Photoluminescence of Eu^{3+} and Tb^{3+} Ions Adsorbed on Oxide Nanosheets

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Photoluminescence properties of TiO ($Ti_{1.825}O_4$) and NbO (Nb_6O_{17}) nanosheets adsorbed with Ln^{3+} ions were studied comparing with those of photoluminescent Gd–Eu–Ti–O and La–Tb–Ta–O perovskite nanosheets. Intense emissions of Ln^{3+} (Eu^{3+} and Tb^{3+}) ions adsorbed on TiO and NbO (Ln^{3+}/MO) nanosheets were observed during UV light illumination. The photoluminescence results from the energy transfer from the band gap excitation of the nanosheets to the adsorbed Ln^{3+}. Coadsorbed H_2O increased the emission intensities of the adsorbed Ln^{3+} for the Ln^{3+}/MO samples. On the other hand, no effect of adsorbed H_2O on the emission intensities of the photoluminescent perovskite nanosheets was observed because of the presence of Ln^{3+} on the inside of the nanosheets. Hydrogen-bonding networks between O^{2-} ions of the nanosheet surface and the adsorbed H_2O surrounding Ln^{3+} will promote the energy transfer for the Ln^{3+}/MO samples. Recombination and photoreaction of the produced electron and hole of the nanosheet, and a phonon due to the adsorbed H_2O suppress the emission, according to the analyses of effects of pH, adsorbed ions and D_2O on the emission.

Semiconducting oxide nanosheets such as Ti–O, Nb–O, and Ta–O nanosheets, have many promising properties such as photoluminescence,[1–8] photocatalysis,[9–11] electrochemistry,[12,13] and so on.[14] In addition, nanosheets might show a peculiar reaction in the presence of Ln^{3+}.[15] In particular, many unique properties concerning photoluminescence have been reported as follows.

1) The photoluminescence of Ln^{3+} results mainly from an energy transfer from the nanosheet band gap excitation to the Ln^{3+}.[1,3–8]

2) Adsorbed or absorbed H_2O promotes the energy transfer to bring about intense emission, especially for Eu^{3+}/TiO systems.[5]

3) The emission intensity depends on solution pH. Usually, the intensity decreases at low pH.[4]

The above photoluminescence properties have been observed for Ln^{3+} intercalated layered oxides with MO/Ln^{3+}/MO (M = Ti, Nb, and Ta) sandwich structure[4,5] and some perovskite oxide nanosheets with Ln^{3+} in the A site.[1,3] Here, we report an intense emission in the photoluminescence of Ln^{3+} adsorbed on the oxide nanosheets, i.e., Ln^{3+}/MO. In this paper, various photoluminescence properties of Ln^{3+}/MO are demonstrated comparing with those of some photoluminescent perovskite oxide nanosheets containing Ln^{3+} inside the nanosheet, and the photoluminescence mechanism is discussed.

Experimental

Materials. In this study, we used some oxide nanosheets such as $Ti_{1.825}O_4$ (TiO), Nb_6O_{17} (NbO), $Gd_{1.4}Eu_{0.6}Ti_3O_{10}$ (GETiO), and $La_{0.7}Tb_{0.3}Ta_2O_7$ (LTTaO). These nanosheets (nanosheet solutions) were prepared by the same methods as reported in previous papers.[1,5] It was proven from the nanosheet thickness measured by atomic force microscopy, that the nanosheets exist as mono-nanosheet (0.84 nm for TiO, 1.03 nm for NbO, 2.4 nm for GETiO, and 1.8 nm for LTTaO).

Preparation of Mono-Nanosheet Films. The nanosheets were attached on a quartz substrate layer by layer (LBL) as follows. A quartz plate was used as a substrate in this study. Substrates were primed in $2.5\,g\,L^{-1}$ aqueous poly(ethyleneimine) (PEI) solution for 20 min to charge the surface of the substrates positively. Primed substrates were dipped into a colloidal solution with negatively charged MO (M = Ti, Nb, Ta, GETi, and LTTa) nanosheets. Mono-nanosheet films were formed on the substrate surfaces for all the samples.

