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# Electrochemistry, Electrodeposition, and Photoluminescence of Eu (III)/Lanthanides (III) on Terpyridine-Functionalized Ti Nanospikes

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**Abstract:** Terpyridine-functionalized Ti nanospike electrodes (TiNS-SiTpy) were developed and applied to cyclic voltammetry and amperometry of Ln (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) ions and mixed Eu (III) + Ln (III) ions in a 0.1 M NaClO<sub>4</sub> electrolyte. Electrodeposition was successfully performed over TiNS-SiTpy electrodes, which were fully examined by scanning electron microscopy, X-ray diffraction crystallography, Fourier-transform infrared spectroscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, photoluminescence (PL), and PL decay kinetics. The Gd and Tb ions were found to increase PL intensities with 10× longer lifetimes of 1.32  $\mu$ s and 1.03  $\mu$ s, respectively, compared with that of the electrodeposited Eu sample. The crystal phase and the oxidation states were fully examined for the mixed Ln (Eu + Gd and Eu + Tb) complex structures.

**Keywords:** lanthanide; Ti nanospike; electrodeposition; cyclic voltammetry; amperometry; photoluminescence

# 1. Introduction

Lanthanide (Ln) elements have very usefully appeared in diverse application fields such as display industry, magnets, bio industry, pyroprocessing technology in nuclear power plants, and energy/environment fields [1-10]. The Ln elements have very unique and similar physicochemical properties because of electronic configurations in 4f-block in the periodic table. To achieve better roles of Ln elements, the studies on Ln elements include Ln coordination chemistry, electrochemical Ln redox reactions, luminescent materials, and selective recovery (for recycling of precious elements) by electrodeposition [11–23]. Bejan et al. synthesized three-dimensional Ln-organic frameworks of [LnL (H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·DMF·yH<sub>2</sub>O with a surface area of about 400  $m^2/g$  by the solvothermal method and demonstrated as a catalyst in acylation reaction of 2-naphthol with acetic anhydride [11]. Lu et al. synthesized Tb (III) and Eu (III)-organic complex-doped silica nanoparticles with high luminescent properties and embedded in transparent membranes by the electrospinning method for their applications to fluorescent clothing, counterfeiting, and labels [14]. Fan et al. synthesized monodispersed  $\alpha$ -NaYF<sub>4</sub>:RE<sup>3+</sup> (RE = Eu, Tb, Ce, Er, and Tm) colloidal spheres and achieved multi-color emissions with orange-red, green, UV emission, bluegreen, and blue depending on the excitation wavelength [17]. They also applied the spheres to in vitro cell imaging. Joo et al. have demonstrated electrodeposition of Ln elements on diverse electrodes such as carbon, Ni, and porous Si, and showed that Ln elements were successfully recovered on the electrodes [21-23].

The main purpose of this study was to examine electrochemical behaviors in mixed Ln ions in an electrolyte and electrodeposit the elements on a Ti nanospike electrode in



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). view of recycling of precious elements and nanomaterial preparations. Eu (III) was chosen as a common ion in mixed Ln ions because it has been extensively used as a luminescence probe as well as hypersensitivity in the local coordination environment [24,25]. Gd (III) and Tb (III) as mixed ions were mainly selected for full characterization because they showed much higher luminescent properties than other electrodeposited materials prepared in other mixed Ln (III) ions. Terpyridine (Tpy)-functionalized Ti electrode was chosen because Tpy has three N atoms and acts as a Lewis basic ligand [26–28]. Therefore, the ligand may strongly interact with Lewis acidic Ln (III) ions at the electrode and electrolyte interface. Consequently, the electrochemistry and electrodeposition will be altered by the surface modification. The nanospike structure was developed to further increase contact areas between metal ions and the electrode surface. The newly developed electrode system and the new electrochemical tests provide valuable information on understanding Ln elements for their diverce applications in displays, bio industry, pyroprocessing technology, and energy/environment materials.

