Supplementary Material (ESI) for Chemical Communications

Shape control of anatase TiO_2 nanoparticles by amino acids in a gel-sol system

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1. General

All amino acids and the corresponding sodium salts of the highest commercial quality were purchased from Nakalai Tesque and were used as received. Water was doubly distilled, deionized, and filtered prior to use. Titanium (IV) tetraisopropoxide (TIPO, 5N) purchased form Kojundo Chemical Laboratory Co., Ltd was used for the preparation of TiO_2 particles. X-ray diffraction (XRD) measurements were carried out on a Rigaku RAD-B system using Ni-filtered CuKα radiation (40 kV, 40 mA). TEM observations were performed by using a JEM-1200EX II and the acceleration voltage was 120 kV. High resolution TEM images were taken by using a JEOL JEM-3010 at 300 kV.

2. Representative procedure for the preparation of TiO_2 particles by the Gel-Sol method.

Representative procedure for the preparation of TiO_2 nanoparticles as follows: A Ti^{4+} stock solution was prepared by mixing TIPO (28.4 g, 0.100 mol) with triethanolamine (TEOA, 29.8 g, 0.200 mol) under dry atmosphere to form a stable complex against hydrolysis of Ti^{4+} at room temperature. After the resulting pale yellow stock solution consisting of the molar ratio of [TEOA] : [TIPO] = 2 : 1 was kept 1 day at room temperature in a dry air, water was added to make an aqueous stock solution of 0.50 M in Ti^{4+}. Then, the 4.0 mL of the stock solution was mixed with the same volume of the 0.10 M amino acid solution. The resulting solution was diluted with 8.0 mL of water, and the pH value of the solution was changed to 9.5, 10.5, or 11.5 by the addition of an aqueous NaOH solution. After the total volume of the solution was adjusted to 20.0 mL by the addition of

water, the mixed solution was ultrasonicated for 30 min at room temperature. The pH value of the resulting solution was measured and recorded as the initial pH of the reaction. The concentrations of Ti^{4+} and amino acids become 0.10 M and 0.020 M, respectively. The solution was transferred into a screw-capped Pyrex bottle, and aged at 100 °C for 24 h for gelation. Finally, the resulting viscous gel was placed into a Teflon-lined autoclave and aged at 140 °C for 3 days to nucleate and grow the TiO_2 particles. Obtained particles were collected by centrifugation (18,000 rpm, 30 min) and washed two times with an aqueous NaOH solution (pH 12), a 2.0 M HNO_3 solution, and water, respectively, by dispersing followed by centrifuging. The resulting dispersion was freeze dried to obtain TiO_2 particles.

3. Effects of the initial pH on the shape controlling properties of amino acids

To examine the effects of the initial pH on the shape controlling properties of amino acids, anatase TiO_2 particles were prepared by changing the initial pH from 1.5 to 11.5 in the gel-sol system. The initial pH was adjusted by the addition of aqueous NaOH or $HClO_4$ solution. The TEM images of TiO_2 particles prepared in the presence or absence of 0.020 M glutamic acid (**GL**) are shown in **Figure S1** and **S2**, respectively. Decrease of the crystal sizes with decreasing initial pH was observed for the systems both in the presence and absence of **GL**. Comparison of the images, the effect of **GL** as a shape controller was not observed for the particles prepared under the acidic conditions. In contrast, spindly TiO_2 particles were obtained by in the presence of **GL** at pH = 10.5. As a consequence, precise control of the initial pH is of vital importance for the shape control. Similar relationship of the initial pH and the resulting particle shapes was observed with aspartic acid as well.

