

Electronic Supplementary Information (ESI)

Journal of Materials Chemistry

“Ultrahigh Dense Electrolytic Nanoreactors composed of Liquid Crystalline Block Copolymer

Template: Water-Electrolysis-induced Deposition of Cerium Oxyhydroxide Nanorod Array”

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I. Experimental procedure and equipments

Film preparation : The BC films were prepared by spin-coating of 2 - 6 wt% BC toluene solution onto an ITO-coated glass (KURAMOTO Co., Ltd., a 150 nm thick ITO layer, resistivity $<10\Omega/\text{sq}$, roughness <1.0 nm) substrate. In order to prevent the BC film from being peeled out, a silane coupling reagent bearing the common chemical structure with the side-chain of the PMA(Az) segment was modified onto the ITO electrode. The BC film was annealed at 140°C for 1 h under vacuum. Thickness of the BC films is 70-350 nm, which can be controlled by spin-coating conditions.

Instruments : All the electrochemical experiments were carried out by using an IVIUM Compact Stat (Ivium technologies). Removal of the BC template was achieved by electron beam irradiation (Min-EB SGP01, USHIO Inc., 60 kV) at $300\ \mu\text{A}$ for 60 min and then calcining at 500°C in air for 3h. Cerium oxide film as a reference was also fabricated on a bare ITO electrode by electrolysis and calcination at the same condition.

Measurements : FE-SEM images were taken with an S-5200 FE-SEM (Hitachi, Japan). XPS measurements were performed on an ESCA-3400 (Shimazu, Japan). Binding energy shifts were corrected using the C1s energy of adventitious carbon at 285.1 eV. GISAXS and GIWAXD were performed on a Nano-Viewer with a PILATUS detector (Rigaku corp. Japan). The X-ray source is a CuK_α radiation beam ($\lambda = 1.541\ \text{\AA}$). Raman spectra were obtained by a RAMANRXN

SYSTEMS microscopic Raman spectrometer (Kaiser optical systems, Inc.) with the exciting line of 532 nm.

II. Preparation of PEO₄₀-*b*-PMA(Az)₁₇ and PEO₁₁₄-*b*-PMA(Az)₅₉ used as BC template.

The block copolymers used in this study (Fig. S1) were synthesized via atom transfer radical polymerization (ATRP) of 11-[4-(4-butylphenylazo)-phenoxy]undecyl methacrylate as the monomer from α -methoxy-poly(ethylene oxide)- ω -(2-bromo-2-methylpropionate) as the macroinitiator by using copper chloride(I) (Kanto Chem. Co., Japan) and 1,1,4,7,10,10-hexamethylenetetramine (HMTETA, Aldrich) as catalyst in anisole according to our previous report. (Y. Tian, K. Watanabe, X. Kong, J. Abe, T. Iyoda, *Macromolecules* **2002**, *35*, 3739.) The degree of polymerization and molecular weight were evaluated by ¹H NMR and gel permeation chromatography (GPC).

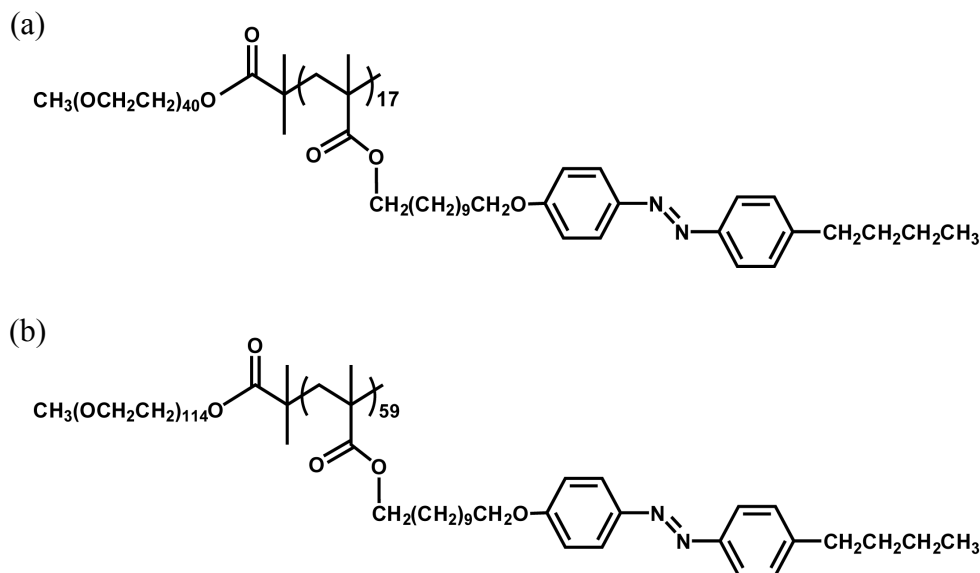


Fig. S1 Chemical structure of (a) PEO₄₀-*b*-PMA(Az)₁₇, (b) PEO₁₁₄-*b*-PMA(Az)₅₉

(a) Synthesis of PEO₄₀-b-PMA(Az)₁₇

A mixture of copper chloride(I) (219.8 mg, 2.22 mmol) and HMTETA(510.6 mg, 2.22 mmol) in anisole solution (50 mL) was added to anisole solution containing α -methoxy-poly(ethylene oxide)- ω -(2-bromo-2-methylpropionate) (1.48 g, 0.74 mmol) and 11-[4-(4-butylphenylazo)-phenoxy]undecyl methacrylate (9.84 g, 20 mmol), and then the mixture was stirred at 80 °C for 12 h. The solution was passed through a neutral Al₂O₃ column with THF as eluent to remove the catalyst. After the solvent was removed under reduced pressure, the residue was taken for ¹H NMR measurement. The conversion of the monomer was 81%. The monomer was removed by soxhlet extraction in hot hexane, and then the polymer was delived by soxhlet extraction in chloroform at 85°C. The extract was reprecipitated into methanol. The yellow polymer was collected by filtration and dried under vacuum. Yield: 8.06g (86% based on the macroinitiator). $M_n(\text{GPC}) = 14\ 000$, $M_w/M_n = 1.18$. ¹H NMR analysis of synthesized block copolymers gave PEO₄₀-b-PMA(Az)₁₇ of polymerization degree, and 10 400 of the molecular weight $M_n(\text{NMR})$. Peak assignments of ¹H NMR spectra are shown in Fig. S2.