Preparation of Ln^{3+}-Adsorbed Oxide Nanosheets. The quartz substrates covered with mono-nanosheets were immersed in a solution containing Eu^{3+} or Tb^{3+} ions (1×10^{-2} M $Ln(CH_3COO)_3$) for 20 min, and then immersed in pure water for 30 s. The samples were dried under pure N_2 at room temperature. The Ln^{3+} adsorbed on the oxide nanosheets prepared by the above simple process are represented as Ln^{3+}/MO in this paper.

Photoluminescence Measurement. Figure 1 shows a schematic illustration of the system used for the measurement of the photoluminescence. Excitation and emission spectra were analyzed with a Jasco FP-6500 spectrofluorometer with a 150 W Xe lamp source. Excitation and emission spectra of Ln^{3+}/MO films were prepared, the films were put in a triangle quartz cell filled with several aqueous solutions (aqueous solution, aqueous metal ion solution, and aqueous methanol solution).

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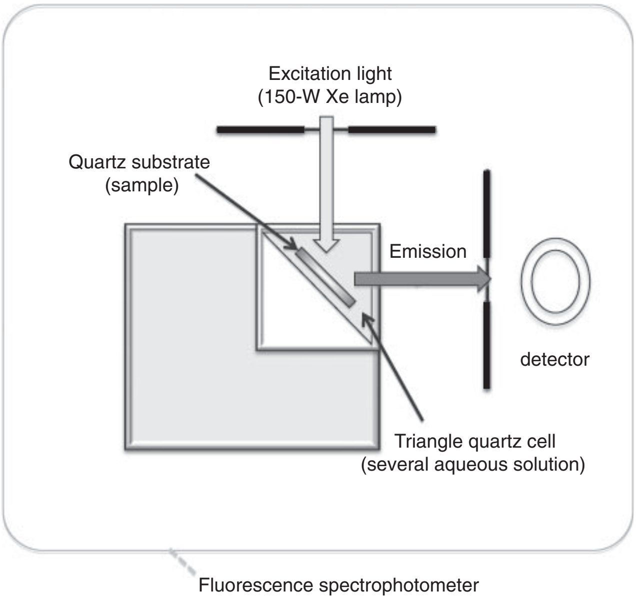

Figure 1. Schematic illustration of method used for the measurement of the photoluminescence.

Characterization and Equipment. The amount of the adsorbed Ln^{3+} was analyzed by means of an inductively coupled plasma (ICP) spectrophotometer (SEIKO Instruments, SPS7800). The emission decay curves were plotted on the basis of the time-resolved emission spectra, which were obtained by using a Perkin-Elmer LS 55 fluorescence spectrometer.

Results and Discussion

Adsorbed H_2O Effect. Figures 2a and 2b show photoluminescence spectra of the Eu^{3+}/TiO and Tb^{3+}/NbO in pure water respectively. Intense characteristic emissions of the adsorbed Ln^{3+} appeared. Both the emissions result from the energy transfer from the band gap excitation of the oxide nanosheets to the adsorbed Ln^{3+}, judging from the excitation spectra. On the other hand, no such intense emission was observed for polycrystalline TiO_2 particle film such as P25 (consisting of about 20 nm particles) on which Eu^{3+} was adsorbed. Thus, the nanosheet with special structure is necessary for the present intense emissions of the adsorbed Ln^{3+}. The photoproduced electron and hole separately exist in the inside and on the nanosheet surface respectively,[14] while those closely exist to bring about easy surface recombination at the polycrystalline particle surface, leading to no energy transfer.