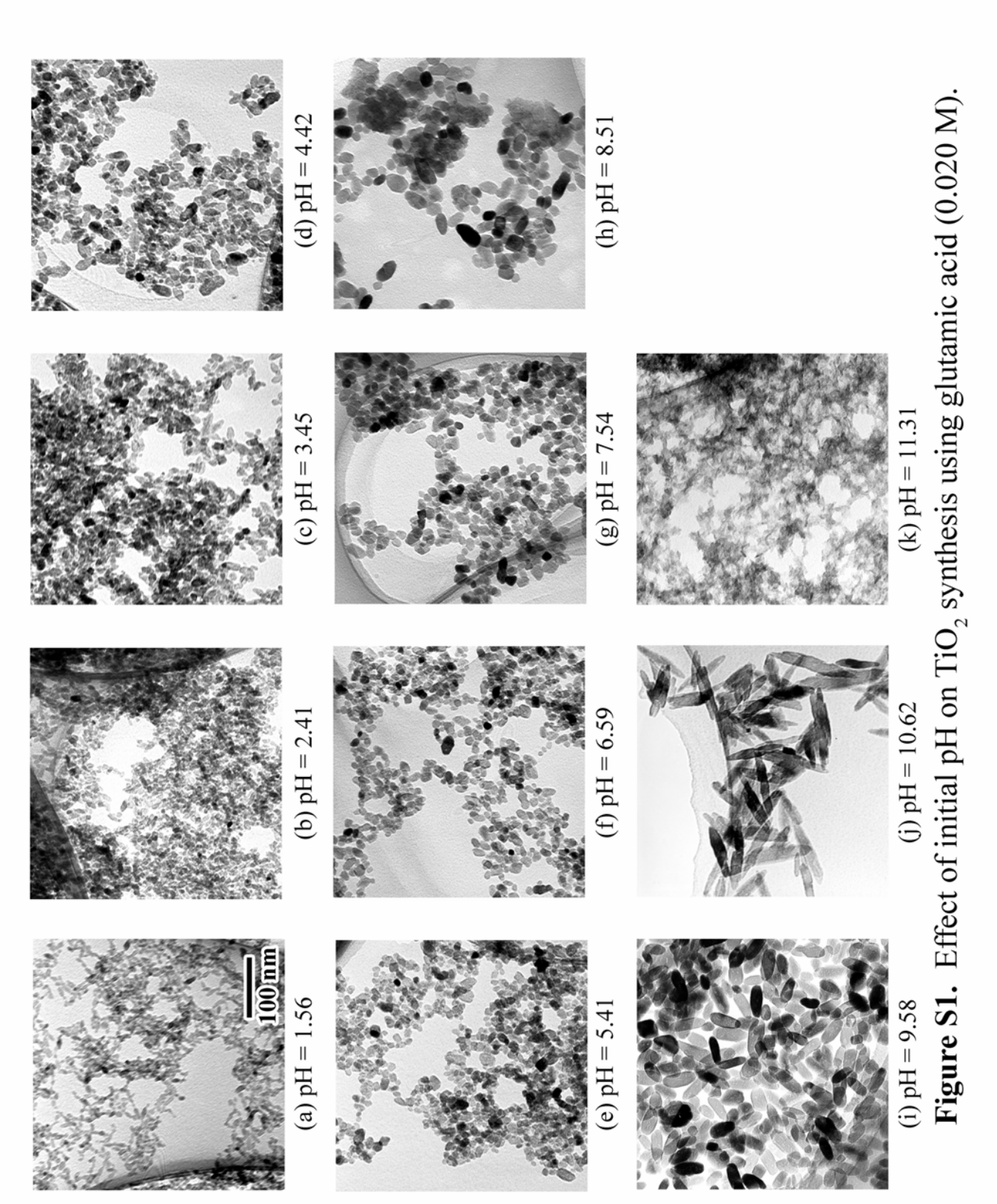

Figure S1. Effect of initial pH on TiO_2 synthesis using glutamic acid (0.020 M).

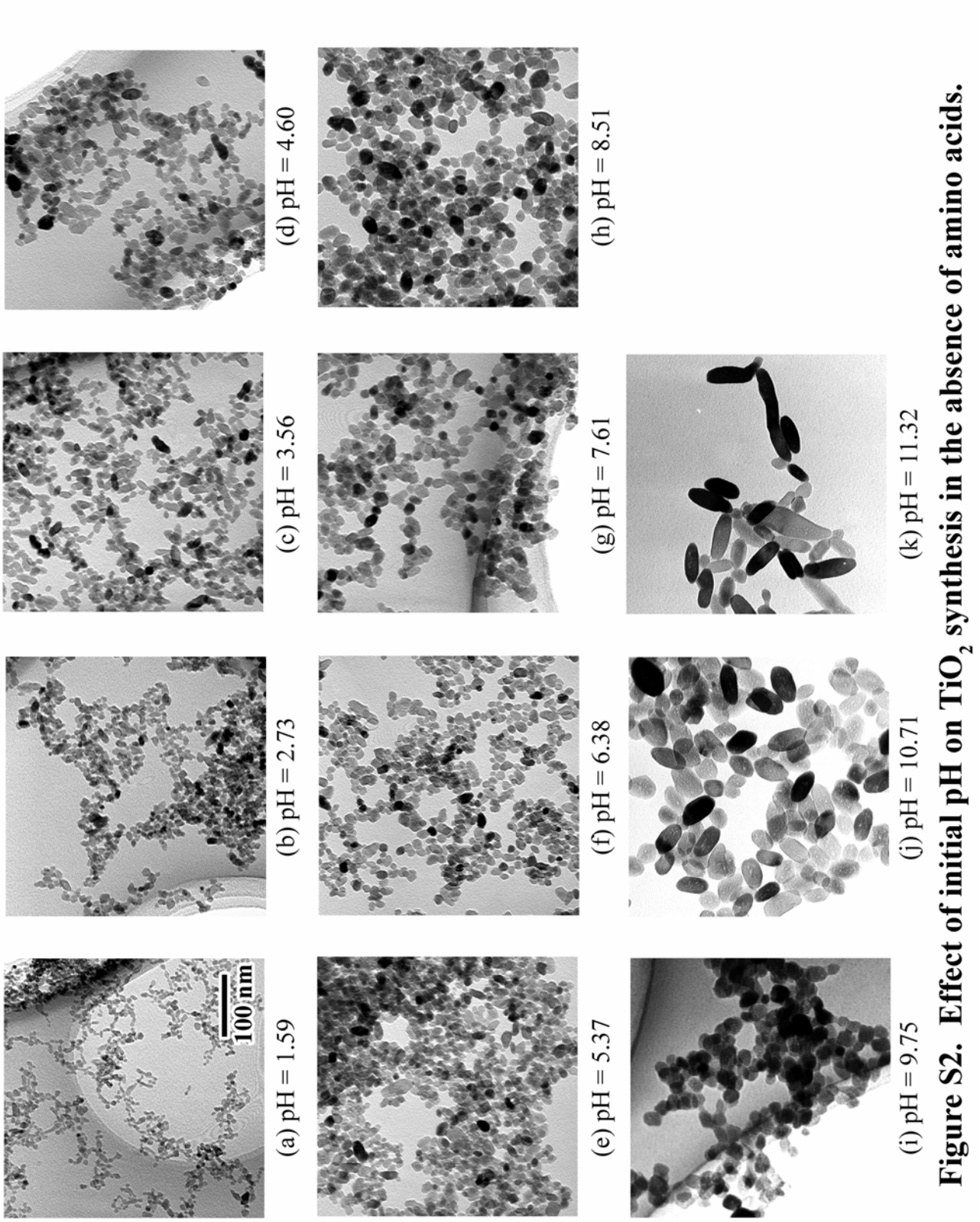

Figure S2. Effect of initial pH on TiO_2 synthesis in the absence of amino acids.