(b) Synthesis of PEO₁₁₄-b-PMA(Az)₅₉

A mixture of copper chloride(I) (91 mg, 0.923 mmol) and HMTETA(212 mg, 0.923 mmol) in anisole solution (50 mL) was added to anisole solution containing

α -methoxy-poly(ethyleneoxide)- ω -(2-bromo-2-methylpropionate) (1.54 g, 0.308 mmol) and 11-[4-(4-butylphenylazo)-phenoxy]undecyl methacrylate (9.84 g, 20 mmol), and then the mixture was stirred at 80°C for 12 h. The solution was passed through a neutral Al₂O₃ column with chloroform as eluent to remove the catalyst. After the solvent was removed under reduced pressure, the residue was taken for ¹H NMR measurement. The conversion of the monomer was 85%. The residue was reprecipitated twice with hot hexane to remove the remaining monomer, and then the residual solid was dissolved in a minimum amount of chloroform, followed by re-precipitation in methanol. The yellow polymer was collected by filtration and dried under vacuum. Yield: 8.77g (89% based on the macroinitiator). M_n (GPC) = 31 100, M_w/M_n = 1.16. ¹H NMR analysis of synthesized block copolymers gave PEO₁₁₄-*b*-PMA(Az)₅₉ of polymerization degree, and 34 000 of the molecular weight M_n (NMR). Peak assignments of ¹H NMR spectra are shown in Fig. S3.

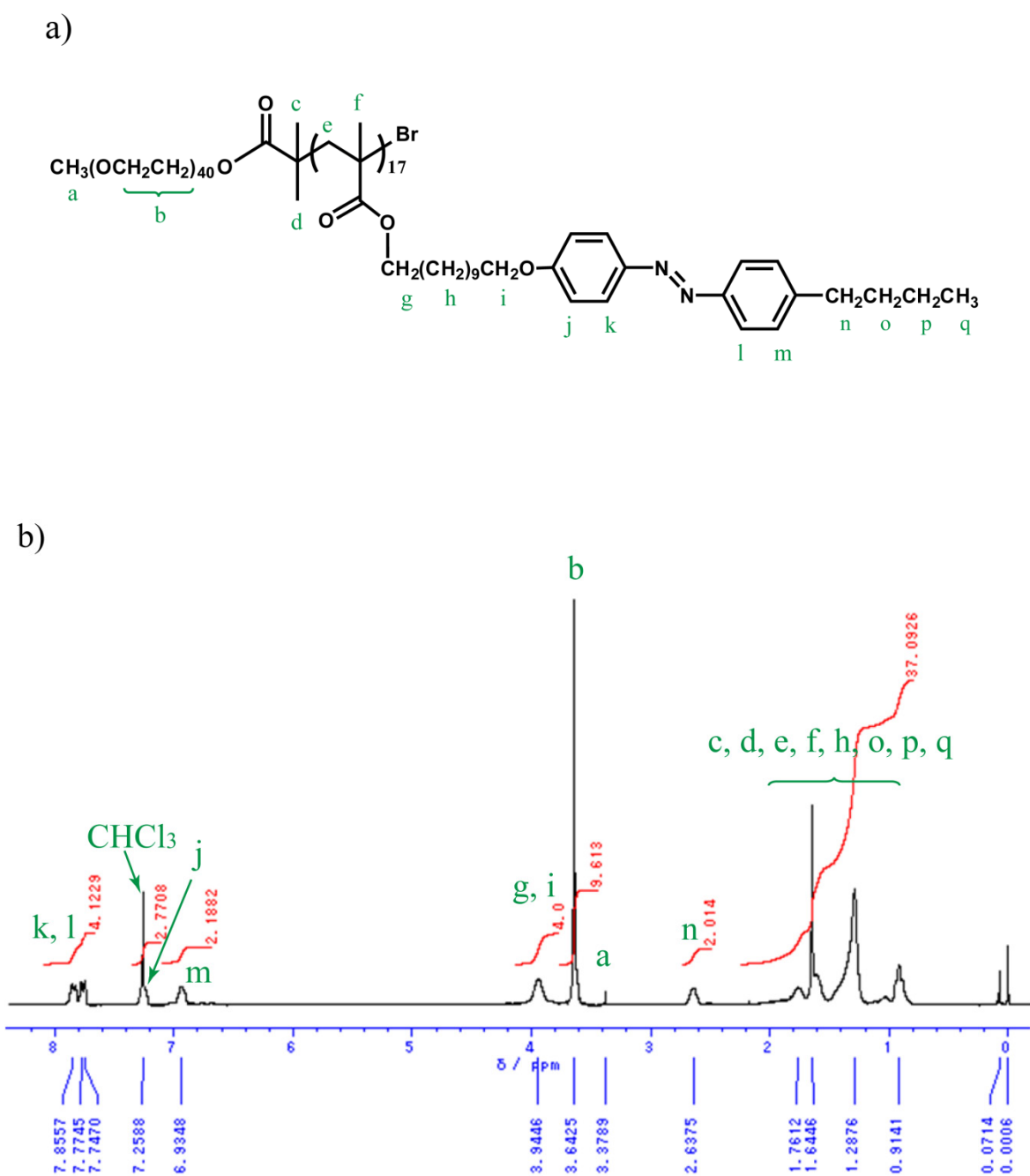


Fig. S2 a) A chemical structure and b) ^1H NMR spectra of $\text{PEO}_{40}\text{-}b\text{-PMA(Azo)}_{17}$ in CDCl_3 .

