

New photocatalyst LnOCl (Ln=Sm,Nd) and novel cocatalytic effect
on BiOCl in humid environment

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Note added after first publication: This Supplementary Information file replaces that originally published on 24th July 2017, in which the supplementary figures were mistakenly omitted. The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

Abstract:

This is the first report on photocatalytic properties of LnOCl (Ln=Sm,Nd) oxychloride compounds, and the novel cocatalytic effect on BiOCl in highly humid environment, evaluated by photoremoval of nitric oxide (NO) gas.

Experimental:

The LnOCl (Ln= Sm, Nd, La, Pr) powders were produced by annealing each corresponding chloride hydrates in air, according to the report by Wendlandt.* Single phase was obtained for all LnOCl powders, confirmed by XRD (X-ray diffractometry), where SmOCl and NdOCl powders were mainly used for further investigation (due to their strong cocatalytic effects exhibited in high humidity). For the former, SmCl₃·6H₂O was annealed at 923 K for 6h, while for the latter NdCl₃·6H₂O was annealed at 723 K for 12h. Purchased BiOCl (99.9% purity) was grafted with the powder through a mechanochemical process in an ambient condition using an automatic agate mortar (Nitto-Kagaku, ANM-1000: Fig. S1, ESI†) for 30 minutes with 120 rpm (2 Hz). Total 2 grams of composite powders were produced for each composition.

The obtained powders were characterized by various standard methods. The crystal structure was investigated by XRD (X-ray diffractometry), the microstructure and surface phase analysis by TEM (transmission electron microscopy), the powder morphology by SEM (scanning electron microscopy), the quantification of elements by EDX (Energy Dispersive X-ray spectrometry), the specific surface area by BET measurements, the optical properties by UV-vis DRS (diffuse reflectance spectroscopy), the electronic surface state analysis by XPS (X-ray photoelectron spectroscopy) and the surface adsorption state by FT-IR (Fourier transform infrared) spectroscopy.

The photocatalytic properties were evaluated by NO gas oxidation, where the NO_x (NO, NO₂) gas monitor (APNA-360 automatic analyzer: Horiba) was used for measuring the concentrations (see Fig. S2, ESI†, for schematic test apparatus). The carrier gas (air, unless specified, with [vol%] 78.1 N₂, 20.9 O₂, and 0.9 Ar) with a flow rate of 3 liter/min was

used at 293 K to adjust the initial NO concentration to be around 0.95 ppm. A xenon lamp was then used for light irradiation (with 2.0 mW/cm² at the sample surface) on the powder (20 mg) dispersed on a glass slide (48 mm by 28 mm) in a container. The quartz plate was used for the irradiation side of the container, and a water filter was used to eliminate the thermal effect on the reaction due to infrared light. The NO_x monitor was positioned downstream side of the container, and the photocatalysis was evaluated by decomposition rate of NO gas at 60 minutes from the start of light irradiation (Fig. S3, ESI†, for the definition) [“Blank” signifies a control test without powder]. Two humidity conditions were selected, i.e. under dry (relative humidity [RH] below 0.1%) and humid (RH: 90 ± 5%) conditions, for photoremoval of NO gas.

* W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 1957, **5**, 118.



Fig. S1 An automatic agate mortar utilized for producing powder composite through mechanical mixing.

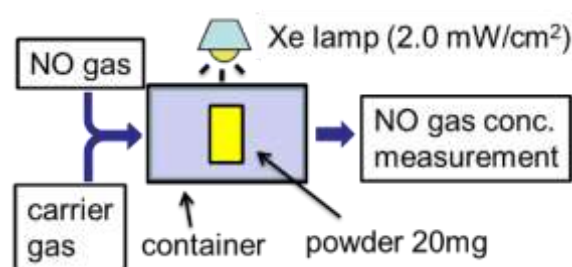


Fig. S2 Schematic diagram for a photocatalytic NO removal test (with 3 L/min flow rate at 293 K).

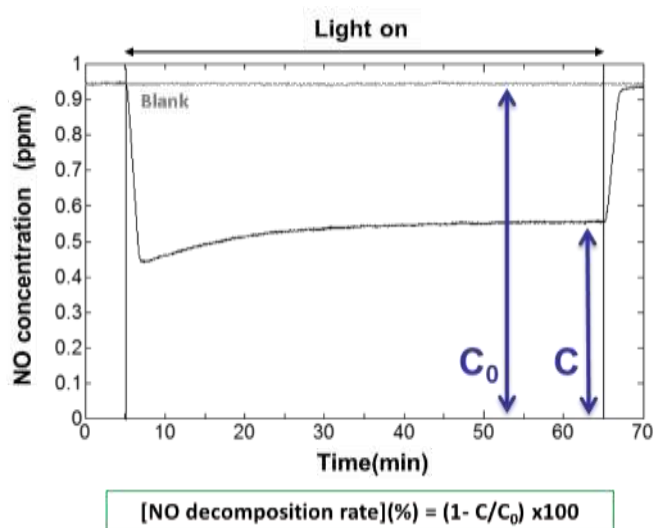


Fig. S3 Evaluation of photocatalysis using “NO decomposition rate”, defined at 60 min after light irradiation.

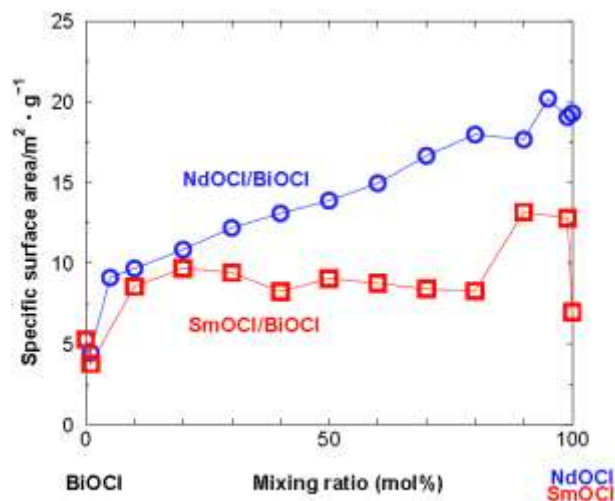


Fig. S4 BET specific surface areas of various SmOCl-BiOCl and NdOCl-BiOCl composite powders after 30 min mechanical mixing.

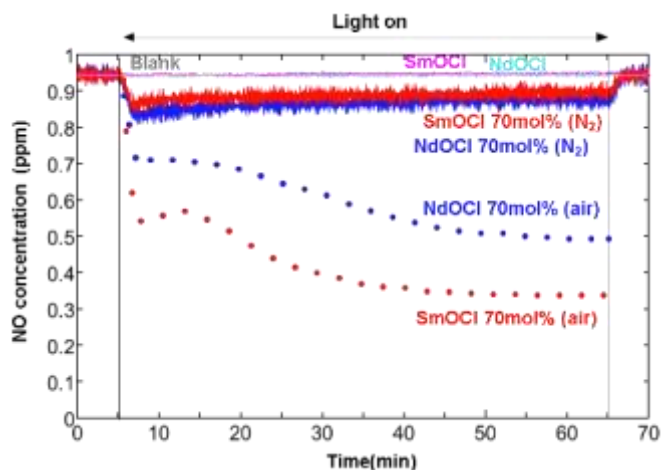


Fig. S5 Photocatalytic NO removal tests for pure LnOCl and BiOCl-70mol%LnOCl (Ln=Sm,Nd) in humid N₂ (solid lines) and in humid air (dotted lines). “Blank” is a control test without powder.

