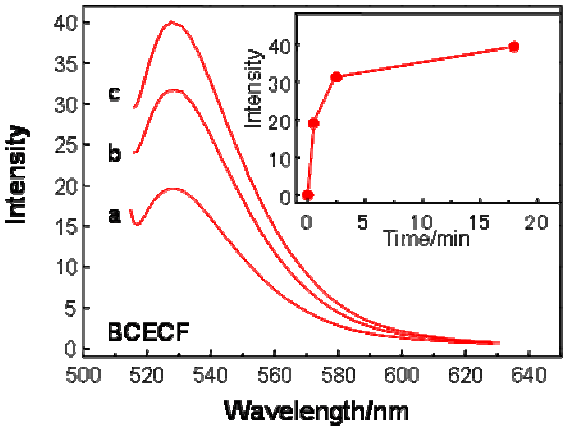

Figure S3. Fluorescence spectra of BCECF released in 0.01 mM *D*-glutamic acid solutions after 30 sec (a), 150 sec (b), and 18 min (c). Inset shows increases in fluorescence intensity at 527 nm.

3. Anion exchange of dipeptides and polypeptides

The anion exchange of SRB with peptides and polypeptides was examined as follows. We chose glycyl-glutamic acid (Gly-Glu), glutamyl-glutamic acid (Glu-Glu), poly(*L*-glutamic acid), and poly(*D*-glutamic acid). For the cases of dipeptides, a quartz substrate coated with PLL and SRB was immersed in the solutions near pH 4. In this condition, Gly-Glu and Glu-Glu adsorb as molecules with one and two negative charges, respectively. As shown in Table S1, relative fluorescence intensities after 18-min immersion were 71 for Gly-Glu and 112 for Glu-Glu. The number of negative charges per molecule seems to be decisive factor for the anion exchange of SRB and dipeptide. Fluorescence intensity obtained for *D*-glutamic acid (see Fig. 4a in our manuscript) is about double of the intensity for Glu-Glu. This suggests that PLL recognizes not only the number of negative charges but also the shape of molecules. In comparison with Glu-Glu, poly(*L*-glutamic acid) gave a little stronger fluorescence intensity. On the other hand, the enantiomer with high molecular length, poly(*D*-glutamic acid), showed relatively weak fluorescence.

Table S1 Anion exchange of dipeptides and polypeptides

Compounds	MW	Negative charges/molecule	Concentration (mg/ml)	pH	PL intensity[c]
Gly-Glu	204.2	1	0.1	4.1	71
Glu-Glu	276.2	2	0.1	3.8	112
poly(*L*-glutamic acid)	17000[a]	113[b]	0.1	7.8	160

poly(*D*- glutamic acid)	38000[a]	254[b]	0.1	8.4	44

[a] Molecular weight of polymers was estimated from the solution viscosity.
[b] Charge density of polymers was assumed to be the same as the degree of polymerization.
[c] Fluorescence intensity after 18-min immersion.