Electronic supplementary information

Moderate Molecular Recognitions on ZnO *m*-Plane and Their Selective Capture/Release of Bio-related Phosphoric Acids

Eisuke Kanao,^{*ab} Katsuya Nakano,^c Ryoma Kamei,^d Takuro Hosomi,^{de} Yasushi Ishihama,^{ab} Jun Adachi,^{ab} Takuya Kubo,^{*c} Koji Otsuka^c and Takeshi Yanagida^d

^aGraduate School of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan ^bNational Institutes of Bio medical Innovation, Health and Nutrition, Ibaraki, Osaka 567-0085, Japan

^cDepartment of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

^dDepartment of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8654, Japan

^ePrecursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Corresponding authors Eisuke Kanao Tel: +81-75-753-4565 Fax: +81-75-753-4601 E-mail: kanao.eisuke.7s@kyoto-u.ac.jp

Takuya Kubo Tel: +81-75-383-2448 Fax: +81-75-383-2450 E-mail: <u>kubo.takuya.6c@kyoto-u.ac.jp</u>

Contents

- Retention behaviors of adenosine, AMP, ADP, and ATP on the column fabricated only the ZnO seed layer (Figure S1)
- SEM images of ZnO nanowalls and ZnO NWs on silicon wafers (Figure S2)
- IR peak shifts of ATP on ZnO nanowires with different immersion time in ATP solution (Figure S3)
- SEM image of the top surface of ZnO NWs (Figure S4)
- Retention behaviors of nucleotides at different temperatures or flow rates on the ZnO-NWs column (Figure S5)
- Physical damage test of ZnO NWs after LC analysis (Figure S6)
- Recovery ratio of ATP in each electrolyte solution as a mobile phase. (Figure S7)
- Chromatogram of nucleotides with the short ZnO-NWs column with phosphate gradient condition (Figure S8)
- Chromatogram of nucleotides in the second phosphate gradient separation (Figure S9)
- Chemical corrosion test of ZnO NWs in electrolyte solutions (Figure S10)
- SEM images of annealed and as-grown ZnO NWs after immersion into phosphate buffer (Figure S11)



Fig. S1 Retention behaviors of adenosine, AMP, ADP, and ATP on the column fabricated only the ZnO seed layer (Seed layer column). (a) Typical chromatograms of adenosine and nucleotides. (b) Recovery ratio of each compound. LC condition: column, seed layer ($30 \text{ cm} \times 100 \mu \text{m}$), bare capillary ($30 \text{ cm} \times 100 \mu \text{m}$); mobile phase, water; flow rate, $5.0 \mu \text{L/min}$; temperature, 25 °C; detection, UV (260 nm).



Fig. S2 SEM images of (a) ZnO nanowalls and (b) ZnO NWs on silicon wafers.



Fig. S3 IR peak shifts of ATP on ZnO NWs with different immersion time in ATP solution. The black line shows the IR spectra of ZnO NWs before immersion.



Fig. S4 SEM image on the top surface of ZnO NWs.



Fig. S5 Retention behaviors of nucleotides at different temperatures or flow rates on ZnO NWs column. (a), (b) Plot of recovery ratio of nucleotides vs temperature. (c), (d) Plot of recovery ratio of nucleotides vs flow rate. LC condition: column, ZnO-NWs ($30 \text{ cm} \times 100 \text{ }\mu\text{m}$), bare capillary ($30 \text{ cm} \times 100 \text{ }\mu\text{m}$); mobile phase, (a), (c) water, (c), (d) ACN; detection, UV (260 nm).



Fig. S6 Physical damage test of the ZnO NWs after LC analysis. (a) Schematic diagram of physical damage test. (b) SEM image of ZnO NWs before LC analysis. (c) SEM image of ZnO NWs after LC analysis at high flow rate of 10 μ L/min, (c) SEM image of ZnO NWs after LC analysis at 50 °C.



Fig. S7 Recovery ratio of ATP in each electrolyte solution as the mobile phase. LC condition: column, ZnO-NWs (30 cm \times 100 μ m), bare capillary (30 cm \times 100 μ m); mobile phase, NaCl solution, Tris-HCl buffer and phosphate buffer; flow rate, 5.0 μ L/min; temperature, 25 °C; detection, UV (260 nm).



Fig. S8 Chromatogram of nucleotides with the short ZnO NWs column with phosphate gradient condition. LC condition: column, ZnO-NWs column ($30 \text{ cm} \times 100 \mu \text{m}$); mobile phase, (A) water, (B) 250 mM phosphate buffer; 0-1 min, 0% B, 1-21 min 0% B to 100% B; flow rate, 1.0 μ L/min; temperature 25 °C; detection, UV (260 nm).



Fig. S9 (a) Chromatogram of nucleotides in the second phosphate gradient separation. (b) Cross section of ZnO NWs column after phosphate gradient separation. LC condition: column, ZnO-NWs column (90 cm \times 100 µm); mobile phase, (A) water, (B) 250 mM phosphate buffer; 0-1 min, 0% B, 1-21 min 0% B to 100% B, 21-30 min 100% B; flow rate, 1.0 µL/min; temperature 25 °C; detection, UV (260 nm).



Fig. S10 Chemical corrosion test of ZnO NWs in electrolyte solutions. The SEM images of ZnO NWs nanowire after soaked in (a) NaCl solution and (b) Tris-HCl buffer. For these electrolyte solutions, the ionic strength was unified to 0.2 M. LC condition: column, ZnO-NWs (30 cm \times 100 µm), bare capillary (30 cm \times 100 µm); mobile phase, NaCl solution, Tris-HCl buffer and phosphate buffer; flow rate, 5.0 µL/min; temperature, 25 °C; detection, UV (260 nm).



Fig. S11 SEM images of annealed and as-grown ZnO NWs after immersion into 100mM phosphate buffer (pH 7.0). Annealed ZnO NWs immersing into phosphate buffer for (a) 1 hour, (b) 5 hours. As-grown ZnO NWs immersing into phosphate buffer for (c) 1 hour, (d) 5 hours.