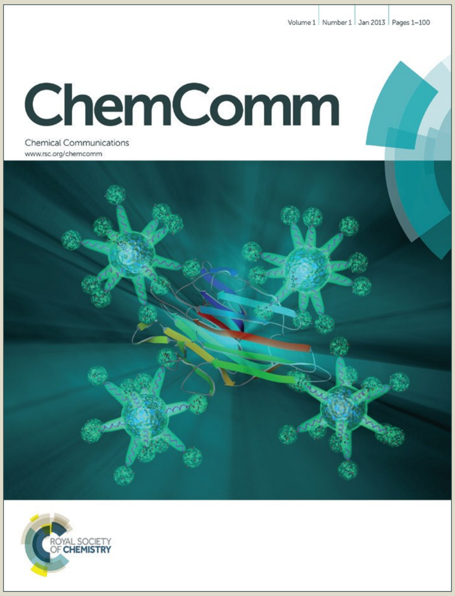
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Multicolour photochromism of colloidal solutions of niobate nanosheets intercalated with several kinds of metal ions

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Colourless and transparent colloidal solutions of niobate nanosheets intercalated with some kinds of metal ions (M-NNS, M: metal) showed quasi-reversible photochromism. Ultraviolet light irradiation to the solutions induced a change in color with maintaining the transparency, and the color changed depending on the metal ions. The coloured solutions were bleached by exposure to oxidizing atmosphere. This cycle could be repeated several times.

Photochromism is well known as a common phenomenon, i.e. colour or transparency of substance alters by photoirradiation. In general, a substance is coloured under irradiation of photons with a specific wavelength, and then returns to the original state by supplying photon energy with a different wavelength or thermal energy. The fact that photochromism occurs repeatedly, suggesting effectiveness for practical application including rewritable memories, optical switches, etc. It has been reported that many classes of organic or inorganic materials have the photochromic properties.[1,2] Organic molecules behave as photochromic materials in several physical states like liquid (solution) and solid (crystal).[3] Regarding inorganic materials, on the one hand, most research efforts have been concentrated in a solid state.

To date, metal halides have been extensively studied and practically applied as inorganic photochromic materials.[4] Moreover, transition metal oxides such as TiO_2, WO_3, and MoO_3 have been also investigated in detail.[5] These semiconducting solid oxides are white or slightly tinged as a result of total reflection of visible light based on their wide band gaps. Photoirradiation with an appropriate wavelength changes their appearances. Recently, some groups have reported that transparent colloidal solutions of nano-sized $Cs_{6+x}W_{11}O_{36}$, WO_3, or MoO_3 have photochromic properties.[6,7] Strictly speaking, small "solid" particles dispersed in a solution change the colour. Photochromism in a liquid state seems to have some advantages like transparency and flexibility in shape.

Most photochromic metal oxides previously reported are nearly white~~,~~ and blued by photoirradiation. In other words, variation in colour is poor for metal oxides as compared with organic materials. The colour change is basically originated from enhanced visible light absorption due to *d*-*d* transition of electrons in an unfilled a *d* orbital of transition metal ions as a result of a reduction under photoirradiation. Recently, Akiyama demonstrated that $BaMgSiO_4$ polycrystals showed a colour change between colorless (white) and pink that is rare for inorganic photochromic compounds, and the two states could be switched by irradiation with different wavelengths of 405 nm (colouring) and 532 nm (bleaching).[8] However, photochromism of oxides is still inferior in the viewpoint of colour diversity as compared to organic molecules or metal nanoparticles with size-dependent photochromic properties.[9]

The present communication reports for the first time multicolour photochromism of transparent basic colloidal solution of niobate nanosheets intercalated with metal ions (denoted below as M-NNS, M: metal). Even though NNS excluding M did not show any change in appearance, intercalation of metal ion made the NNS photochromic materials. Under ultraviolet (UV) light irradiation, colourless and transparent colloidal solutions of M-NNS were stained along with reduction of dopants and regenerated to the original state by exposure to oxidizing atmosphere. In addition, the change could be repeated several times. The colour induced by the UV light irradiation depended on a metal ion, realizing multicolour photochromism. The transparency of colloidal solutions was preserved over the whole process. Here we briefly discuss mechanism of the photochromism of the M-NNS colloidal solutions based on experimental findings.

