Experimental Methods

Material Synthesis

The titania colloid dispersed in aqueous solution of nitric acid was purchased from Ishihara Sangyo Kaisha, Ltd. (STS-01: particle diameter~7 nm, pH=1.7, anatase phase). Poly (ethylene oxide), PEO, with viscosity average molecular weight \( M_v \) of 100,000, 300,000 and 1,000,000 was obtained from Aldrich. All the other solvents were purchased from Wako Pure Chemicals Industrials, Ltd.

Sample gels were prepared from the starting compositions listed in Table 1. First, a given amount of PEO was homogeneously dissolved in the aqueous solution of nitric acid. Then, titania colloid dispersed solution and formamide were added to the mixture under stirring in an ice cooled condition. After stirring for 5 min, the resultant homogeneous solution was poured into a test tube. The test tube was sealed and kept at 40 °C for 24 h for gelation and ageing. The wet gels thus obtained were subjected to solvent exchange with 2-methyl-2-propanol and freeze-dried using a vacuum device (VFD-21S, Sinku Device Co, Japan).

Measurements

The morphology of dried and heated gels was observed by a scanning electron microscope (SEM) (S-2600N, Hitachi Ltd., Japan, with Pt coating) and a field emission-scanning electron microscope (FE-SEM) (JSM-6700F, JEOL Ltd., Japan, without coating). The size distribution of macropores was determined for the gel samples heat-treated at 1000 °C using a mercury porosimetry (PORESIZER-9320, Micromeritics Co., USA). For the Hg porosimetry measurement, the heat treatment was required to enhance the mechanical strength of gel skeleton because the dried gels could not stand the applied high pressure due to the low connectivity between the particles. Mesoporous structure was characterized by a nitrogen adsorption-desorption isotherm (ASAP-2010 Micromeritics Co., USA).
The pore size distribution was calculated from the adsorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method, and the surface area was obtained by the Brunauer-Emmett-Teller (BET) method.
Figure S1. a-c) SEM images of dried P1-T215 gels prepared with $w_{PEO} = 0.12$, $w_{PEO} = 0.13$, and $w_{PEO} = 0.14$, respectively. d-f) SEM images of dried P3-T215 gels prepared with $w_{PEO} = 0.0275$, $w_{PEO} = 0.030$, and $w_{PEO} = 0.035$, respectively. Bicontinuous structure can be obtained in both the systems when PEO contents is large, but the degree of connectivity of continuous gel skeletons is higher is P3-T215 systems than in P1-215 systems. The use of P3 with larger $M_v$ can provide the viscosity for the gel phase enough to withstand the fragmentation during the coarsening process of the phase separation, which increases the connectivity and thus makes the pore size distribution sharper.

Figure S2. XRD pattern of dried P3-T215 gel recorded on a Regaku RINT 2500 diffractmeter with CuK$\alpha$ ($\lambda = 1.5418 \text{ Å}$) radiation, which reveals the single phase of anatase-type titania. The crystallite size estimated by Scherrer’s equation is about 10 nm.