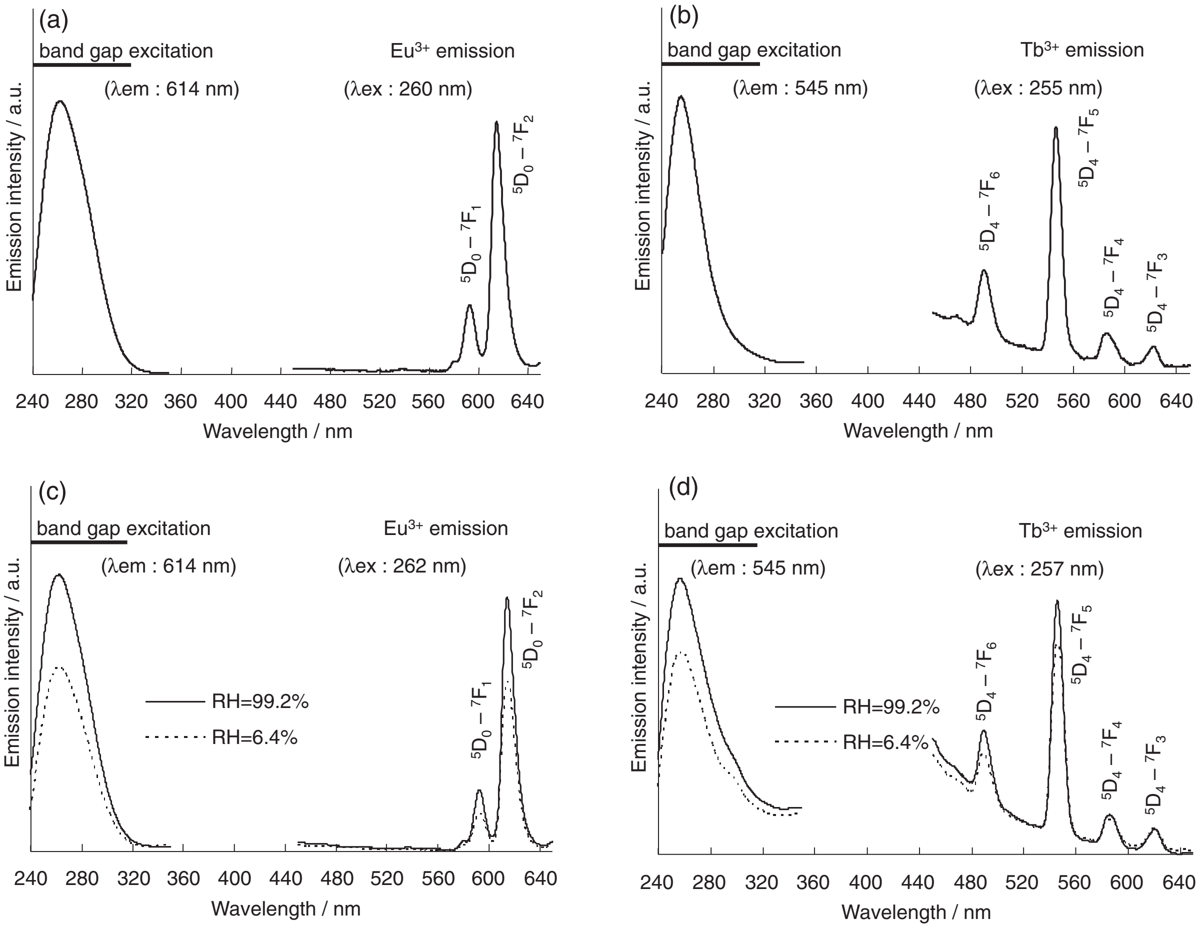

Figure 2. Photoluminescence spectra of the Eu^{3+}/TiO (a and c) and Tb^{3+}/NbO (b and d) in water (a and b) and air with relative humidities (RH) (c and d).