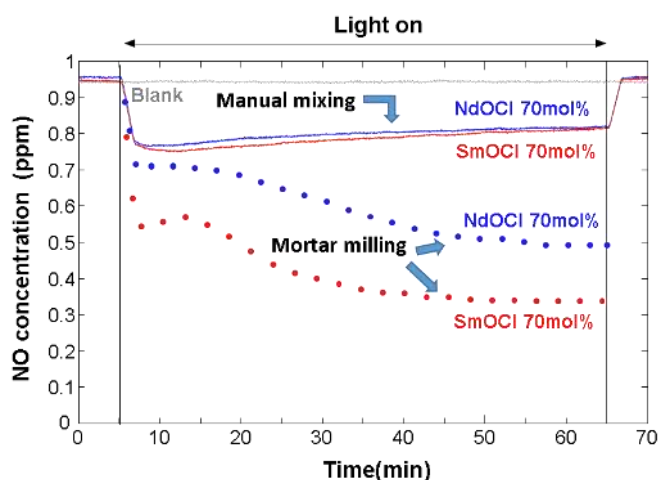


Fig. S6 Photocatalytic NO removal tests in humid air for BiOCl-70mol%LnOCl (Ln=Sm,Nd) powders mixed manually (solid lines), compared with mortar milling (dotted lines). "Blank" is a control test without powder.

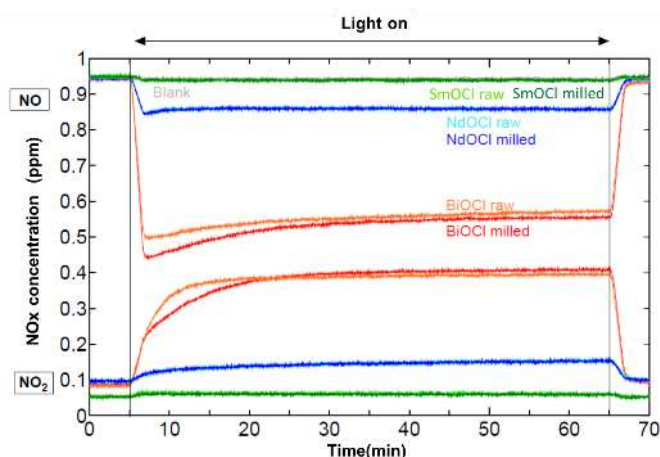


Fig. S7 Photocatalytic NO_x (NO and NO₂) tests for pristine (raw) and milled MOCl (M=Bi, Sm, Nd) powders in dry air. The NO₂ gas increases with removal of NO gas.

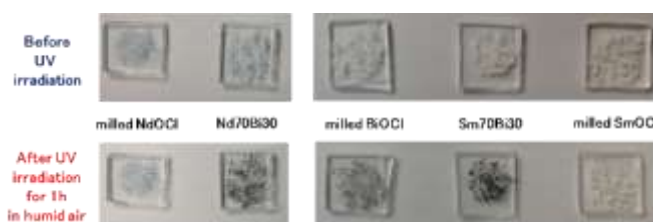


Fig. S8 After UV irradiation test for 1h in humid air, the color of composite powder often becomes darker, especially those exhibiting high NO removal rates with distinguished behavior: for example, Sm70Bi30 or Nd70Bi30 (BiOCl-70mol%LnOCl [Ln=Sm, Nd]) powders.

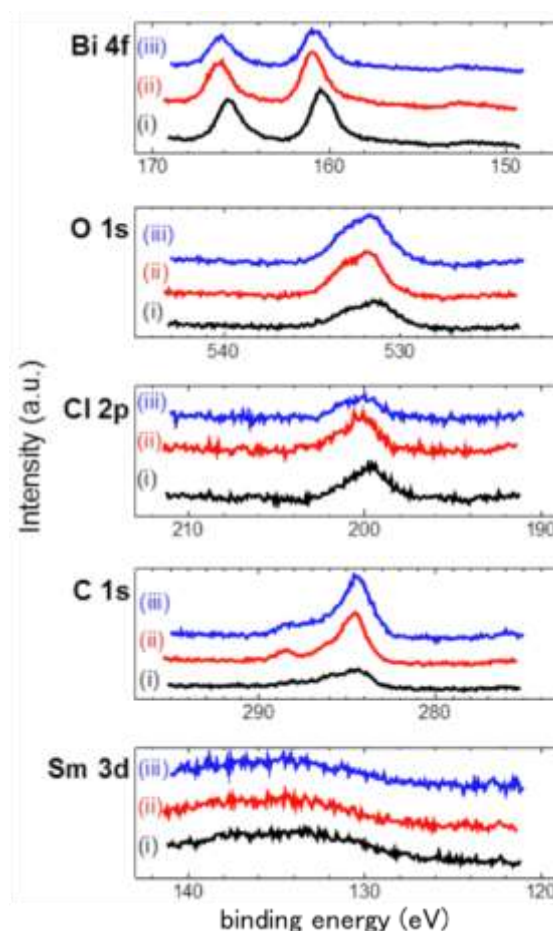


Fig. S9 XPS spectra on surface of Sm70Bi30 powders in 3 conditions: (i) without light irradiation, (ii)(iii) after 1h irradiation by a Xe lamp, in dry air (ii), or in humid air (iii) [calibrated by C1s binding energy at 284.5 eV].

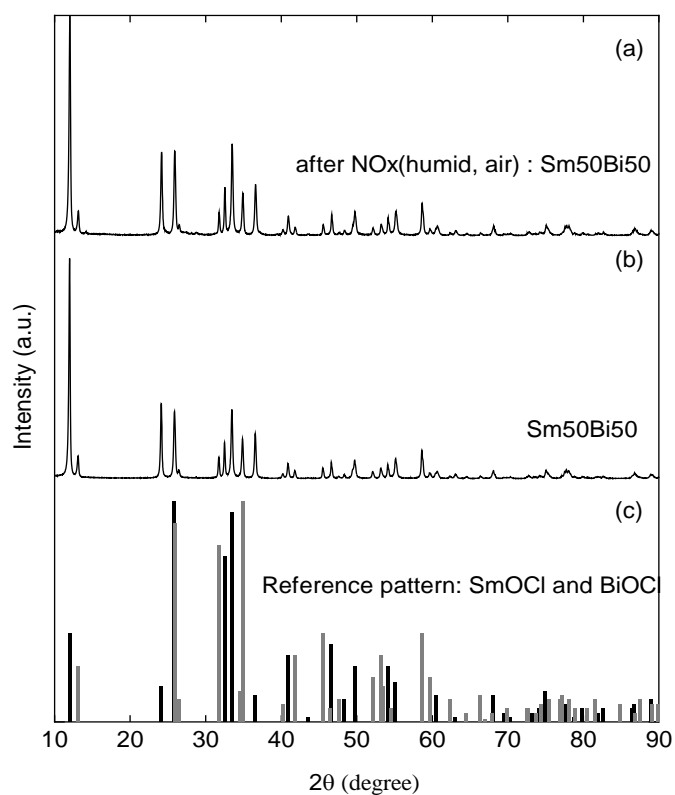


Fig. S10 X-ray diffraction patterns for: (a) Sm50Bi50 (SmOCl-50mol%BiOCl) powder composites after photocatalytic NO removal test in humid air, (b) Sm50Bi50 composites before the test, (c) SmOCl (gray) and BiOCl (black) references.