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†Electronic Supplementary Information (ESI) available: Experimental details, schematic illustration of an experimental setup for photochomism, emission spectrum of a UV light source, Raman spectrum and XRD pattern of NNS, photoluminescence spectrum of Eu-NNS, transient absorbance of Eu-NNS under UV light irradiation, photographs and absorption spectra of coloured colloidal solutions with different metal ions, and effect of Ti content on absorbance of irradiated Ti-NNS. See DOI: 10.1039/x0xx00000x

Transparent colloidal solutions were formed as a result of hydrolysis of niobium(V) ethoxide including or excluding another metal source ($EuCl_3$, $LaCl_3$, $CuCl_2$, or Ti(IV) tetraisopropoxide) with an aqueous tetramethylammonium (TMA^+) hydroxide solution followed by aging at 333 K for 24 h.[10] The experimental details are explained in the ESI†. Mean colloid sizes and photochromic properties of the obtained solutions are summarized in Table 1. The NNS was colourless. Similarly, the samples including another metal (M-NNS) except for M = Cu were also colourless, while the Cu-NNS was only slightly tinted to green even at a small concentration (0.5 mol%), probably due to presence of Cu^{2+}. All colloidal solutions had mean sizes less than 10 nm, which were much smaller than that of micrometric niobate nanosheets prepared by a solid state reaction at high temperature followed by exfoliation with bulky tetraalkylammonium ions.[11] Such dimensions brought about the transparencies of the solutions. According to the Raman spectrum of a solid thin film prepared by drying the NNS colloidal solution, crystal structure was akin to a layered hexaniobate ($Nb_6O_{17}^{4-}$) intercalated with TMA^+ in the interlayer space (Fig. 1S(a)†), implying the formation of NNS by using the hydrolysis reaction. This was also confirmed by measuring an X-ray diffraction pattern of the thin film, which was analogous to that of hydrated $K_4Nb_6O_{17}$ (Fig. 1S(b)†).[10] Considering the small dimensions of the particles as stated already, the layered niobate should exist as small particles consisting of a few layers of $Nb_6O_{17}^{4-}$ sheet with 0.41 nm in thickness. With respect to the M-NNS (M = Eu, La, Cu, or Ti), Ti^{4+} (6-coordination, 61 pm) having a close ionic radius to Nb^{5+} (64 pm) appears to substitute for Nb sites, while larger Cu^{2+} (74 pm), La^{3+} (103 pm), and Eu^{3+} (95 pm) were expected to occupy interlayer space between anionic layers ($Nb_6O_{17}^{4-}$) together with TMA^+ and H_2O.[12] In the case of the NNS containing a large amount of Ti (80 mol%), crystal structure might be closed to tetratitanate ($Ti_4O_9^{2-}$) rather than hexaniobate.[13] As a result, it was clarified that the simple hydrolysis reaction realized the formation of a colloidal solution of M-NNS.

To study photochromic performance, the colloidal solutions of M-NNS in a closed quartz cuvette were exposed to UV light from a Hg-Xe lamp at 303 K, and UV-Vis optical absorption spectrum was measured before and after the irradiation. Schematic illustration of experimental setup and emission spectrum of the light source are displayed in Fig. 2S† and 3S†, respectively. Fig. 1 shows the absorption spectra of (a) the NNS and (b) the Eu-NNS accompanied by photographs of solutions before and after the UV light irradiation. Prior to the irradiation, the NNS had no absorption in a visible range and an absorption edge at *ca.* 345 nm that corresponds to band gap energy of n-type semiconducting NNS. As shown in Fig. 1a, the absorption spectrum of NNS had hardly changed by the UV light irradiation, indicating that the NNS itself had no photochromic abilities. In contrast, the colourless and transparent Eu-NNS was changed to orange while holding the transparency (Fig. 1b). The coloured state was stable even after switching off the UV light unless the cuvette was not opened. The change in appearance largely affected the absorption spectrum, that is, the absorption edge was significantly red-shifted to around 650 nm. Moreover, the orange colour was completely bleached to the original state under exposure to air, and hence the spectrum returned to the original state. Visible light irradiation using a UV cut filter (λ > 420 nm) did not induce the colour change, band gap excitation of NNS appears to trigger off the colouring. Moreover, Eu-NNS with a small size (1.7 nm) that were formed after aging extended to 100 h also occurred the photochromism. This means that the photochromic property of Eu-NNS is independent of particle dimensions within the size range investigated.