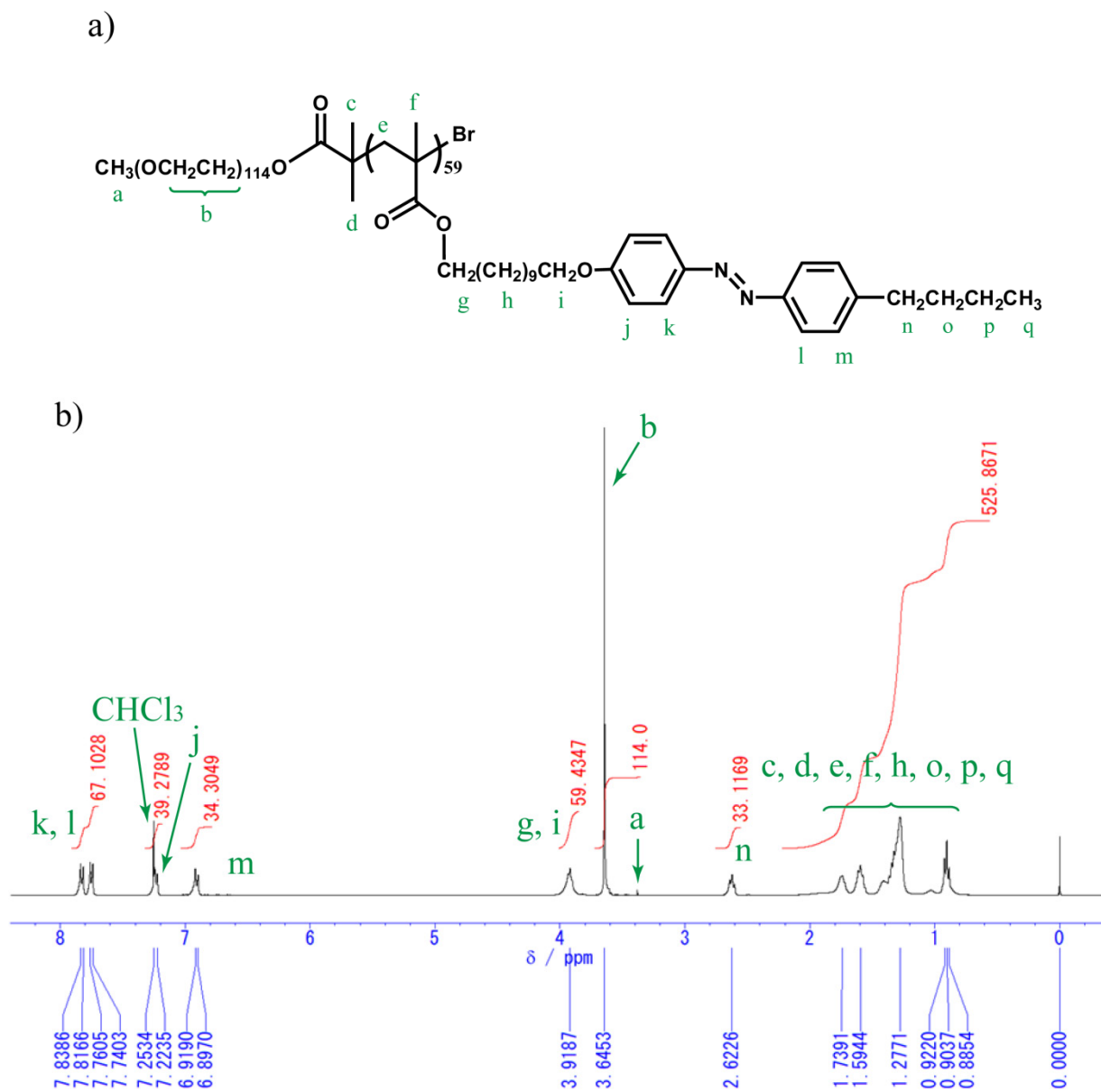


Fig. S3 a) A structure and b) ^1H NMR spectra of $\text{PEO}_{114}\text{-}b\text{-PMA(Azo)}_{59}$ in CDCl_3 .

III. Preparation of self-assembled monolayer to anchor the BC template on the ITO electrode.

We have designed and synthesized the silane-coupling molecule bearing the common chemical structure with the side-chain of the PMA(Az) segment (Fig. S4 (a)) so as to prevent the spin-coated BC film from being peeled out in an electrolytic solution, as the concept is shown in Fig. S4 (b). The detail was described in our previous report; T. Goda, S. Hadano, T. Iyoda, *Materials Research Society Symposium Proceedings* **2011**, 1302, W06, 09. The molecule anchored to hydroxyl groups of the ITO surface through silane coupling would be miscible with the side-chains of the PMA(Az) microdomains in smectic phase. Improved adhesion of the BC template to ITO and silicon wafer surfaces would result from an interdigitated structure between the molecule and the side-chain of the undermost layer of the PMA(Az) microdomains, as so-called a molecular glue.

The NMR and IR data of the silane-coupling molecule are as follows. ¹HNMR (CDCl₃, ppm) δ: 7.89 (d, 2H, aryl H), 7.79 (d, 2H, aryl H), 7.30 (d, 2H, aryl H), 6.99 (d, 2H, aryl H), 4.88(s, 1H, NH), 4.03 (tt, 4H, aryl-O-CH₂-, -CH₂-O-CO-), 3.82 (q, 6H, Si-O-CH₂-), 3.18 (q, 2H, -N-CH₂-), 2.68 (t, 2H, -CH₂-aryl), 1.82 (quin, 2H, -CH₂-), 1.58 (m, 6H, -CH₂-), 1.47 (quin, 2H, -CH₂-), 1.30 (m, 14H, -CH₂-), 1.23 (t, 9H, -Si-O-C-CH₃), 0.94 (t, 3H, -CH₃), 0.63 (t, 2H, -CH₂-Si-). FT-IR (KBr, cm⁻¹) ν_{max}: 3346 (ν_{N-H}), 1691 (ν_{amideI}), 1540 (ν_{amideII}).

The ITO surface was cleaned by a sequence of wet and dry processes. The ITO-deposited glass electrode (KURAMOTO Co., Ltd., a 150 mm thick ITO layer, resistivity < 10 Ω / square

centimeters, roughness < 1 nm) was rinsed with methanol for 5 min in an ultrasonic bath, immersed in a mixed solution of deionized water, 35% hydrogen peroxide and 25% ammonia (5/1/1) (APM) at 80°C for 20 min, and then rinsed with deionized water under ultra-sonication. After drying with N₂ blow, vacuum ultraviolet (VUV: $\lambda = 172$ nm, 5.0×10^2 Pa) light was irradiated on the ITO surface for 30 min. Then, the as-cleaned ITO electrode was immersed in a chloroform containing the silane-coupling molecule (10 mM) for 10 min. The modified ITO electrode was annealed at 120°C in oven for 30 min. Finally, the annealed ITO was washed in CHCl₃ by sonication and dried in oven at 120 °C for 30 min.