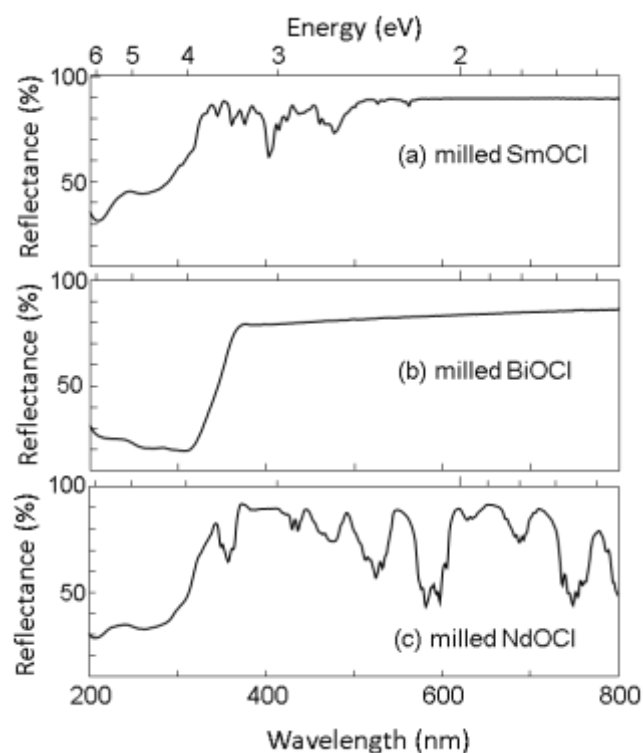


Fig. S11 UV-vis DRS spectra of pure powder samples milled for 30 min in air using an automatic agate mortar: (a) SmOCl (b) BiOCl (c) NdOCl.

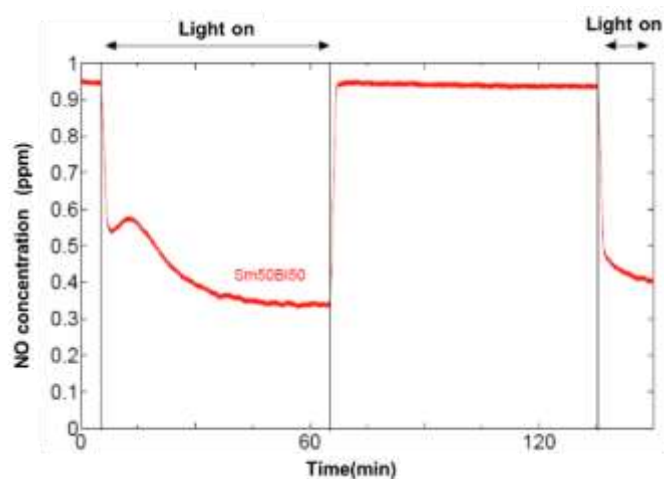


Fig. S12 Repeated NO photoremoval test, using a Xe lamp, on Sm50Bi50 (BiOCl-50mol%SmOCl) powder in humid air.

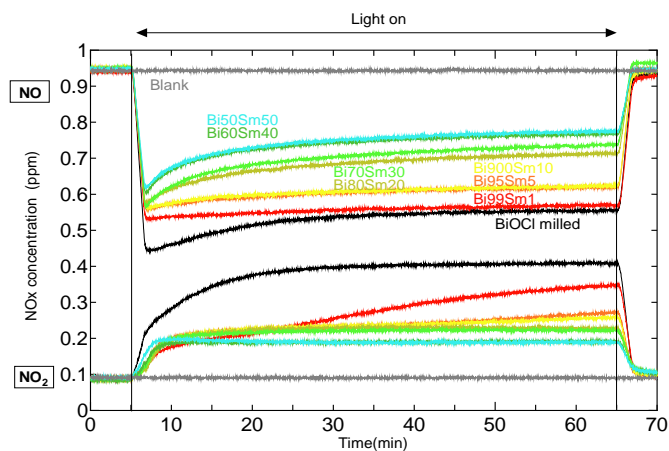


Fig. SS1 Photocatalytic NO_x (NO and NO₂) tests for various BiOCl-SmOCl (0, 1, 5, 10, 20, 30, 40, 50 mol% SmOCl) powder composites in dry air.

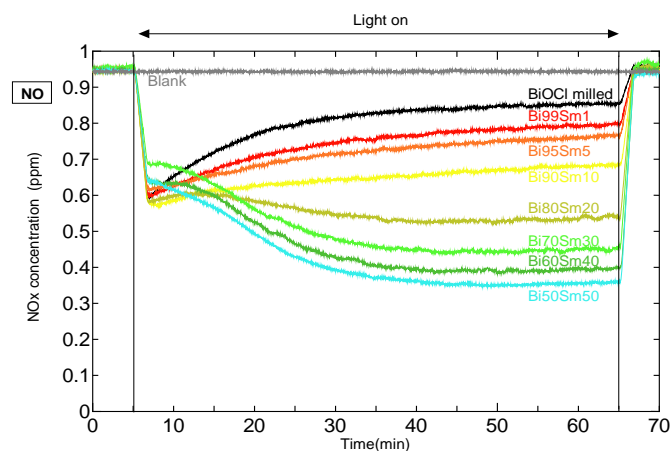


Fig. SS3 Photocatalytic NO removal tests for various BiOCl-SmOCl (0, 1, 5, 10, 20, 30, 40, 50 mol% SmOCl) powder composites in humid air.

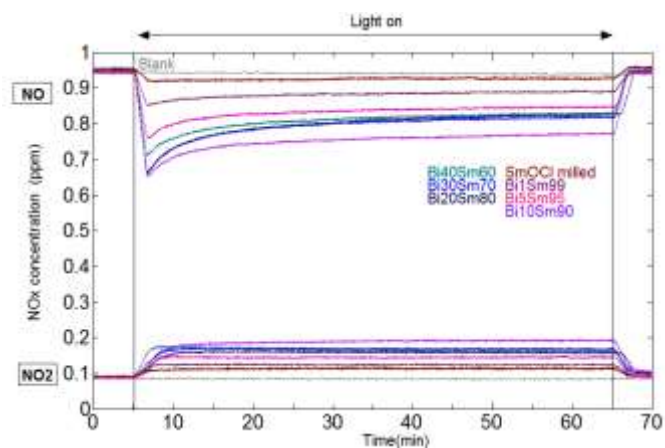


Fig. SS2 Photocatalytic NO_x (NO and NO₂) tests for various BiOCl-SmOCl (60, 70, 80, 90, 95, 99, 100 mol% SmOCl) powder composites in dry air.

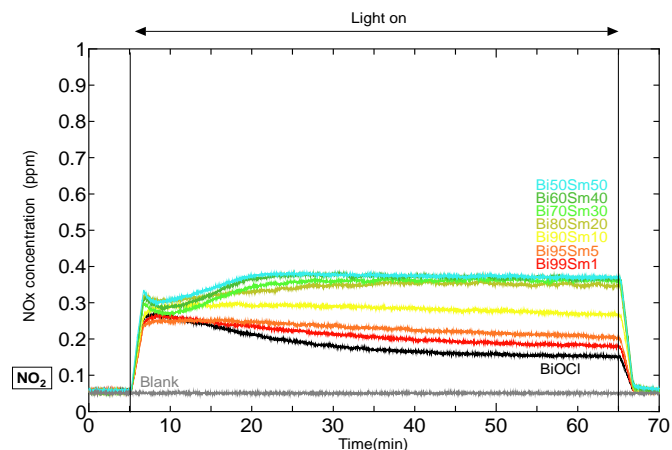


Fig. SS4 Photocatalytic NO removal tests (NO₂ generation) for various BiOCl-SmOCl (0, 1, 5, 10, 20, 30, 40, 50 mol% SmOCl) powder composites in humid air.

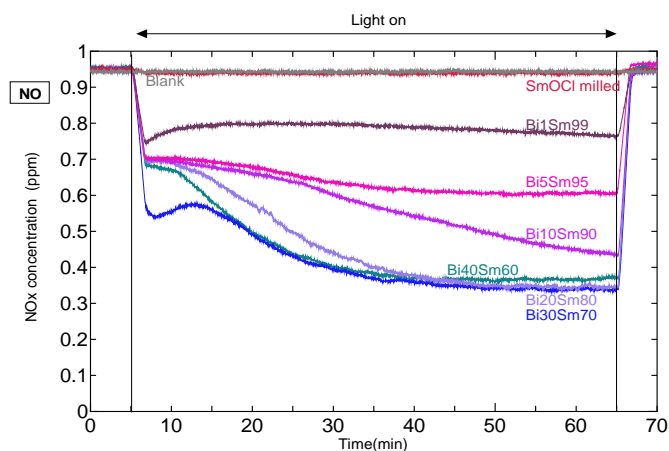


Fig. SS5 Photocatalytic NO removal tests (NO_2 generation) for various BiOCl-SmOCl (60, 70, 80, 90, 95, 99, 100 mol%SmOCl) powder composites in humid air.