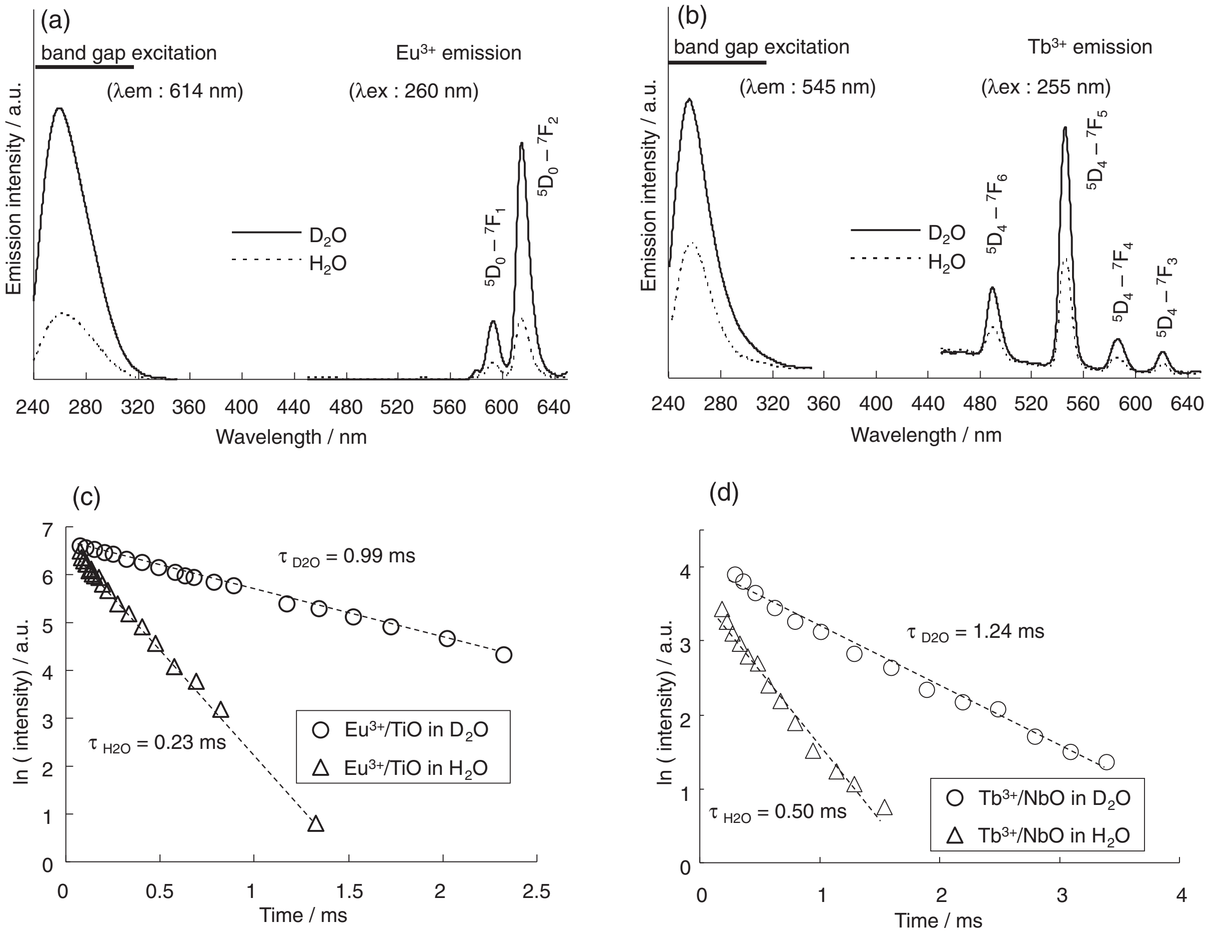

Figure 3. Photoluminescence spectra of the Eu^{3+}/TiO (a) and Tb^{3+}/NbO (b) in H_2O and D_2O. Time-resolved emission of the Eu^{3+}/TiO and Tb^{3+}/NbO are shown in (c) and (d) respectively.