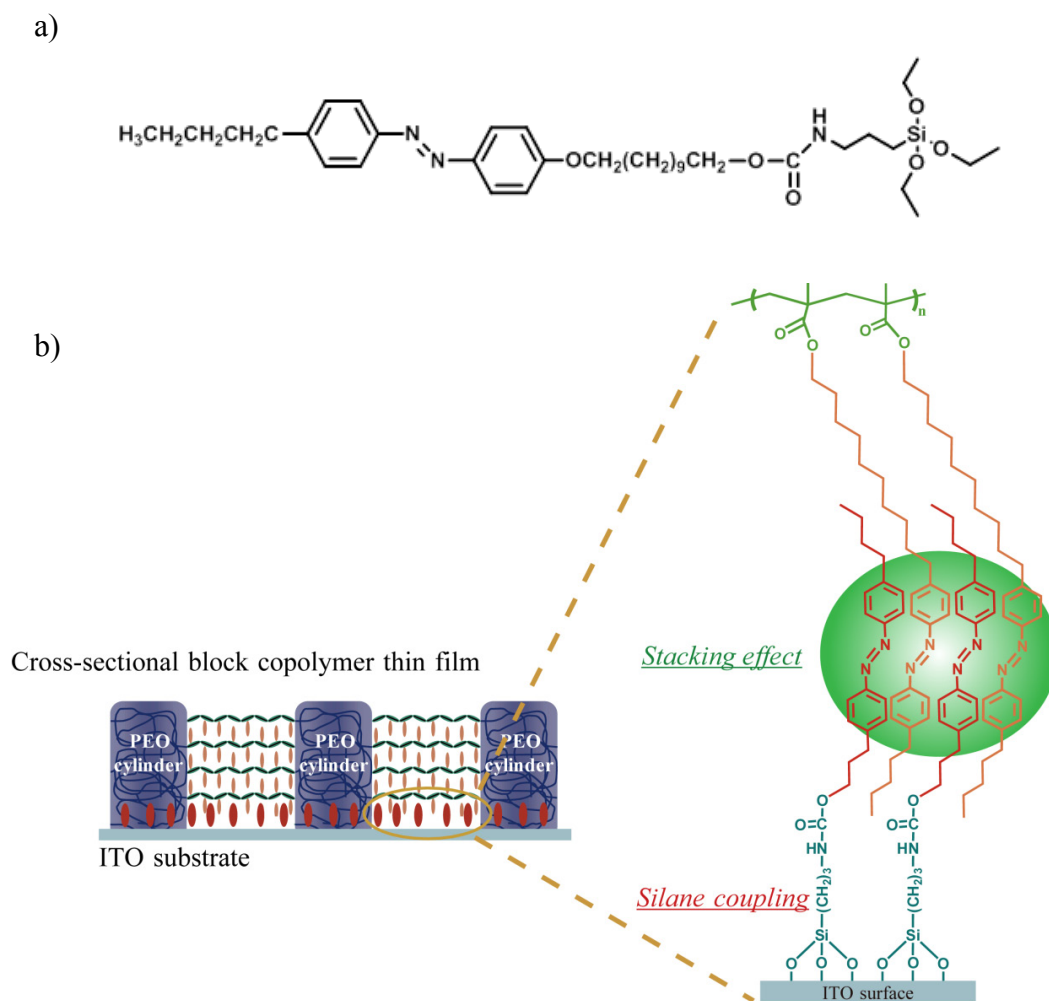


Fig. S4 a) A structure of the self-assembled monolayer bearing LC moiety and b) schematic image of anchoring effect between the ITO surface and BC template by the SAM.

IV. Nanostructural analyses of microphase-separated BC films on the ITO substrate by AFM and GI-SAXS.

Nanostructure and arrangement of the PEO cylindrical microdomains formed in the microphase-separated BC films were analyzed by atomic force microscopy (AFM) and grazing incidence small-angle X-ray scattering (GI-SAXS).

Typical AFM height images of PEO₄₀-*b*-PMA(Az)₁₇ and PEO₁₁₄-*b*-PMA(Az)₅₉ films coated on the ITO electrodes after thermal annealing at 140°C for 1 hour under vacuum are shown in Fig. S5. Prior to the coating of the BC film, the surface of the ITO electrode was modified with the silane-coupling molecule described in section II of Supporting Information. The insets are their Fast Fourier transform (FFT) images. These observations indicate highly dense PEO cylindrical microdomains (dark orange dots) are hexagonally arranged in the PMA(Az) matrix (light orange area). The diameter and average center-to-center distance of the PEO cylindrical microdomains are 6 nm and 13 nm for PEO₄₀-*b*-PMA(Az)₁₇, 11 nm and 24 nm for PEO₁₁₄-*b*-PMA(Az)₅₉, respectively.

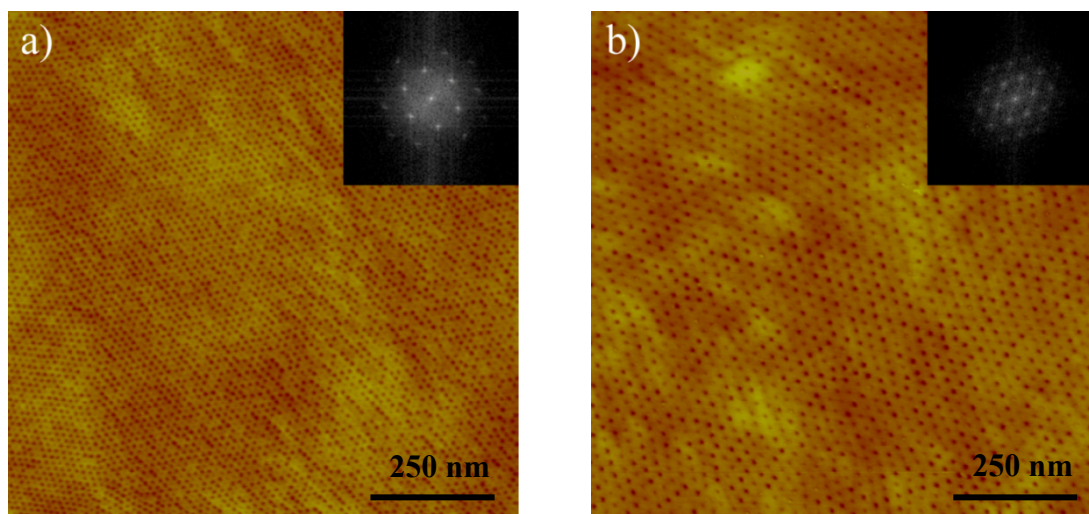


Fig. S5 AFM height images of surface morphology of a) PEO₄₀-*b*-PMA(Azo)₁₇ and b) PEO₁₁₄-*b*-PMA(Azo)₅₉ template films on ITO electrodes after thermal annealing at 140°C for 1 hour under vacuum condition. The insets are their FFT images.