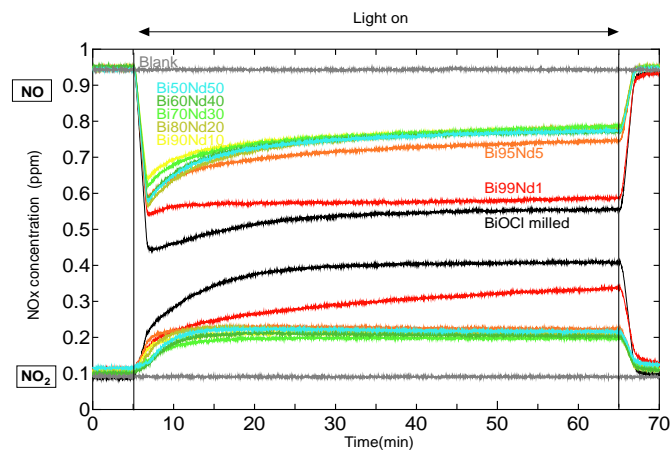


Fig. SS7 Photocatalytic NOx (NO and NO_2) tests for various BiOCl-NdOCl (0, 1, 5, 10, 20, 30, 40, 50 mol% NdOCl) powder composites in dry air.

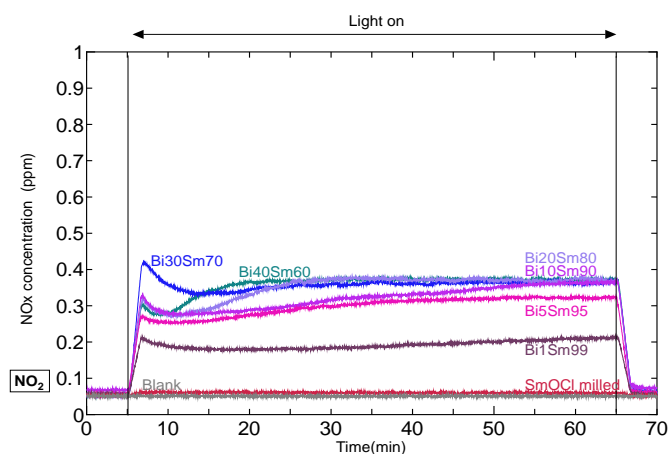


Fig. SS6 Photocatalytic NO removal tests (NO_2 generation) for various BiOCl-SmOCl (60, 70, 80, 90, 95, 99, 100 mol% SmOCl) powder composites in humid air.

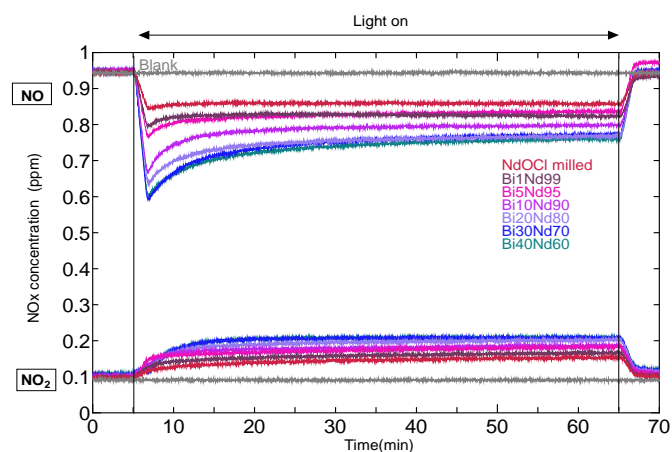


Fig. SS8 Photocatalytic NOx (NO and NO_2) tests for various BiOCl-NdOCl (60, 70, 80, 90, 95, 99, 100 mol% NdOCl) powder composites in dry air.

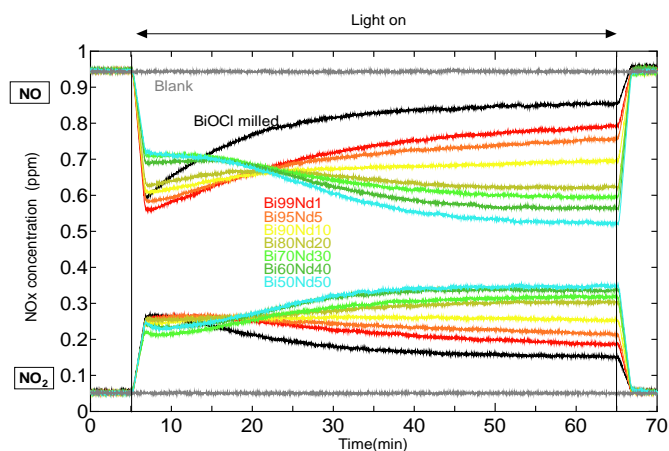


Fig. SS9 Photocatalytic NO_x (NO and NO₂) tests for various BiOCl-NdOCl (0, 1, 5, 10, 20, 30, 40, 50 mol% NdOCl) powder composites in humid air.

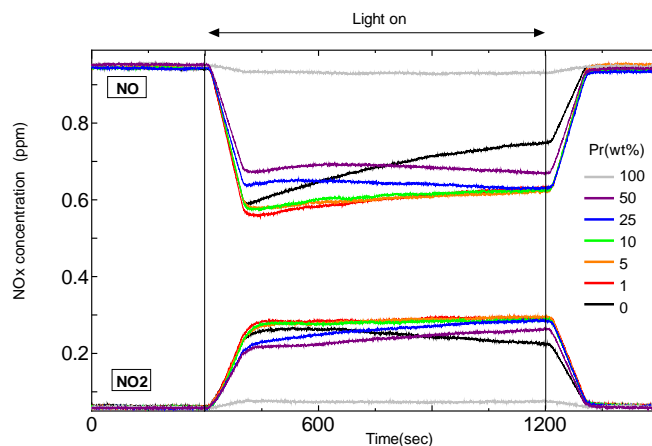


Fig. SS11 Photocatalytic NO_x (NO and NO₂) tests for various BiOCl-PrOCl (0, 1, 5, 10, 25, 50, 100 mol% PrOCl) powder composites in humid air.

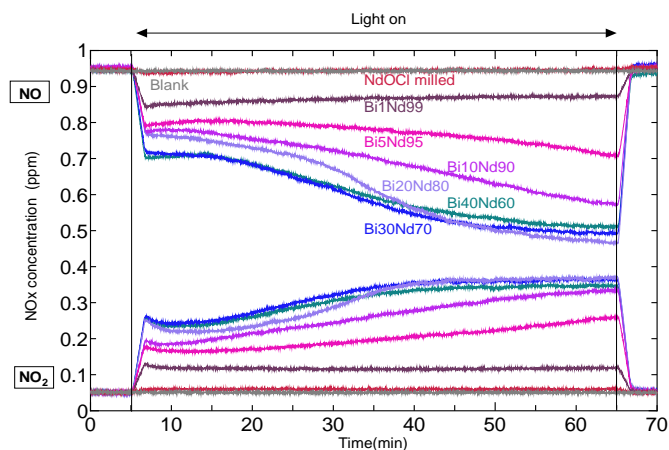


Fig. SS10 Photocatalytic NO_x (NO and NO₂) tests for various BiOCl-NdOCl (60, 70, 80, 90, 95, 99, 100 mol% NdOCl) powder composites milled in humid air.