Figures 2c and 2d show photoluminescence spectra of the Eu^{3+}/TiO and Tb^{3+}/NbO in air respectively, where relative humidity (RH) was changed by setting a cell containing various H_2SO_4/H_2O solutions in the measurement chamber. The emission intensity increased with the increase of RH for both the samples. This (together with the results in Figures 2c and 2d) indicates that the energy transfer from the nanosheet band gap excitation to the adsorbed Ln^{3+} is promoted by the coadsorbed H_2O on the surface. As a matter of course, no effect of the adsorbed H_2O was observed for either the GETiO or LTTaO nanosheets, because the Ln^{3+} exists on the inside of the nanosheets and therefore H_2O in air does not directly attach to the Ln^{3+}.

D_2O Effect. Figures 3a and 3b show photoluminescence spectra of the Eu^{3+}/TiO and $Tb^{3+/}$NbO in D_2O and H_2O solutions respectively. Emission intensities in D_2O stronger than those in H_2O were observed for both the samples. The lifetimes calculated from the decay curves shown in Figures 3c and 3d were longer in D_2O than in H_2O for both the samples (The lifetimes in D_2O and H_2O were 0.99 and 0.23 ms for the Eu^{3+}/TiO respectively, and those in D_2O and H_2O were 1.24 and 0.50 ms for the Tb^{3+}/NbO respectively.).

It is known that, in general, the excited states relax via two competitive paths. One is by light emission, and the other is by phonon emission (radiationless quenching); the latter path applies to the present case. The rate of phonon emission, ω, depends on the phonons simultaneously emitted to bridge the energy gap, and is expressed as

$$\omega \propto \exp(-k\Delta E/h\nu_{\max}) \qquad (1)$$

Where ΔE is the energy gap to the nearest lower level and $h\nu$ is the maximum energy of phonons coupled to the emitting state[16,17] The phonon emission rate, ω, decreases rapidly with increasing ΔE, so that the competitive light emission or radiative process becomes dominant. Large values of $h\nu_{\max}$ also quench light emission. Therefore, in general, the photoluminescence of Ln^{3+} ions strongly depends on the chemical environment of the ions, and Ln^{3+} ions exhibit a stronger luminescence in D_2O than in H_2O because of the smaller phonon energy of D_2O ($\nu_{\text{O–D,stretch,max}} \approx 2800\,\text{cm}^{-1}$) than that of H_2O ($\nu_{\text{O–H,stretch,max}} \approx 3600\,\text{cm}^{-1}$).[18] This indicates that the general quenching effect of Ln^{3+} emission by H_2O occurs in the interlayer of Ln^{3+}/MO. Thus, the photoluminescence properties of Ln^{3+}/MO films are dependent on the hydration state of the water molecules surrounding the Ln^{3+} ions in the interlayer, as occurs in general with Ln^{3+} ions in aqueous solution. From the lifetimes of Ln^{3+} in H_2O and D_2O, it is possible to evaluate the number of water molecules directly coordinated to interlayer Ln^{3+}, q^{Ln}, by the following equation:

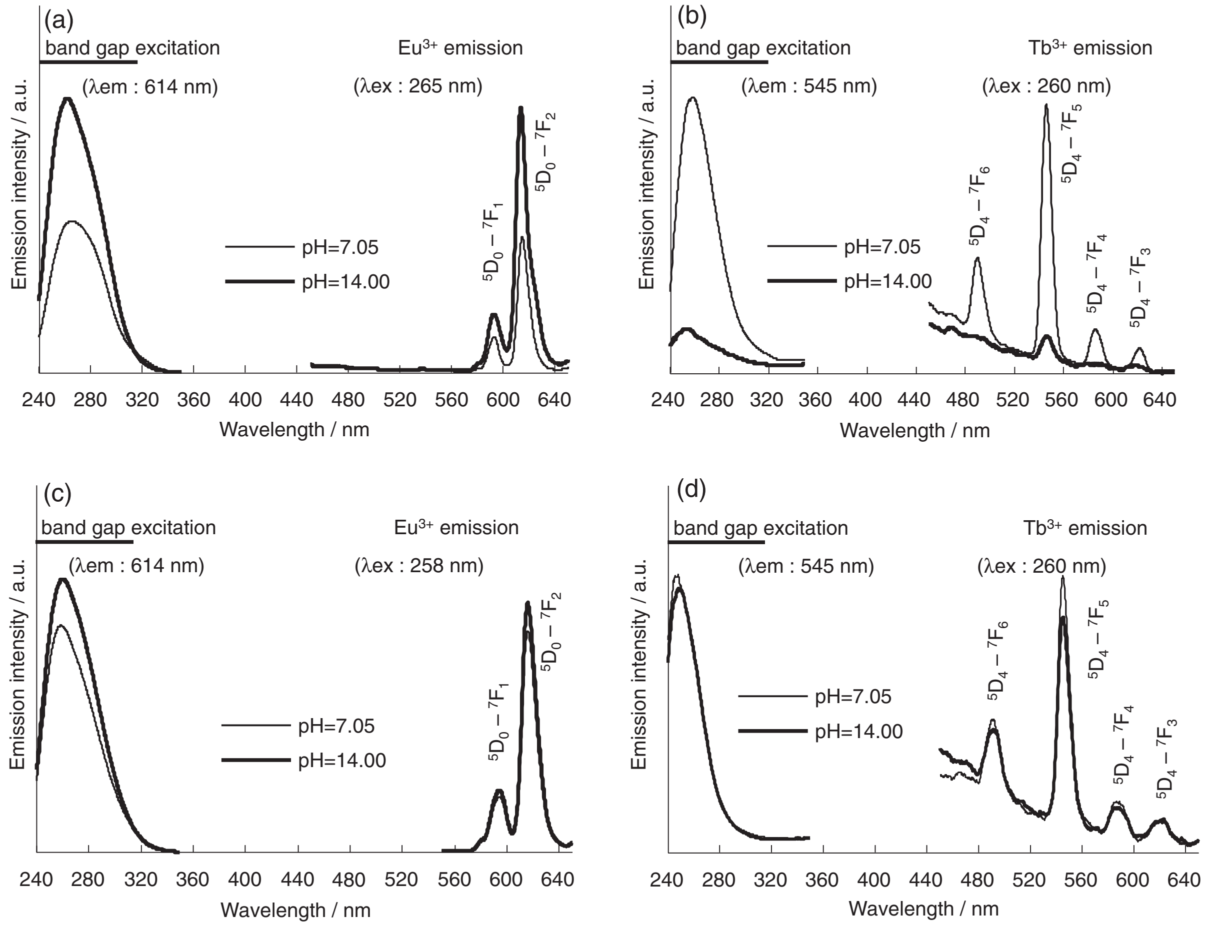

Figure 4. pH Dependences of emission intensities of Eu^{3+}/TiO (a), Tb^{3+}/NbO (b), $Gd_{1.4}Eu_{0.6}Ti_3O_{10}$ (GETiO) (c), and $La_{0.7}Tb_{0.3}Ta_2O_7$ (LTTaO) (d).

$$q^{\mathrm{Eu}} = 1.2[(1/\tau_{\mathrm{HEu}}) - (1/\tau_{\mathrm{DEu}}) - 0.25] \tag{2}$$

$$q^{\mathrm{Tb}} = 5.0[(1/\tau_{\mathrm{HTb}}) - (1/\tau_{\mathrm{DTb}}) - 0.06] \tag{3}$$

Where τ_{HLn} and τ_{DLn} are luminescence lifetimes of Ln^{3+} in H_2O or D_2O, respectively.[19–22] Thus the Eu/TiO film has 3.7 inner sphere water molecules, and the Tb/NbO film has 5.7 inner sphere water molecules.

pH Effect. Figures 4a and 4b show pH dependences of the emission intensities of the Eu^{3+}/TiO and Tb^{3+}/NbO respectively. The intensity for the Eu^{3+}/TiO decreased at low pH, while that for the Tb^{3+}/NbO decreased at high pH. Similar pH dependences of the emission intensities of the GETiO and LTTaO samples were observed as shown in Figures 4c and 4d respectively, although the effects were small. The following two mechanisms can be surmised for the pH dependence.