Matsumoto and co-workers claimed that UV light irradiation to a thin film of solid Pt-loaded layered niobate induced a similar red shift of an absorption shoulder.[14] They explained the shift was caused by doping of nitrogen originated from co-existent tetrabutylammonium ions. On the other hand, Zhang et al. reported that white $K_4Nb_6O_{17}$ microspheres dispersed in an aqueous methanol solution had turned black under irradiation of UV light.[15] The behaviour was interpreted that electrons excited to the conduction band of $K_4Nb_6O_{17}$ were trapped by Nb^{5+} along with oxidation of methanol as a sacrificial agent by holes left in the valence band. As a result, *d-d* transition of formed Nb^{4+}, which had one electron in a 4*d* orbital, was the origin of visible light absorption. Our experimental results seem to be close to the latter literature, because the colloidal solutions included alcohols as by-products derived from the raw materials (niobium(V) ethoxide, ethanol solutions of the metal chlorides, and titanium(IV) tetraisopropoxide). In contrast to the Zhang's report, however, the NNS excluding another metal did not give a rise to any change in appearance by the UV light irradiation. Nb^{5+} in the NNS might be stable in the basic colloidal solution (pH = 11.2), because a redox potential of solid metal oxides in an aqueous solution is generally shifted to negative direction with an increase in pH.[16] On the contrary, the presence of Eu (Eu-NNS) resulted in the colouring. It was validated that the Eu ions in the Eu-NNS were trivalent by measuring a fluorescence spectrum of the colloidal solution that was absolutely different from that of Eu^{2+} (Fig. 4S†). That is, two major red emissions from an excited energy level ($^5D_0$) of Eu ($^7F_2$: 618 nm and $^7F_1$: 593 nm) were observed by excitation with UV ray.[17] The fluorescence originated from Eu^{3+} was also confirmed even after dialysis against pure water to reduce the solution pH, suggesting Eu^{3+} was intercalated into the NNS. According to the literature, it is anticipated that redox potentials of metal ions located between anionic layers are not so far from those of free metal ions in an aqueous solution.[18] Since the redox potential of a $Eu^{3+/2+}$ couple has been reported to be more positive (E^o = -0.429 V vs. NHE, independent of pH[16]) than the conduction band edge of niobate (estimated to be -1.00 V at pH = 11.2),[19] the excited electrons might contribute to a reduction of the Eu^{3+} in the interlayer space. An Eu^{2+} ion has a half-closed shell (electron configuration: $[Xe]4f^7$), and hence has to be colorless.[20] Unfortunately, the coloured (reduced) Eu-NNS did not show blue fluorescence, which is an indication of Eu^{2+}.[21] The emission might be quenched by the visible light absorption of Eu-NNS as shown in Fig. 1b. The reduction of Eu^{3+} would also cause generation of oxygen vacancies in anionic niobate layers to maintain a charge balance in the Eu-NNS. As a result, the vacancies played a role as a colour centre,[8] resulting in the colour change of the Eu-NNS. At the same time, the holes left in the valence band would be consumed by oxidizing the alcohols as sacrificial reagents. The importance of alcohols for the photochromism was indirectly demonstrated by the fact that little absorbance change during the UV light irradiation was observed for a solid thin film of the Eu-NNS covering a quartz plate. Additionally, to investigate feasibility of photochromism of the simple mixture of free (not intercalated) Eu^{3+} and NNS, a small amount of aqueous $EuCl_3$ solution was added to the basic colloidal solution of NNS. As a result, white precipitates were produced in the solution probably due to formation of $Eu(OH)_3$ and/or aggregation of NNS. This fact indicates that the intercalation of Eu^{3+} into the NNS is important to induce the photochromism while maintaining the transparency.

Fig. 1b indicates that the coloured Eu-NNS solution was bleached by exposing to an ambient atmosphere (air), in other words, the solution returned to the original colourless and transparent state. This fact was attributed to reoxidation of the Eu^{2+} together with disappearance of the oxygen vacancies, and reinforced the validity of the aforementioned mechanism and reversibility of the photochromism. In addition, in-situ monitoring of absorbance at 550 nm during UV light irradiation (Fig. 5S†) revealed that there was an induction period having little increase in absorbance for about 300 s at the initial stage of the irradiation. In this period, electrons excited would preferentially reduce oxygen gas dissolved in the solution until the gas was consumed. Considering all results above, it was confirmed that the liquid state reversible photochromism of the Eu-NNS was accomplished under irradiation of UV light.

Effect of another metal (M) on the photochromic property of the M-NNS was also evaluated. As summarized in Table 1, various colours depending on the M were observed by the UV light irradiation. As similar to Eu-NNS, the coloured solutions returned to the original state by exposing to an oxidizing atmosphere. Photographs and absorption spectra of the irradiated M-NNS are given in Fig. 6S and 7S†, respectively. In the case of Ti^{4+}, a small doping amount (5 mol%) did not cause the photochromism, but the highly doped Ti-NNS (80 mol%) turned bluish due to formation of Ti^{3+}, which is a typical colour of photochoromic TiO_2. The absorbance in a visible range increased with an increase in a molar concentration of Ti^{4+} (Fig. 8S†). On the other hand, the Cu-NNS turned red probably due to photoreduction of Cu^{2+} ions to metallic Cu nanoparticles in the interlayer because a sharp absorption peak (574 nm) based on localized surface plasmon resonance was observed after the irradiation.[22] These results can be also explained by valence fluctuation (reduction/oxidation) of the metal ions in the irradiated M-NNS, except for La^{3+} that has no lower and higher oxidation number than +3 besides zero. Hence, it was confirmed that NNS is useful as a host material for the multicolour photochromism.