The ordered nanostructures of the micro-phase-separated BC template film on the ITO electrode were investigated by GI-SAXS (Fig. S6 and S7). X-ray incidence angle was set to 0.2 near the critical total reflection angle of an ITO substrate. A series scattering peaks appeared in the in-plane direction, indicating vertical arrangement of the PEO cylindrical microdomains on the ITO electrode. The scattering peaks in the in-plane direction are observed at 0.56 and 0.96 for PEO₄₀-*b*-PMA(Az)₁₇, and 0.29, 0.48, 0.57, and 0.77 for PEO₁₁₄-*b*-PMA(Az)₅₉ of *q*-vector, corresponding to 1 and $\sqrt{3}$ as the (10) and (11) faces, and 1, $\sqrt{3}$, 2, and $\sqrt{7}$ as the (10), (11), (20), and (21) faces of the hexagonally arranged cylindrical structure, respectively. And, a pair of peaks in the out-of-plane direction indicates a layered structure (3.1 nm of spacing) of the smectic phase

of the PMA(Az) microdomains. The lower and the higher peaks originated from scattering of transmitted X-rays and X-rays reflected on a ITO substrate, respectively. The details were described in our previous report; M. Komura, K. Watanabe, T. Iyoda, T. Yamada, H. Yoshida, Y. Iwasaki, *Chem. Lett.* 2009, 38, 408.

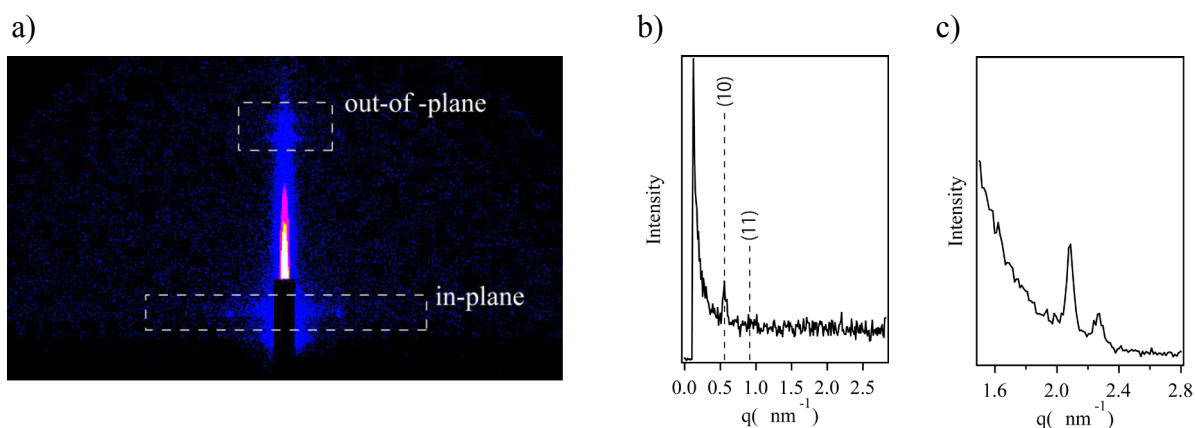


Fig. S6 A GI-SAXS 2D patterns a) 2D patterns, b) in-plane, and c) out-of-plane profile obtained for PEO₄₀-*b*-PMA(Azo)₁₇ film on ITO substrate modified with SAM.

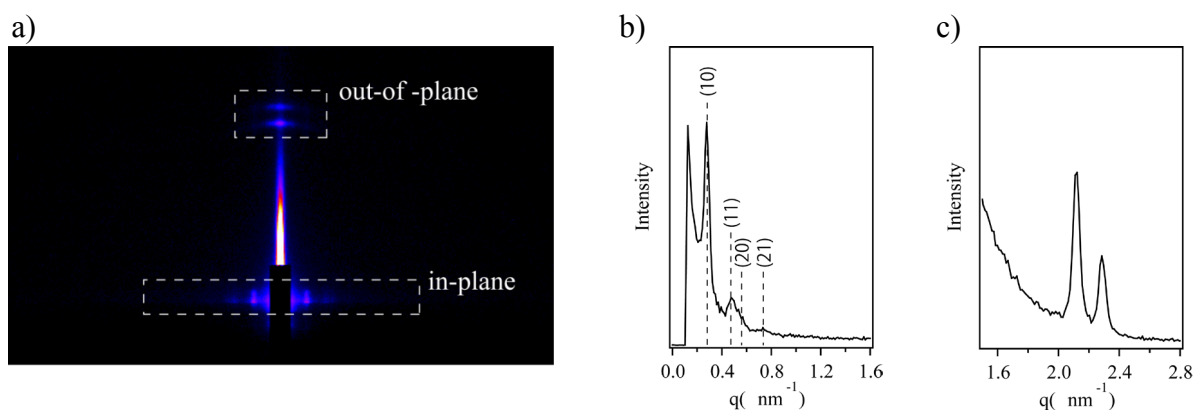


Fig. S7 A GI-SAXS a) 2D patterns, b) in-plane, and c) out-of-plane profile obtained for PEO₁₁₄-*b*-PMA(Azo)₅₉ film on ITO substrate modified with SAM.

V. Current density with time curve and FE-SEM observation during electrolytic deposition of Cerium oxyhydroxide.

The electrolyses through the PEO₄₀-*b*-PMA(Az)₁₇ (blue line in Fig. S8) and PEO₁₁₄-*b*-PMA(Az)₅₉ (black line) templates, and non-templated electrolysis (green line) gave similar current–time behaviors. In case of the non-templated electrolysis, a bare ITO electrode was used under the same electrolytic conditions. Cathodic current density of the templated electrolysis was normalized by effective electrode area, i.e., a fraction of the cross sectional area of the PEO microdomains to the total surface area of the BC template film (0.18 for PEO₄₀-*b*-PMA(Azo)₁₇ and 0.16 for PEO₁₁₄-*b*-PMA(Azo)₅₉), which is determined by the AFM images (Fig. S5). Such spiky current indicates that the concerned electrolyses were almost completed within several decade seconds. Passed charge densities (this is normalized by the surface area of PEO domain of the BC template) of the electrolyses for the first 600 s through PEO₄₀-*b*-PMA(Azo)₁₇ and PEO₁₁₄-*b*-PMA(Azo)₅₉ templates and without template are 611 mC/cm², 364 mC/cm², and 261 mC/cm², respectively.

A series of cross-sectional FE-SEM images at different electrolysis periods were taken. No nanorod was observed in the BC template (Fig. S9a) before electrolysis, when the BC-modified ITO electrode was placed into the electrolytic bath, the NRA has reached the top surface of the PEO cylindrical microdomains in the first 60 sec electrolysis with 131 mC/cm² of passed charge density, in good agreement with that (121 mC/cm²) expected to fill the cerium oxyhydroxide into

the PEO cylindrical microdomains. This evidence indicates that the water-electrolysis-induced deposition of metal oxyhydroxide should be indirect *Faradaic* process and the growth of NRA can be controlled by the passed charge.