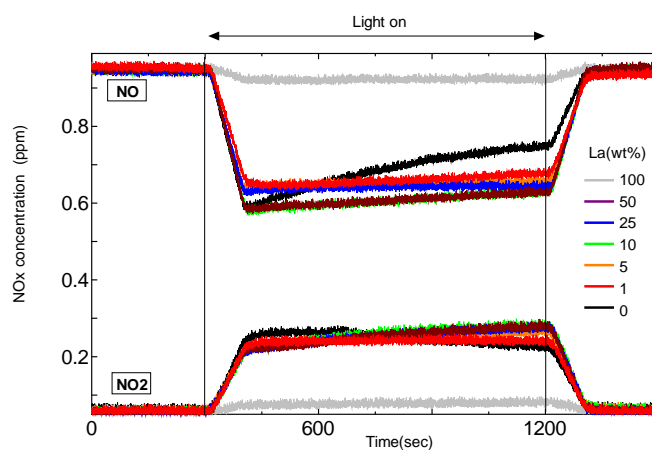


Fig. SS12 Photocatalytic NO_x (NO and NO₂) tests for various BiOCl-LaOCl (0, 1, 5, 10, 25, 50, 100 mol% LaOCl) powder composites in humid air.

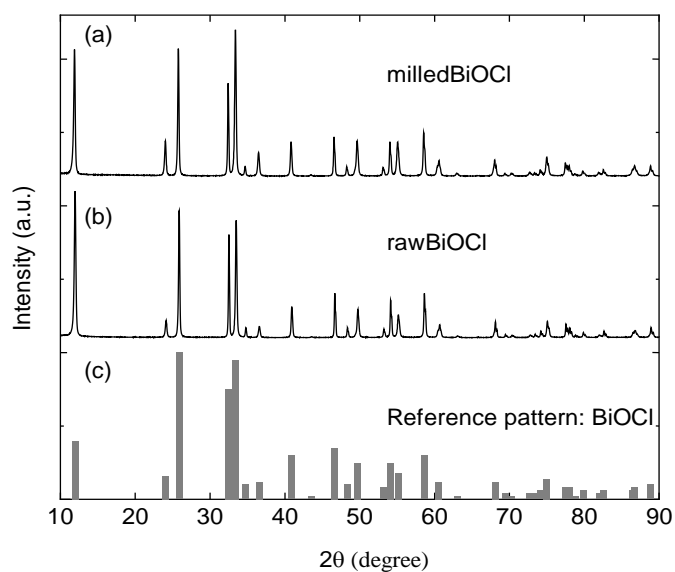


Fig. SS13 XRD patterns for (a) milled BiOCl, (b) raw BiOCl, and (c) BiOCl reference.

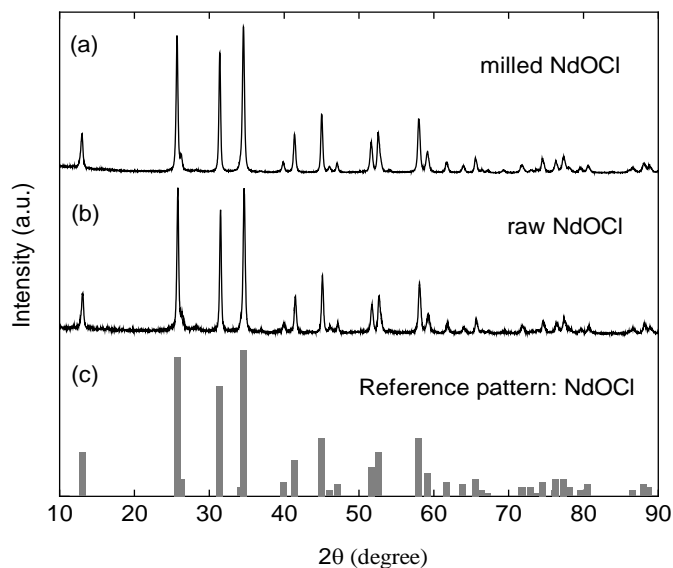


Fig. SS15 XRD patterns for (a) milled NdOCl, (b) raw NdOCl, and (c) NdOCl reference.

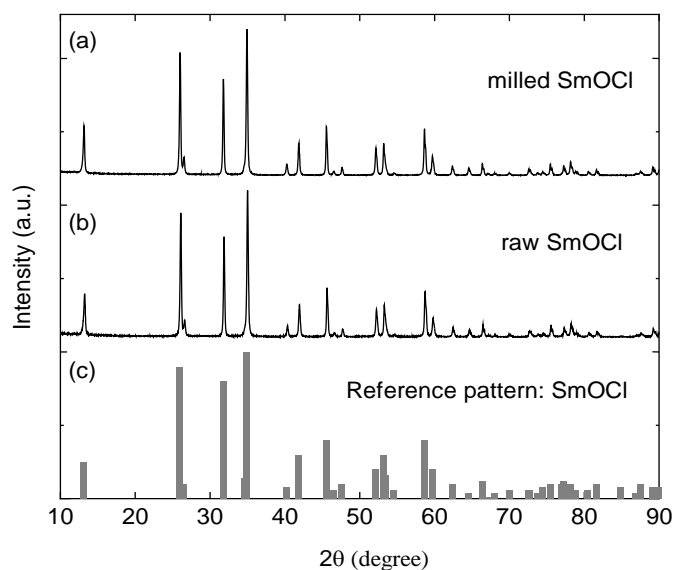


Fig. SS14 XRD patterns for (a) milled SmOCl, (b) raw SmOCl, and (c) SmOCl reference.

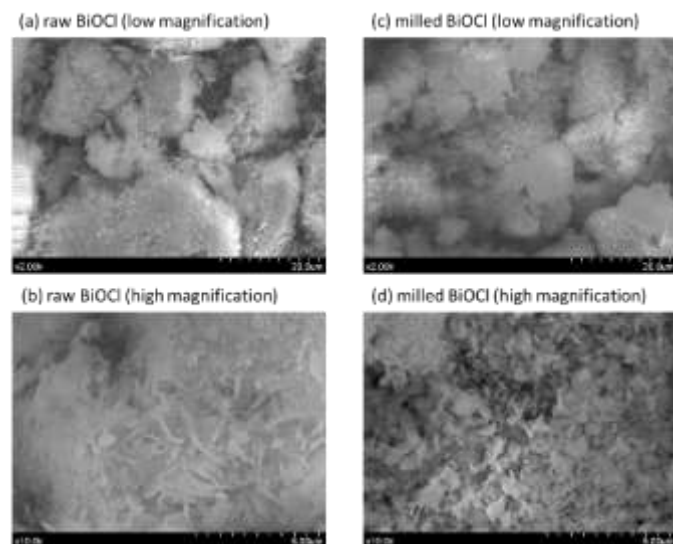


Fig. SS16 SEM images of BiOCl: (a)(b) pristine (raw) powder, (c)(d) milled powder. [(a)(c): low magnification (x2000), (b)(d): high magnification (x10000)].

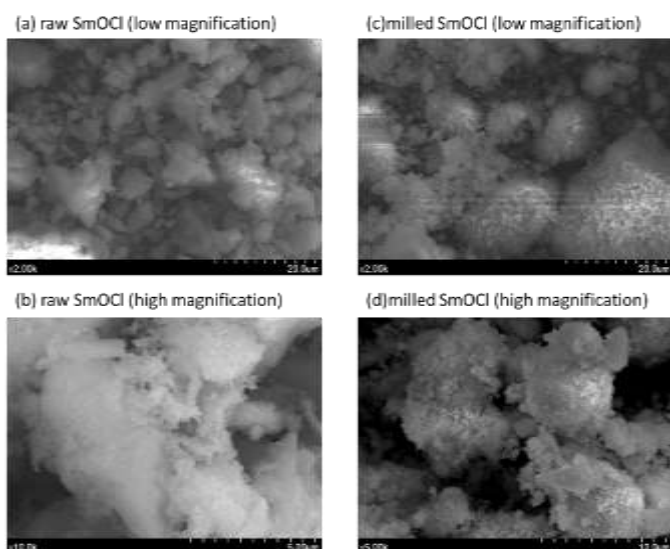


Fig. SS17 SEM images of SmOCl powders: (a)(b) as-synthesized (raw) powder, (c)(d) milled powder. [(a)(c) x2000, (b) x10000, (d) x5000].