Since photochromism is required to occur repeatedly, cyclic performance of the photochromism was evaluated by alternating the UV light irradiation to the Eu-NNS solution (3 h) and the subsequent oxidation. Fig. 2 shows fluctuation in absorbance at 550 nm when the cycle was repeated several times. As can be seen in the figure, the repeatable photochromic activity was achieved accompanied by a minor increase in absorbance when bleached.

In the present communication, we have demonstrated for the first time that the colloidal solutions of niobate nanosheets intercalated or doped with another metal (M-NNS) possess the photochromic properties under UV light irradiation and the colour could be adjusted by selecting an appropriate metal ion. In the present photochromism system, when reduced metal species can absorb visible light (e.g. Cu^0, Ti^{3+}), the appearance is determined by the colour. On the other hand, in the case of colourless metal ions such as Eu^{2+}, the colour change is originated from generation of oxygen vacancies. The origin of photochromism will be systematically elucidated for combinations of various metal ions and host layers hereafter. More concretely, influence of location of metal ions (intercalation or doping into oxide layers) on the photochromism will be clarified in our future study. Besides the photochromism, the broad absorption wavelength range of the coloured materials may be effective as semiconductor photocatalysts driven by visible light irradiation.[14,15,19] Our further study will also be devoted to development of photochromic M-NNS showing unfound colours like green by introduction of different metal ions.

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Table 1 Particle sizes and photochromic properties of colloidal solutions of M-NNS.

M	[M] / mol%	Size[a] / nm	Appearance		
			Before irradiation	After irradiation	After exposure to air
None	0.0	4.8	CT	CT	CT
Eu^{3+}	0.5	7.2	CT	Orange	CT
La^{3+}	3.0	1.2	CT	Pale yellow	CT
Cu^{2+}	0.5	1.9	CT[b]	Red	CT[b]
Ti^{4+}	5.0	1.3	CT	CT	CT
	80.0	6.0	CT	Pale blue	CT

CT: colourless and transparent, [a]estimated by DLS measurements, [b]tinged only slightly with green.

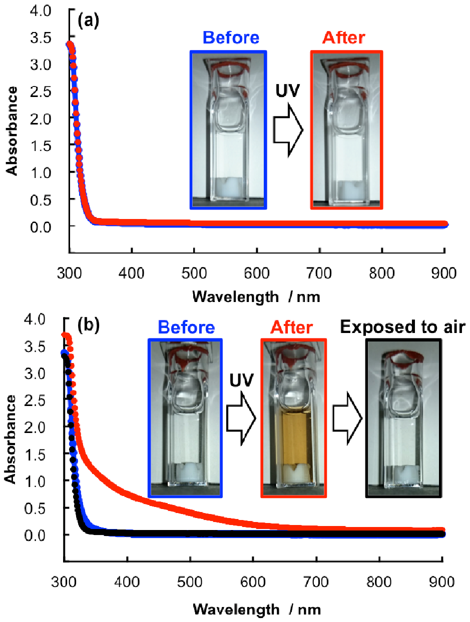

Fig. 1 UV-Vis absorption spectra of (a) NNS and (b) Eu-NNS colloidal solutions before (blue) and after (red) UV light irradiation for 6 h. The spectrum of coloured solution of Eu-NNS after exposing to air atmosphere (black) is also displayed in (b). The photographs inserted in each figure indicate appearances of solution of which the spectrum was measured.

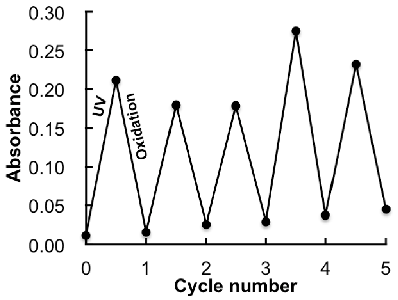

Fig. 2 Variation in absorbance (λ = 550 nm) of a colloidal solution of Eu-NNS during repeated UV irradiation and re-oxidation. A cycle consists of UV irradiation for 3 h and subsequent exposure to air atmosphere.

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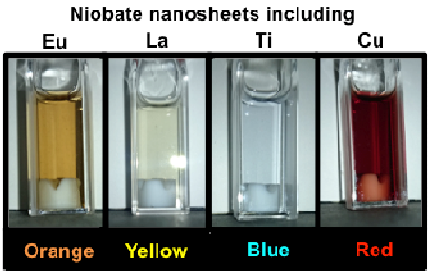

Niobate nanosheets show multicolour photochromism depending on a kind of coexistent metal ions.