#### 2. Materials and Methods

Chemicals used in this study were (3-aminopropyl)trimethoxysilane (APTMS, 97%, Sigma-Aldrich, Saint Louis, MO, USA), 2,2':6',2''-terpyridine-4'-carboxylic acid (Tpy-COOH, 95%, Alfar Aesar, Ward Hill, MA, USA), La (III) nitrate hexahydrate (99.999%, Sigma-Aldrich), Dimethyl sulfoxide (anhydrous,  $\geq$ 99.9%, Sigma-Aldrich), Ce (III) nitrate hexahydrate (99%, Sigma-Aldrich), Pr (III) nitrate pentahydrate (99.9%, Alfa Aesar), Nd (III) nitrate hexahydrate (99.9%, Alfa Aesar), Sm (III) nitrate hexahydrate (99.9%, Alfa Aesar), Sm (III) nitrate hexahydrate (99.9%, Alfa Aesar), Eu (III) nitrate hexahydrate (99.9%, Alfa Aesar), Gd (III) nitrate hexahydrate (99.9%, Sigma-Aldrich), Tb (III) nitrate hydrate (99.9%, Alfa Aesar), Dy (III) nitrate pentahydrate (99.9%, Sigma-Aldrich), Ho (III) nitrate pentahydrate (99.9%, Alfa Aesar), Er (III) nitrate hydrate (99.9%, Sigma-Aldrich), Tm (III) nitrate hydrate (99.9%, Alfa Aesar), Er (III) nitrate hydrate (99.9%, Sigma-Aldrich), Tm (III) nitrate hydrate (99.9%, Alfa Aesar), and Yb (III) nitrate hydrate (99.9%, Sigma-Aldrich).

Titanium (Ti) sheets (5 mm  $\times$  20 mm) were cleaned by sonication in acetone, isopropyl alcohol, and water repeatedly. After that, the cleaned Ti sheets were dipped in a 1% HF solution for 30 min. Then, a nanospike morphology was finally achieved. For surface functionalization with terpyridine group, Ti nanospikes (abbreviated as TiNS) were first dipped in a H<sub>2</sub>O/NH<sub>3</sub> (aq. 25.0–30.0%)/H<sub>2</sub>O<sub>2</sub> (aq. 34.5%) (5:3:1, v/v) solution at 60 °C for 1 h, rinsed with deionized water, and dried under N<sub>2</sub> gas blowing. The OH-terminated TiNS substrate was dipped in methanol with 1% APTMS for 12 h, rinsed with methanol, and dried under N<sub>2</sub> gas blowing. The APTMS-functionalized TiNS substrate was then dipped in a 1 mM Tpy-COOH/DMSO solution for 6 h, rinsed with pure DMSO solvent, and dried under N<sub>2</sub> gas blowing. The details of the functionalization procedure are described elsewhere [26–28]. Consequently, terpyridine-functionalized TiNS was achieved and abbreviated as TiNS-SiTpy.

Electrochemical experiments of cyclic voltammetry (CV) and amperometry were performed in a three-electrode system (a working, a Pt wire counter, and a Ag/AgCl reference electrodes) using a ZIVE SP 1 Potentiostat/Galvanostat/EIS (WonATech Co., Ltd. Seoul, Korea). For the electrochemistry of a single Ln element, the concentration of Ln ions was 10 mM in a 0.1 M NaClO<sub>4</sub> supporting electrolyte. For the electrochemistry of mixed Ln ions (Eu and another Ln), the concentrations were 5 mM (Eu) and 5 mM (Ln), respectively, in a 0.1 M NaClO<sub>4</sub> electrolyte. The CV was performed between -1.8 V and +0.5 V (vs. Ag/AgCl). The fixed potential for amperometry was based on the CV profiles and amperometry electrodeposition was performed for 2 h. After the electrodeposition, the electrode samples were gently washed with deionized water and dried under an IR lamp.