1) The recombination between the produced hole and electron will be promoted at low pH. The photoproduced electron and hole exist inside the nanosheet and on the surface O^{2-} respectively.[14] Adsorbed H^+ on the surface at low pH will push the hole from the surface to the inside and attract the electron from the inside to the surface by electrostatic force, and therefore the recombination will be promoted to suppress the energy transfer at low pH. This effect will be pronounced for the Ti oxide nanosheets (Figures 4a and 4c).

2) The bonding state of the adsorbed H_2O surrounding Ln^{3+} for the Ln^{3+}/MO samples will be changed by pH.[4] At high pH, the number of H_2O molecule surrounding Ln^{3+} increases, resulting in the increase of the energy transfer. This effect will be pronounced for the Tb^{3+}/NbO (Figure 4b). As previously explained a difference of number of the inner sphere water molecules affects the emission of light in Eu/TiO and Tb/NbO.

Other Ions and Solvent Effects. Figure 5 shows effects of added Co^{2+}, Ag^+, and CH_3OH on the photoluminescence spectra. The addition of transition-metal cations such as Co^{2+} and Ag^+ (2.5×10^{-2} M) brought about a decrease in the emission intensities for all the Ln^{3+}/MO samples (Figures 5a and 5b). This is due to photoreaction (photodeposition) leading to consumption of the photoproduced electron and hole. As a result, the energy transfer decreases to bring about a decrease in the emission intensity. Table 1 shows the quantity of each ion (Ln^{3+}) of several aqueous solutions after immersing samples for five minutes. It was found that ion exchange occurred to the greatest degree in water, however the very small degree to which it occurred did not affect the emission.

CH_3OH brought about change in the emission intensity (Figures 5c and 5d). Two mechanisms can be rationalized. One as in the case of Co^{2+} and Ag^+ adsorptions, is photooxidation of alcohol. The other is the decrease of the amount of adsorbed