Figures S9b and S9c show top surface and cross-sectional FE-SEM images of the electrodeposited cerium oxyhydroxide film (400 nm of thickness) on a bare-ITO electrode in 0.25 M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ethanol solution at -2.0 V (vs Ag/AgCl) for 1800sec (430 mC/cm^2) were shown. The surface looks rough with many cracks.

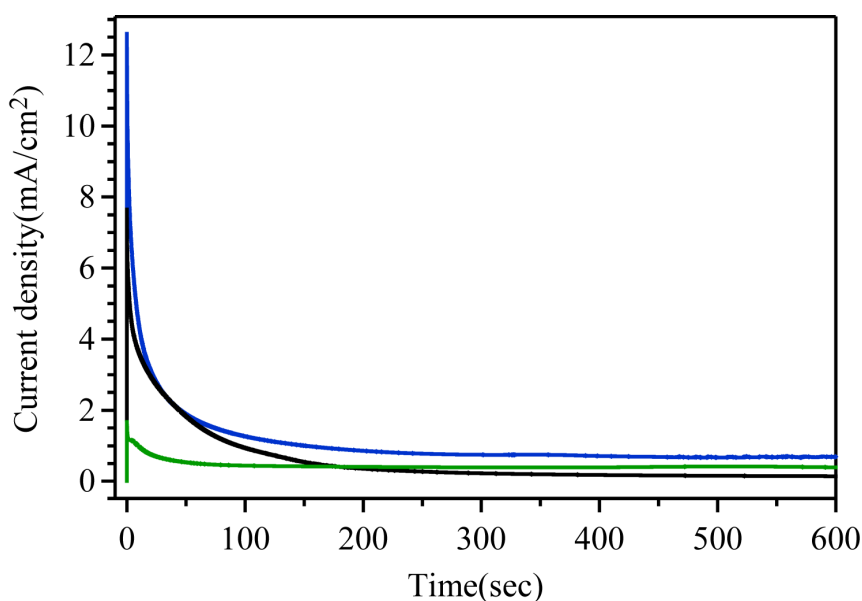


Fig. S8 The current density with time curve during electrolysis of water for deposition of cerium oxyhydroxide in 0.25 M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ethanol solution at -2.0 V (vs Ag/AgCl) on BC/SAM/ITO electrode. The BC films of $\text{PEO}_{40}\text{-}b\text{-PMA(Az)}_{17}$ (blue line) and $\text{PEO}_{114}\text{-}b\text{-PMA(Az)}_{59}$ (black line) were used as templates, respectively. The current density was normalized by the surface area of PEO domain of the BC template.

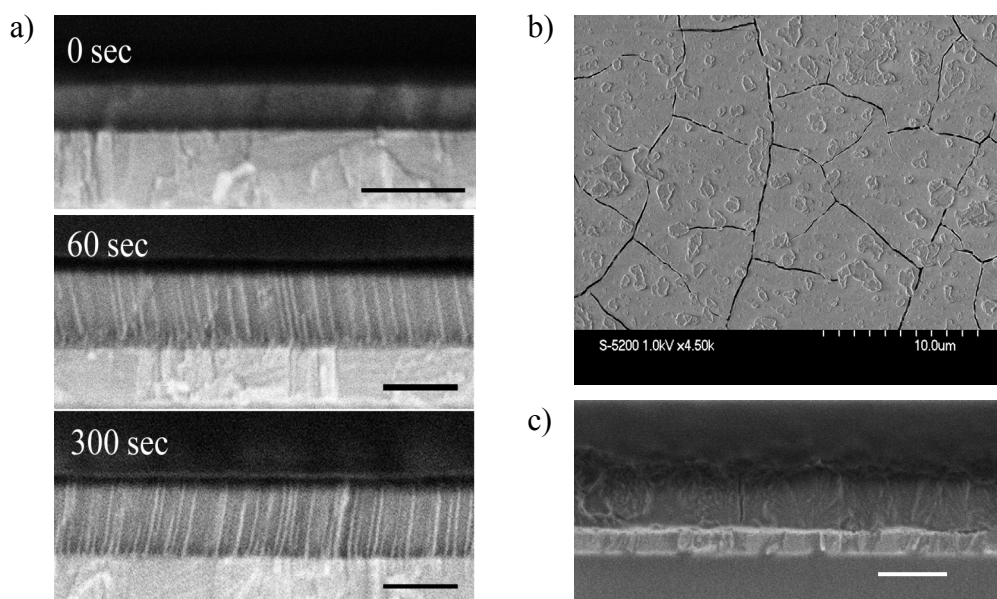


Fig. S9 (a) The cross-sectional FESEM images of the electrodeposited cerium oxyhydroxide NRAs on the ITO electrodes through $\text{PEO}_{114}\text{-}b\text{-PMA(Az)}_{59}$ after 0, 60, and 300 sec electrolyses. The inset scale bar is 250 nm. The film thickness of each BC template is 100, 250, 250 nm for 0, 60, 300 sec, respectively. The 0 sec image was observed after immersion in 0.25 M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ethanol solution for 3 hours. (b) Top view and (c) cross-sectional FESEM images of the cerium hydroxide film electrodeposited at -2.0 V in 0.25M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ethanol solution for 1800 sec on ITO substrate without BC film. The inset scale bar is 500 nm.

VI. GISAXS images of the electrodeposited NRAs in BC templates.

The ordered nanostructures of the as-electrodeposited NRA in the BC film were investigated by GI-SAXS in the similar manners. A series of intense scattering peaks with the same peak positions as those of the BC template film are observed in the in-plane direction, indicating the vertical and hexagonal arrangement of the electrodeposited nanorods in the BC template film. The pair of peaks in the out-of-plane direction were preserved as the layered structure of the smectic phase of the PMA(Az) microdomains.