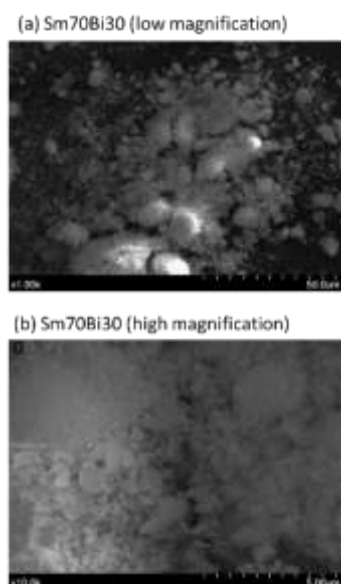


Fig. SS18 SEM images of Sm70Bi30 composite powder: (a) low magnification (x1000), (b) high magnification (x10000).

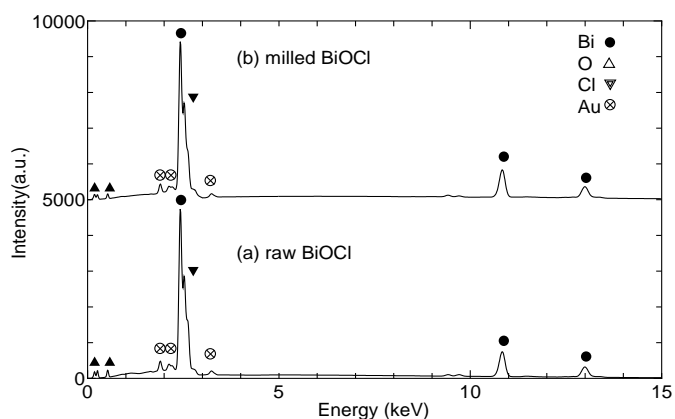


Fig. SS19 EDS analyses on (a) raw BiOCl powder, and (b) milled BiOCl powder: The Au signal is from sputtered Au film to obtain electrical conductivity.

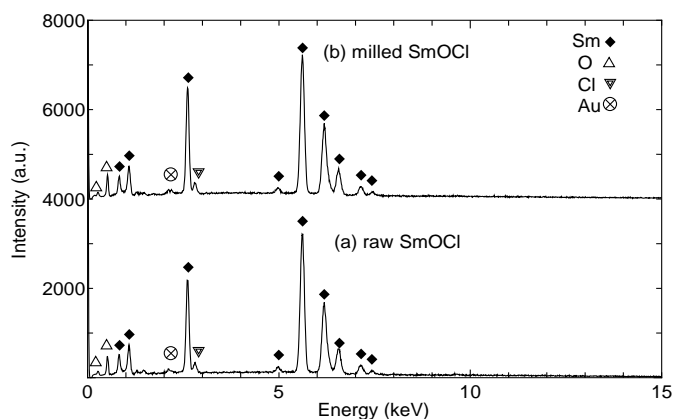


Fig. SS20 EDS analyses on SmOCl: (a) raw (as-synthesized) powder, and (b) milled powder.

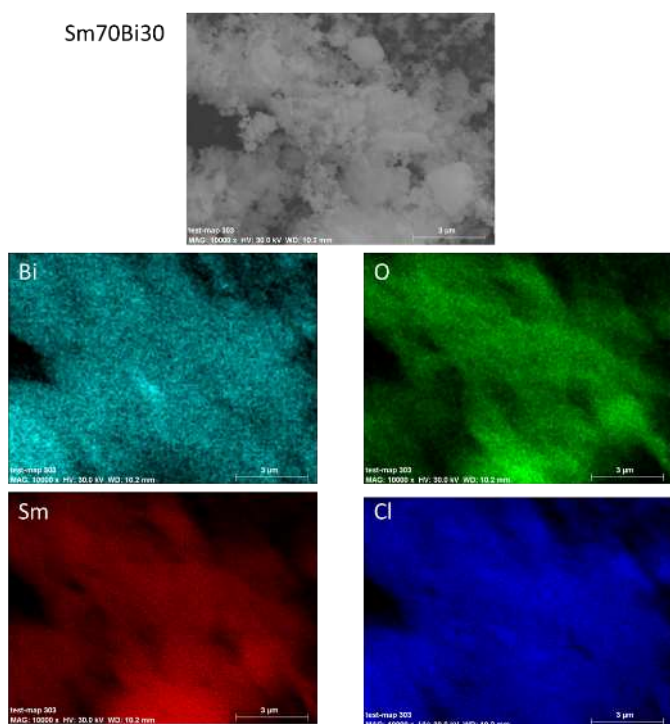


Fig. SS21 Element mapping analyses by EDS systems on Sm70Bi30 (BiOCl-70mol%SmOCl) composite powder (x10000).

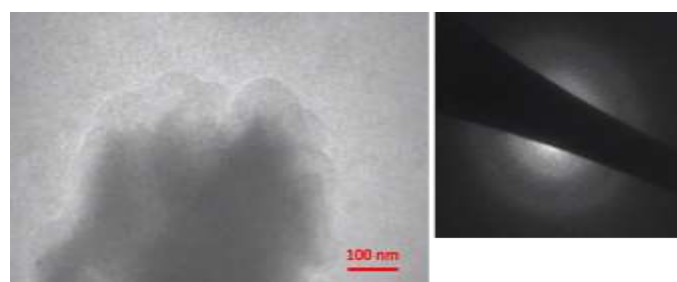


Fig. SS22 TEM image of SmOCl powder irradiated with a Xe lamp for 3h in humid air. Amorphous core (gray region) is further covered with another amorphous film.

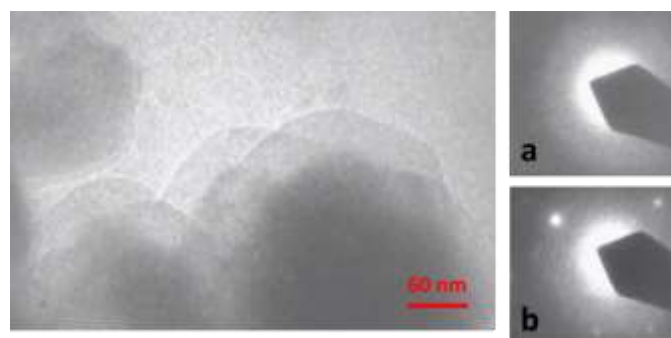


Fig. SS23 TEM image of SmOCl powder irradiated with a Xe lamp for 3h in humid air. A halo ring pattern (a) is obtained from glassy films, while it is spotty (b) for a crystalline gray region.

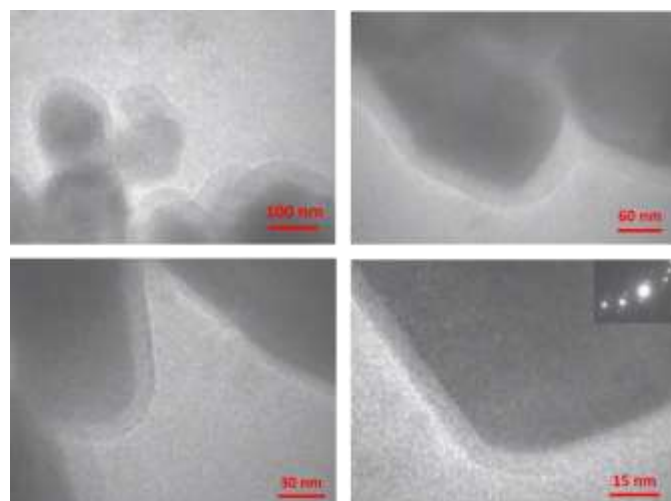


Fig. SS24 TEM images of SmOCl powder irradiated with a Xe lamp for 3h in humid air. Crystalline powder is often covered with amorphous film. Glassy debris is also found near powder.

