Supporting Information

Low temperature *in-situ* formation of cobalt in silicon nitride toward functional nitride nanocomposites

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Sample synthesis

Perhydropolysilazane (PHPS, NN110-20, 20 wt% in butyl ether solution) was provided by Merck KGaA, Darmstadt, Germany. The butyl ether was substituted by super-anhydrous toluene (99.5 % purity, Wako Pure Chemical Industries, Ltd., Osaka, Japan). $CoCl_2$ (97% purity, Sigma-Aldrich Japan, Tokyo, Japan) was used as-received. The handling of the chemicals and reagents was performed using standard Schlenk techniques. The synthesis of the cobalt-modified PHPS labeled Co-PHPS was performed according to a Co/Si atomic ratio of 1/5. A 100 mL two-neck round-bottom flask equipped with a magnetic stirrer was charged with the solvent-substituted PHPS (10 mL, 4.25 mmol, 19 wt% in toluene) and anhydrous toluene (50 mL). $CoCl_2$ (1.137 g, 0.85 mmol) was added to the solution at room temperature (RT), and refluxed for 12 h. Then, the solvent was removed under vacuum at RT. The Co-PHPS sample was subsequently pyrolyzed under flowing ammonia (NH_3) at specific temperatures of 400, 500, 800 and 1000 °C for 2 h with a heating rate of 5 °C min^{-1}. The as-pyrolyzed samples were labelled as **Co/SiNX** (**X** denotes pyrolyzed temperature).

Characterizations

The chemical modification performed in this study was monitored by attenuated total reflection flourier transform infra-red (ATR-FTIR) spectroscopy using FTIR spectrometer (FT/IR-4200IF, JASCO Corporation, Tokyo, Japan) with attachment of ATR equipment (ATR PRO 550S-S/570S-H, JASCO Corporation, Tokyo, Japan) at a resolution of 4 cm^{-1}.

Elemental analyses were performed for oxygen and nitrogen (inert-gas fusion method, Model

EMGA-930, HORIBA, Ltd., Kyoto, Japan), and carbon (non-dispersive infrared method, Model CS844, LECO Co., St Joseph, MI, USA). Then, the composition of **Co/SiNX** samples was calculated as:

$$wt\%(Si + Co) = 100\% - wt\%(C) - wt\%(N) - wt\%(O) \quad (1)$$

The Co content in the **Co/SiNX** samples was analyzed by the energy dispersive X-ray spectroscopy (EDS) mounted on a scanning electron microscope (SEM, Model JSM-6010LA, JEOL Ltd., Tokyo, Japan), and evaluated as Co/Si atomic ratio.

XRD measurements were performed on powder samples using CoKα radiation (Model Miniflex 600NB, Rigaku Co., ltd., Tokyo, Japan). The average crystallite size, *L* was obtained from Scherrer equation,

$$L = K\lambda/\beta cos\theta \quad (2)$$

where *l* is the X-ray wavelength in nanometer, β is the peak width of the diffraction peak at half maximum height in radian and *K* is a constant related to crystallite shape, normally taken as 0.9.
TEM observations were performed on the **Co/SiN800** sample using an atomic-resolution analytical microscope (Model JEM-ARM200F, JEOL Ltd., Tokyo, Japan) operated at an accelerating voltage of 200 kV.

The simultaneous TG-MS analyses up to 1000 °C under flowing helium (He) was performed on Co-PHPS sample by TG-DTG (Model STA7200, Hitachi High-Tech Science Corporation, Tokyo, Japan, heating rate of 10 °C min^{-1}) coupled with a quadrupole mass-spectrometry (Model JMS-Q1500GC, JEOL Ltd., Tokyo, Japan).

Ultraviolet-Visible (UV-Vis) absorption spectra in the range of 200–800 nm were recorded on Co-PHPS sample and pure $CoCl_2$ using a ultraviolet-visible near-infrared spectrometer (Model: V-670SP, JASCO Corporation, Tokyo, Japan) with integrating sphere attachment (Model: ISN-723, JASCO Corporation, Tokyo, Japan).

Supplementary Figures

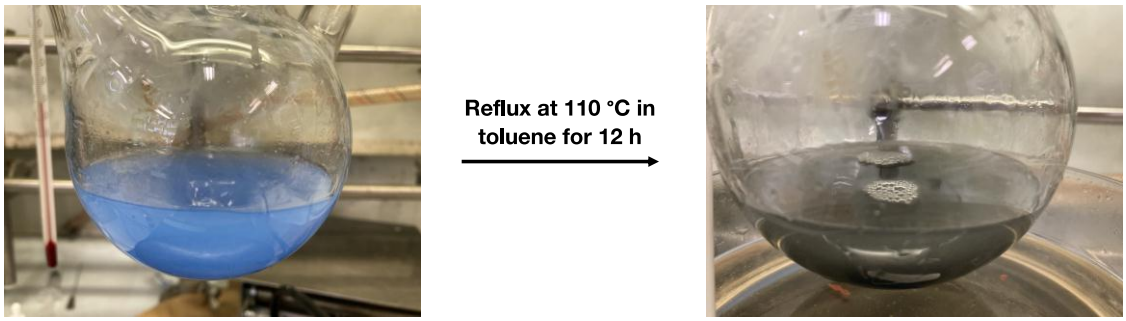

Fig. S1 A color change of $CoCl_2$-dispersed PHPS solution observed after reflux at 110 °C for 12h.

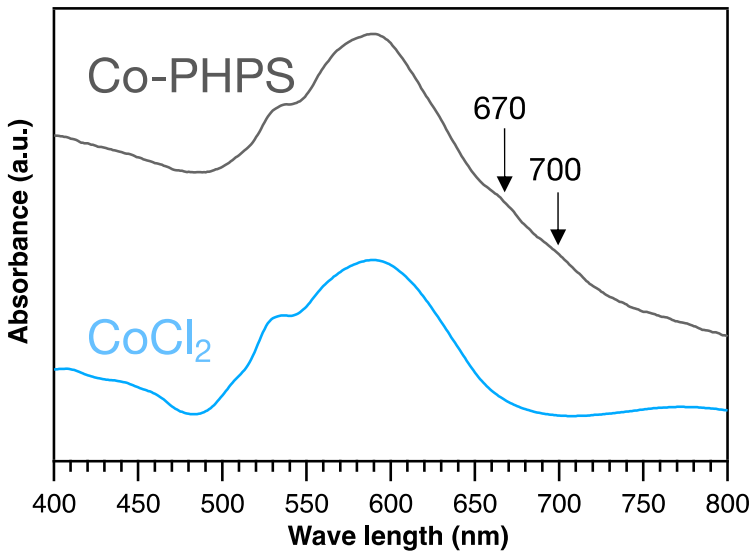

Fig. S2 UV-Vis absorption spectra of Co-PHPS sample and pure $CoCl_2$.