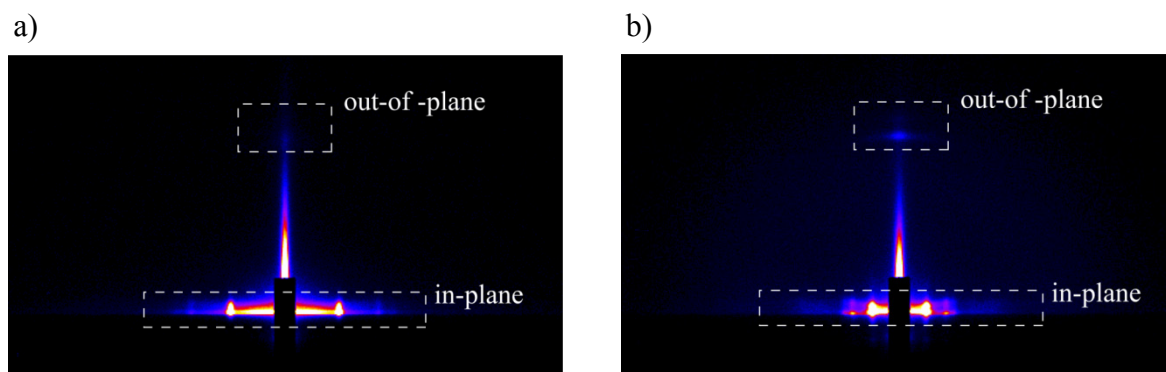


Fig. S10 GI-SAXS 2D patterns obtained a) $\text{PEO}_{40}\text{-}b\text{-PMA(Az)}_{17}$ b) for $\text{PEO}_{114}\text{-}b\text{-PMA(Az)}_{59}$ film after electrolysis at -2.0 V in 0.25M $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ethanol solution for 600 sec.

VII. FE-SEM observation of the cerium oxyhydroxide NRA after removal of the BC template by electron beam irradiation.

A 60 kV electron beam in 300 μ A for 60 min under vacuum was irradiated to the electrodeposited cerium oxyhydroxide NRA so as to remove the BC template film. Figure S9 shows an FE-SEM image of the as-irradiated NRA. Individual nanorods look like wet hairs, which seem to be tightly connected to the ITO surface and their upper parts tend to be aggregated. There remains a little amount of the residue from the BC template film, so that the following calcination is required to completely remove the BC template.

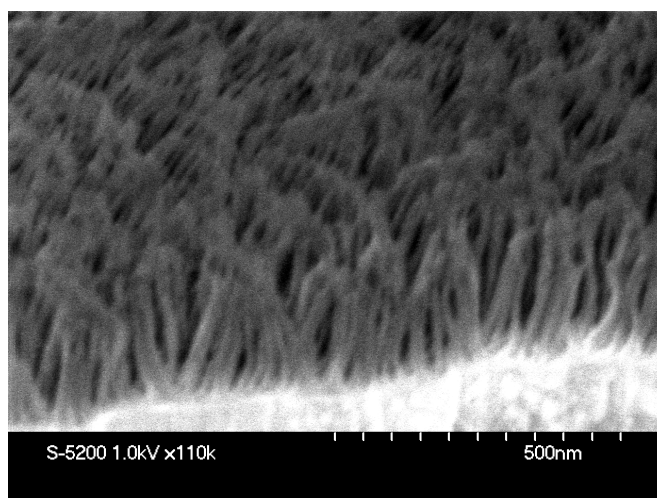


Fig. S11 FE-SEM image at 35° of tilting angle of NRA after removal of BC thin film by electron beam irradiation (acceleration voltage/60keV, current/300 μ A for 60 min).

VIII. XPS analysis of NRA before and after calcination.

Figure S12 shows the XPS spectra of Ce 3d core level with the Gaussian fits based on the least square method. The characteristic peaks are labeled as v_0 , v_2 , u_0 , and u_2 for Ce(III) states, and v_1 , v_3 , v_4 , u_1 , u_3 , and u_4 for Ce(IV) states, respectively, according to the previous report. (V. Fernandes, J. J. Klein, W. H. Schreiner, N. Mattoso, D. H. Mosca, *J. Electrochem. Soc.* **2009**, *156*, E199.)

Figure S13 shows O1s spectra of the as-electrodeposited and calcined NRAs. We assigned the fitted two peaks (at 529.3 and 531.7 eV) as lattice oxygen (O-Ce) and hydroxide group, based on the literature (V. Perrichon *et al.*, *J. Chem. Soc. Faraday Trans.*, 1991, 87(10), 1601.). However, there has been arguments on the assignment of these two peaks. Golden *et al.* reported that the low- and high- energy peaks are lattice oxygen (O-Ce) and oxide ion in the defective CeO_x ($x < 2$) or that chemisorbed on the surface such as CO, CO₂, respectively. (T. D. Golden *et al.*, *Journal of Vacuum Science & Technology B* 2003, 21, 1169.) In either assignment, a strong major signal of Ce(IV) in Ce 3d core level spectra and the higher intensity of lower binding energy corresponding to (O-Ce) after calcination, indicates oxidation of the oxyhydroxide NRA.

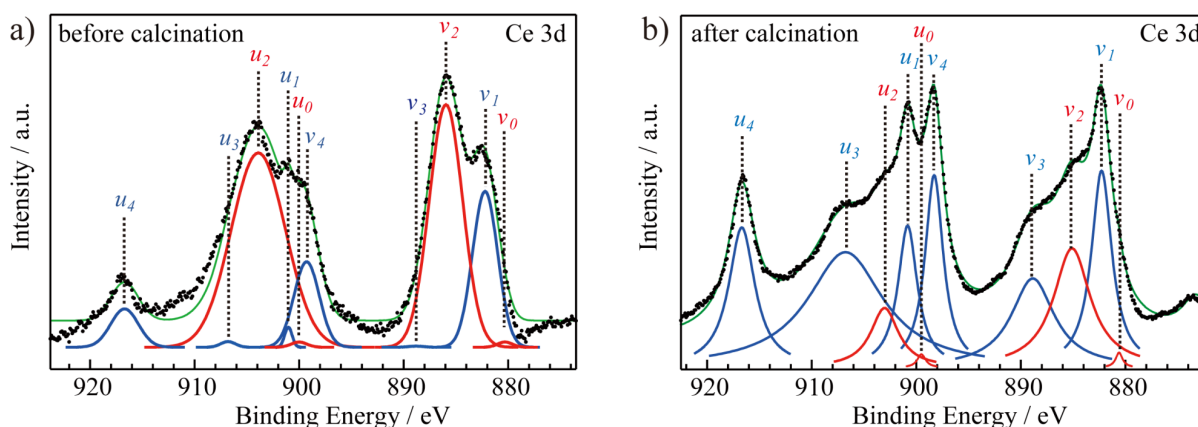


Fig. S12 XPS spectra of Ce 3d (green line denotes Gaussian fitted spectra) of a) the electrodeposited NRA through PEO₁₁₄-*b*-PMA(Azo)₅₉ film on ITO substrate and b) the calcined NRA at 500 °C in air. The letters *u* and *v* refer to 3d_{3/2} and 3d_{5/2} spin-orbit components. The characteristic peaks of Ce(III) states are labeled as *v*₀, *v*₂, *u*₀, and *u*₂, while the peaks of Ce(IV) states are labeled as *v*₁, *v*₃, *v*₄, *u*₁, *u*₃, and *u*₄.