The morphology of the electrodeposited samples was examined using a Hitachi SE-4800 field emission scanning electron microscope (FE-SEM, Hitachi Ltd., Tokyo, Japan) with an operating voltage of 10 kV. Optical microscope images ( $300 \times$  amplification) were also obtained to confirm the electrodeposition using a EG Tech EGVM-452M video microscope system (EG Tech., Gyounggi, Korea). Elemental composition of the electrodeposited samples was evaluated by energy dispersive X-ray spectroscopy (EDXS) analysis using a TESCAN LYRA3 XMU focused ion beam-SEM (Brno, Czech Republic). Fourier-transform infrared (FT-IR) spectra were obtained using a Thermo Scientific Nicolet iS10 spectrometer (Thermo Scientific Korea, Seoul, Korea) with attenuated total reflectance mode. Photoluminescence (PL) emission spectra of the electrodeposited samples were taken using a AvaSpec spectrometer (model ULS2048CL-EVO-RS, Louisville, CO, USA) equipped with a high-power deuterium halogen lamp (model AvaLight-DH-S-BAL, Louisville, CO, USA). 2D and 3D PL profiles were obtained using a Fluorescence spectrometer (FS-2, Scinco, Seoul, Korea) equipped with a 150 W Xe lamp. PL decay profiles were obtained using a FluoroLog 3 spectrometer (Horiba-Jobin Yvon, Kyoto, Japan) with a single photon counting photomultiplier tub and a pulsed laser diode 374 nm ( $\pm 10$ ). The crystal phases of the electrodeposited samples were investigated by X-ray diffraction crystallography using a MiniFlex II powder X-ray diffractometer (Rigaku Corp., Tokyo, Japan, CNU chemistry core-facility) with Cu K $\alpha$  radiation. The chemical states of the electrodeposited samples were examined by X-ray photoelectron spectroscopy (XPS) using a Thermo-VG Scientific K-alpha<sup>+</sup> spectrometer (Waltham, MA, USA) with a hemispherical energy analyzer and a monochromatic Al  $K\alpha$  X-ray source.

### 3. Results and Discussion

Figure 1 shows the cyclic voltammetry curves (initial cycle) at a scan rate of 0.2 V/s over TiNS-SiTpy electrodes in 5 mM Eu (III) + 5 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolytes, compared with the CV profiles in a blank 0.1 M NaClO<sub>4</sub>, 10 mM Ln (III)/0.1 M NaClO<sub>4</sub>, and 10 mM Eu (III)/0.1 M NaClO<sub>4</sub> electrolytes. For a single Ln element, cyclic voltammetry profiles were also obtained at 0.2 V/s over bare TiNS and TiNS-SiTpy electrodes in a 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte and are provided in the Supplemental Materials Figure S1 and Figure S2, respectively. In a blank 0.1 M NaClO<sub>4</sub> electrolyte, the CV profile (dotted gray line) between +0.5 V and -1.8 V (vs. Ag/AgCl) showed no meaningful redox peaks, except a sharp current increase (starting from -0.8 V during the negative-going scan) due to the hydrogen evolution reaction [21–23]. Upon addition of Ln (III) ions, the CV profile became meaningfully changed and a new curvature appeared between -0.9 V and -1.5 V. In 5 mM Eu (III) + 5 mM La (III)/0.1 M NaClO<sub>4</sub> electrolyte (Figure 1a), a curvature (or a CV peak) appeared around -1.25 V (vs. Ag/AgCl). Other CV profiles (Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Yb mixed Eu ions) showed the curvature between -1.4 V and -1.2 V. The peak position  $(\pm 0.01 \text{ V})$  was determined by the intersection point of the two crossing lines as depicted in the corresponding CV profile in Figure 1. Joo et al. also observed similar CV profiles for Ln (III) ions on carbon, Ni, and porous Si electrodes [21–23]. There was a weak inclination that the CV peak became slightly shifted to a positive direction, as shown in Figure 1n. This is plausibly due to sizes of lanthanide ions, known as lanthanide contraction, where the size is known to be decreased as the atomic number increases from La (No. 57) to Yb (No. 70) [21-23]. For Eu (III) ions, the CV peak position was observed to be around -0.9 V, about -0.3 V lower than other Ln (III) ions. It is possible that the reduction (Eu<sup>3+</sup> + e<sup>-</sup>  $\rightarrow$  Eu<sup>2+</sup>) of free Eu (III) ion was involved in this region [21–23].