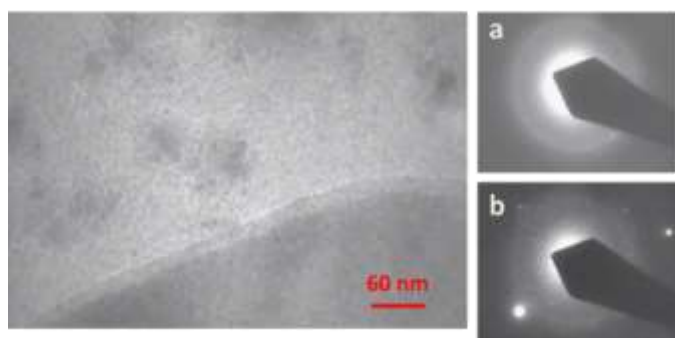


Fig. SS25 TEM images of BiOCl powder irradiated with a Xe lamp for 3h in humid air. Crystalline powder is sometimes covered with amorphous film, and surrounded by glassy/nanocrystalline debris: electron diffraction obtained for (a)debris (b)powder.

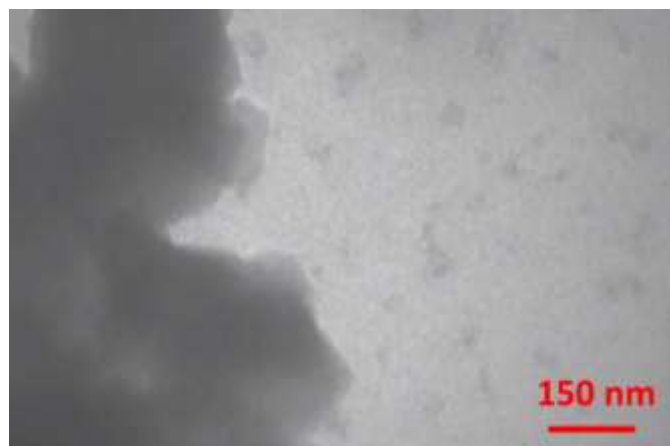


Fig. SS27 TEM image of Bi₃₀Sm₇₀ (70mol%SmOCl) powder irradiated with a Xe lamp for 3h in humid air. Crystalline powder is covered with amorphous patches, exhibiting jagged surface. Glassy debris is often found near powder.

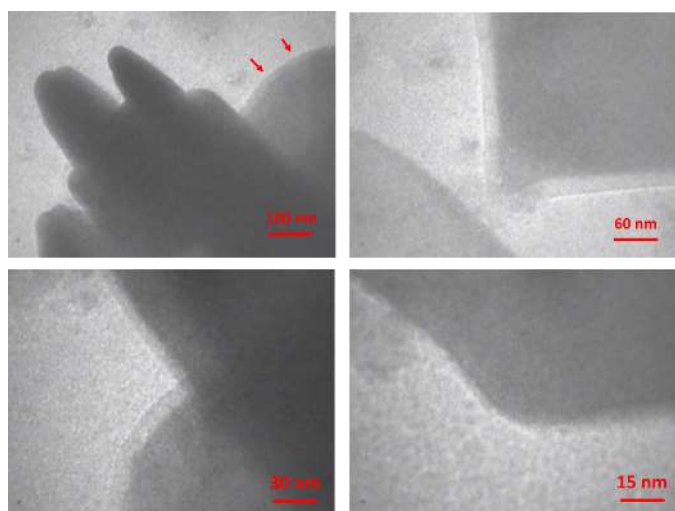


Fig. SS26 TEM images of BiOCl powder irradiated with a Xe lamp for 3h in humid air. Crystalline powder is sometimes covered with amorphous film. Seemingly clean surface is often covered with ultrathin film. Glassy debris is found near powder.

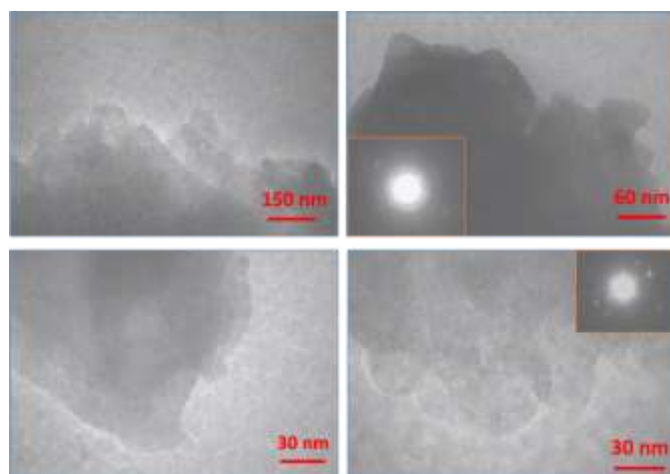


Fig. SS28 TEM images of composite Bi₃₀Sm₇₀ (70mol%SmOCl) powder irradiated with a Xe lamp for 3h in humid air. Crystalline powder is usually covered with amorphous patches, exhibiting jagged surface.

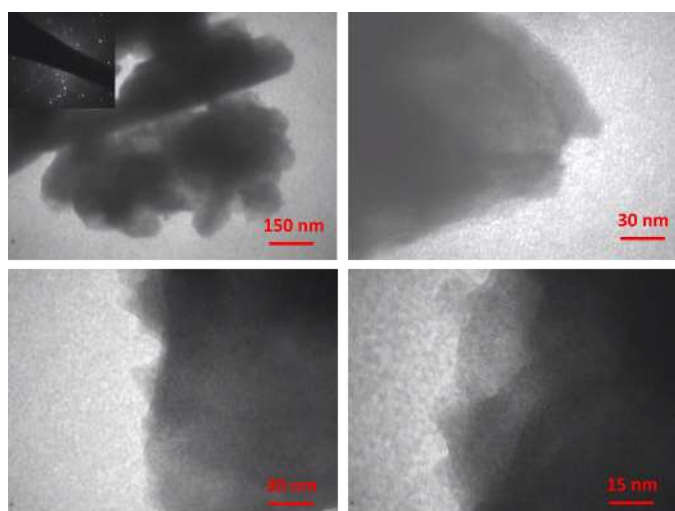


Fig. SS29 TEM images of composite Bi₃₀Sm₇₀ (70mol%SmOCl) powder after the NO_x test in humid air (irradiated with a Xe lamp for 60 min). Crystalline powder is often covered with amorphous patches, exhibiting jagged surface.

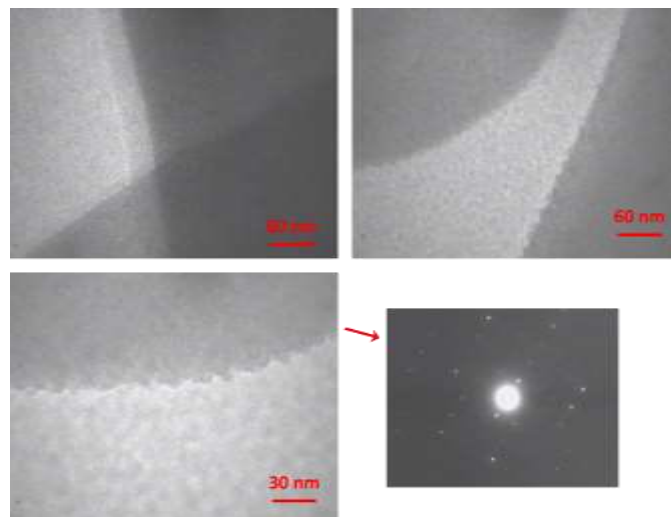


Fig. SS31 TEM images of BiOCl powder irradiated with a Xe lamp for 70 min in dry air. Seemingly clean surface is often covered with ultrathin film or numerous small crystalline protrusions.