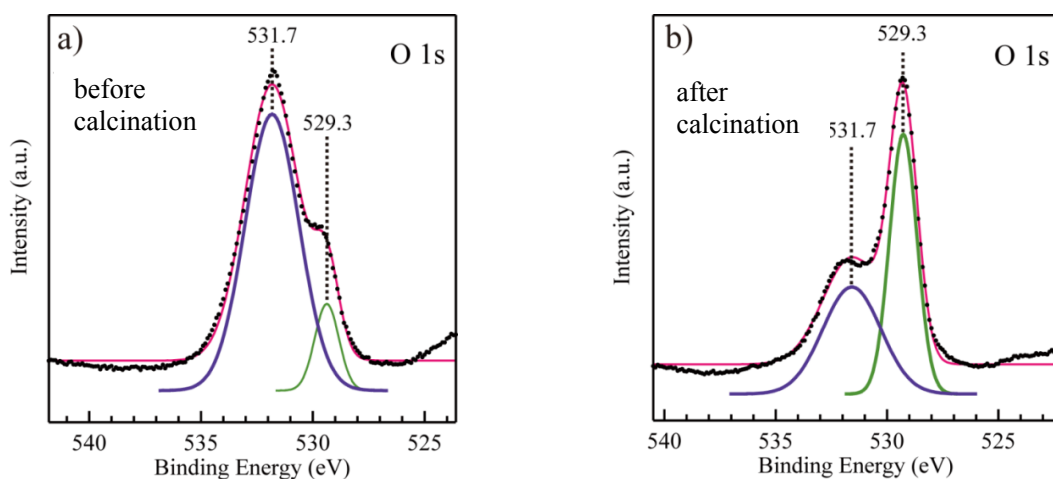


Fig. S13 XPS spectra of O1s (pink line denotes Gaussian function-fitted spectra) of NRA a) before and b) after calcination at 500 °C, which were electrodeposited through PEO₁₁₄-*b*-PMA(Azo)₅₉ film on ITO substrate. The two peaks of O1s represent the existence of the lattice oxygen (Ce-O, 529.3 eV) and hydroxyl group (O-H, 531.7 eV).

IX. Two dimensional GI-WAXD images of the calcined NRA.

Figure S14 shows two dimensional GI-WAXD image of the NRA calcined at 500 °C for 3 h in air. Ring shaped reflections corresponding to cerium oxide and ITO as the electrode were observed.

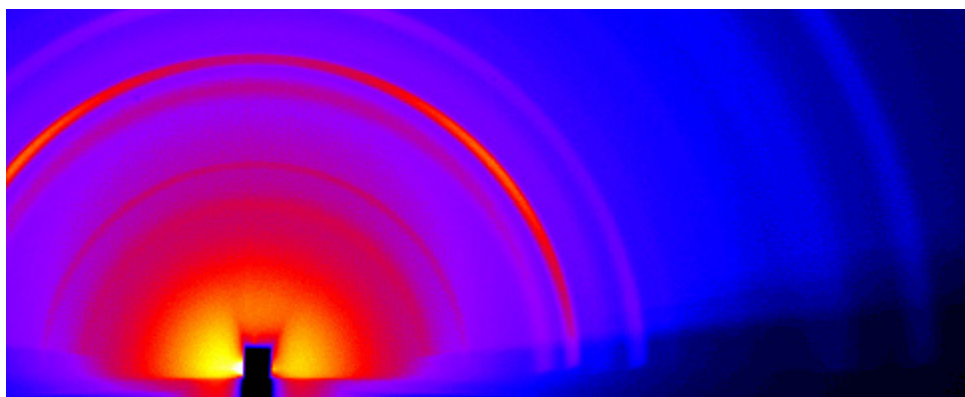


Fig. S14 GI-WAXD 2D pattern of calcined NRA at 500 °C on ITO substrate.

X. Raman spectra of calcined NRA at various temperatures.

The cerium oxyhydroxide NRA calcined at different temperatures in air was investigated by Raman spectroscopy. An intense vibration peak around 465 cm^{-1} was observed in the calcined NRA at 500 °C for 3 h, which is assigned to a symmetric breathing mode of oxygen atoms around cerium atom and characteristic of CeO_2 F_{2g} in fluorite structure (R. Kostic, S. Askrabic, Z. Dohcevic-Mitrovic, Z. V. Popovic, *Applied Physics a-Materials Science & Processing* **2008**, *90*, 679-683). The peak appears at 456 cm^{-1} in the NRAs calcined at 300 °C . Upon the elevating temperature for calcination, the peak shifts to 463 cm^{-1} and becomes sharpened, suggesting oxidation of the remaining cerium oxyhydroxide to CeO_2 and further crystallization.

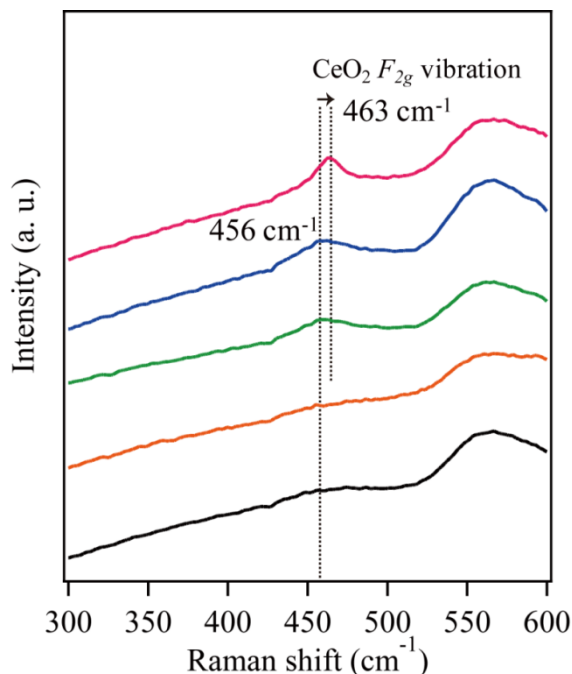


Fig. S15 Raman spectra of ITO substrate (black line) and as-electrolyzed NRA (orange line) and after calcined at 300 (green), 400 (blue), and 500 (red) °C in air.