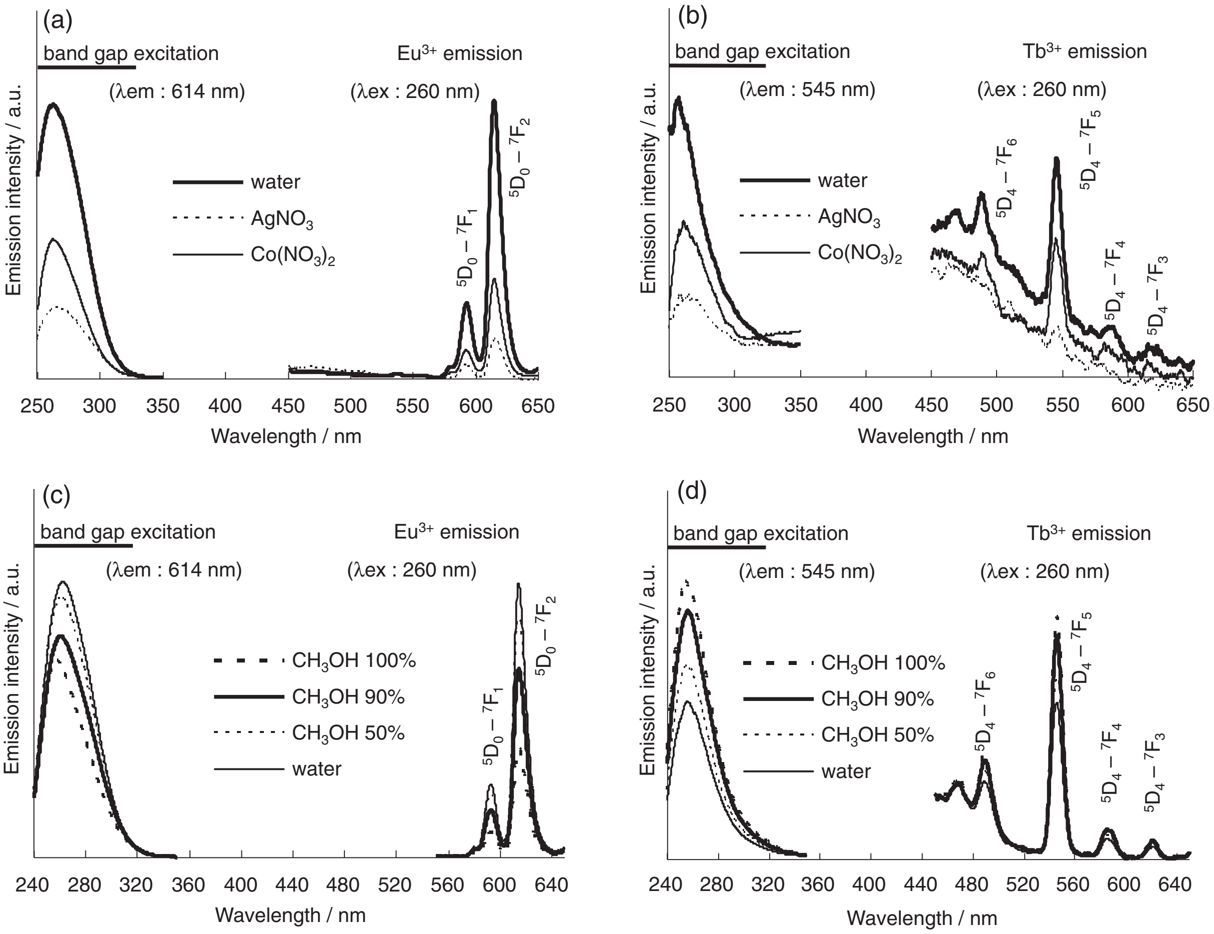

Figure 5. Photoluminescence spectra of the Eu^{3+}/TiO (a and c) and Tb^{3+}/NbO (b and d) in Ag^+ and Co^{2+} solutions (a and b), and CH_3OH (c and d) solutions.

Table 1. Quantity of Exchange of the Ln^{3+} Ions of Solvents

Solvent	Eu^{3+}/ppm	Tb^{3+}/ppm
H^+	0	0.037
Co^{2+}	0	0
Ag^+	0	0.002

H_2O on the nanosheet surface in alcohol solutions. These will bring about a decrease in the emission intensity as in the case of Eu^{3+}/Ti (Figure 5c). However, the increase in the intensity for Tb^{3+}/NbO suggests direct promotion by CH_3OH of the emission. Consequently, the change of the emission intensity by addition of transition-metal ions and alcohol suggests that the Ln^{3+}/MO will act as a sensor using photoluminescence to analyze ions and organic molecules in solution.

Conclusion

Intense emissions of Ln^{3+} ions (Eu^{3+} and Tb^{3+}) adsorbed on TiO and NbO nanosheets were observed. This photoluminescence results from the energy transfer from the band gap excitation of the nanosheets to the adsorbed Ln^{3+}. Coadsorbed H_2O increased the emission intensities of the adsorbed Ln^{3+}. Hydrogen-bonding networks between O^{2-} ions of the nanosheet surface and the adsorbed H_2O surrounding Ln^{3+} will promote the energy transfer for Ln^{3+}/MO. The intensity increased in D_2O because of the decrease of phonon effect of coadsorbed water molecules. Consequently, the energy transfer promotion by the coadsorbed H_2O is stronger than the phonon effect, leading to the increase of the emission intensity in high humidity and water. The emission intensity of the Eu^{3+}/TiO and the Tb^{3+}/NbO, while Co^{2+} and Ag^+ addition decreased the emission intensity because the photoproduced electron and hole in the nanosheets are consumed by photoelectrochemical reactions.

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