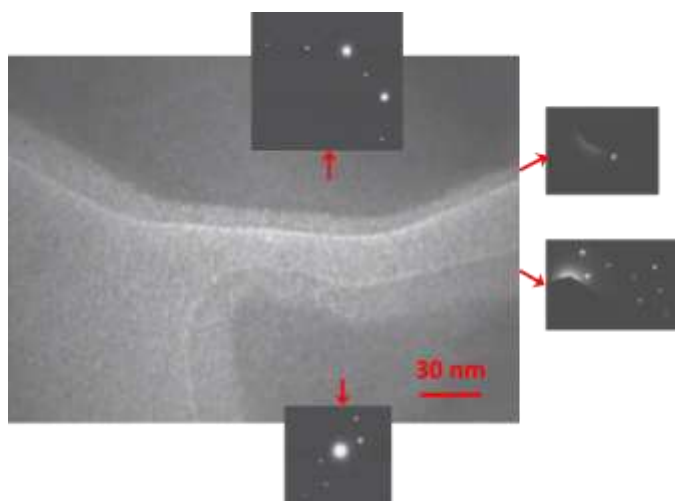


Fig. SS30 TEM image of BiOCl powder irradiated with a Xe lamp for 70 min in dry air. Crystalline powder is sometimes covered with epitaxial crystalline film.

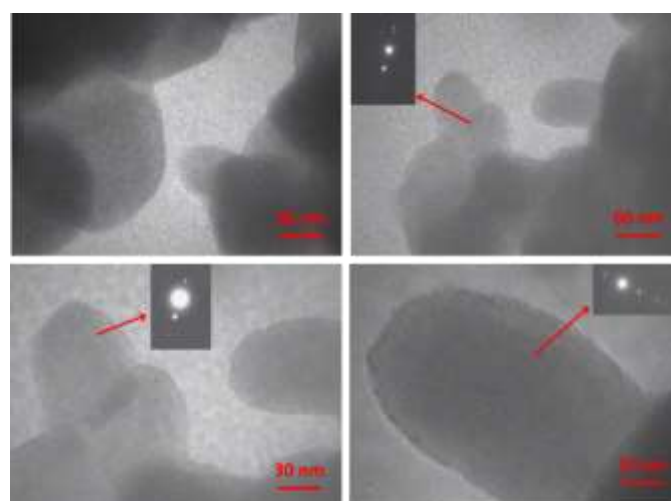


Fig. SS32 TEM images of SmOCl powder irradiated with a Xe lamp for 70 min in dry air. Though the surface is generally cleaner than BiOCl, slightly different contrast is often exhibited at the outermost ultrathin layer of crystalline powder.

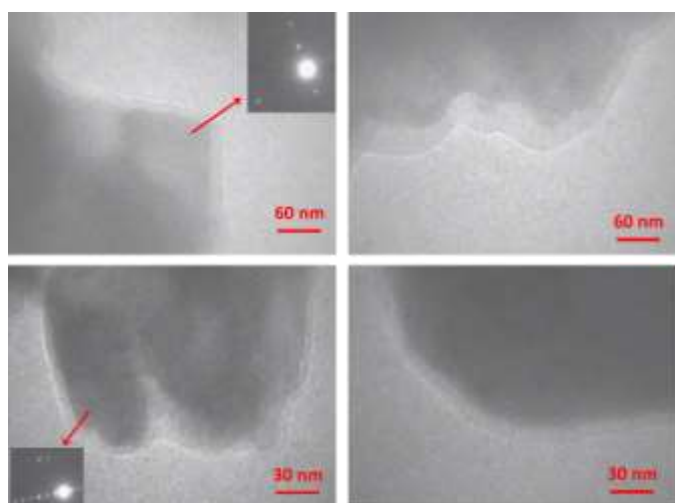


Fig. SS33 TEM images of composite Bi₃₀Sm₇₀ (70mol%SmOCl) powder irradiated with a Xe lamp for 70 min in dry air. Crystalline powders are sometimes covered with crystalline films. No debris is found around powder.

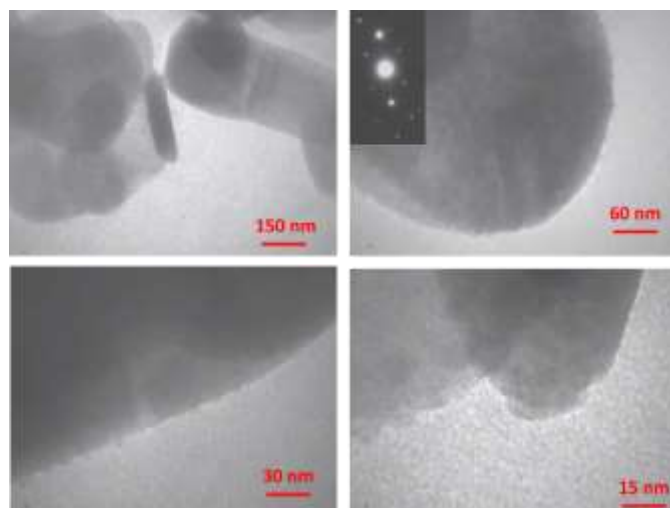


Fig. SS35 TEM images of BiOCl powder milled for 30 min. Without UV light irradiation, there is no film formation found, while the surface is sometimes covered with numerous small protrusions.

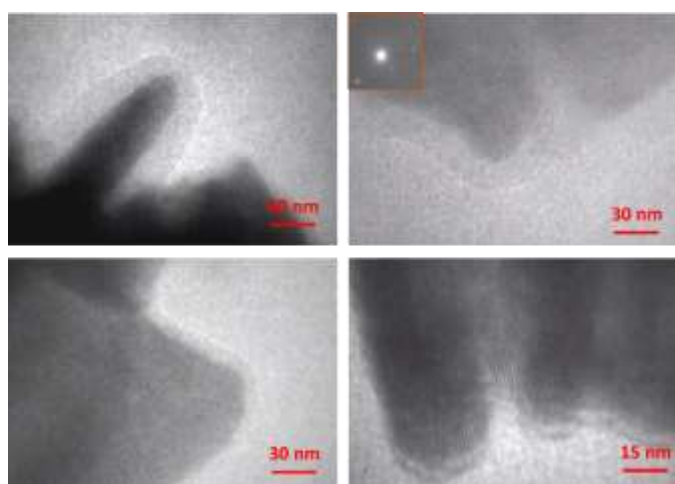


Fig. SS34 TEM images of composite Bi₃₀Sm₇₀ (70mol%SmOCl) powder after the NO_x test in dry air (irradiated with a Xe lamp for 60 min). Crystalline powders are sometimes covered with crystalline films. No debris is found around powder.

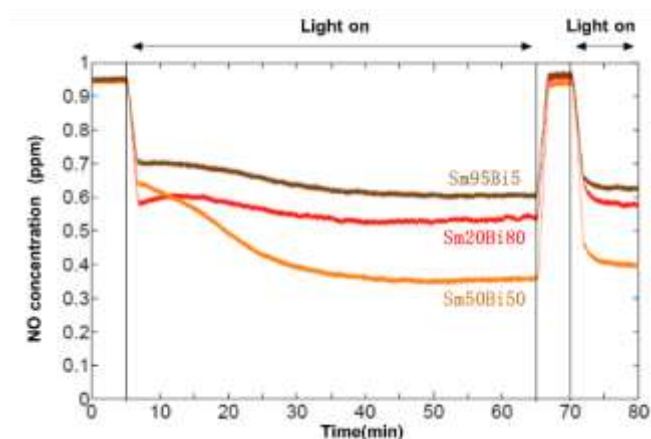


Fig. SS36 Repeated NO photoremoval tests, using a Xe lamp, on various BiOCl-SmOCl (20, 50, and 95 mol% SmOCl) powder composites in humid air.