**Figure 1.** Superimposed cyclic voltammetry profiles (**a**–**m**) at 0.2 V/s over TiNS-SiTpy electrodes in a blank 0.1 M NaClO<sub>4</sub> (thin gray lines), 5 mM Eu (III) + 5 mM Ln (III)/0.1 M NaClO<sub>4</sub> (thick lines), 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> (broken lines), and 10 mM Eu (III)/0.1 M NaClO<sub>4</sub> (red lines) electrolytes, the new peak positions (V vs. Ag/AgCl) with mixed Ln ions (**n**), and a schematic of the three electrode electrochemical system with a TiNS-SiTpy electrode (**o**). Each arrow indicates the intersection point of two crossing lines.

For the CV profiles over bare TiNS electrodes in unmixed (pure) Ln (III) ions of 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte, as displayed in the Supplemental Materials Figure S1, the CV peak for La (III) ion was observed around -1.5 V (vs. Ag/AgCl), and the potential was

observed at -1.35 V for Yb (III) ion. Except for the Eu (III) ion, the CV peak was observed between -1.5 V and -1.3 V for other Ln ions. For the CV profiles over bare TiNS-SiTpy electrodes in a 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte, as displayed in the Supplemental Materials Figure S2, except for the Eu (III) and La (III) ions, the CV peak was observed between -1.3 V and -1.15 V for other Ln ions. Generally, the functionalized electrodes showed lower negative potentials. The functionalized terpyridine appears to play a role in the electrochemical behavior, as depicted in Figure 10. Joo et al. performed CV using plain Ti and Ti-SiTpy sheets in a 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte. They observed that CV peaks were observed between -1.6 V and -1.4 V (vs. Ag/AgCl) and between -1.5 V and -1.2 V (vs. Ag/AgCl) in plain Ti and Ti-SiTpy sheets, respectively [28]. Compared with the present study (Supplemental Materials, Figures S1 and S2), the nanospike structure showed lower negative potentials than those for the plain Ti surfaces.

Electrodeposition of the Ln (III) species was performed by the amperometry method in a 5 mM Eu (III) + 5 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte at a fixed applied potential for 2 h. The applied potentials (La + Eu: -1.2 V, Ce + Eu: -1.4 V, Pr + Eu: -1.3 V, Nd + Eu: -1.3 V, Sm + Eu: -1.2 V, Eu: -1.2 V, Gd + Eu: -1.3 V, Tb + Eu: -1.2 V, Dy + Eu: -1.2 V, Ho + Eu: -1.2 V, Er + Eu: -1.3 V, Tm + Eu: -1.3 V, Yb + Eu: -1.2 V) were based on the CV profiles and the peak positions seen in Figure 1n. As seen in the selected superimposed CV profiles taken in 10 mM Eu (III)/0.1 M NaClO<sub>4</sub>, 5 mM Ln (III)+5 mM Eu (III)/0.1 M NaClO<sub>4</sub>, and 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolytes (Supplemental Materials Figure S3), the CV profiles in the mixed ions (5 mM Eu (III) + 5 mM Gd (III) or 5 mM Eu (III) + 5 mM Tb (III)) showed stronger CV peaks (marked by an up arrow,  $\uparrow$ ) compared with those in 10 mM Eu (III)/0.1 M NaClO<sub>4</sub> and 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolytes. This indicates that the newly enhanced signal was associated with the electrodeposition signal. The CV signal volume was increased and the peak position was shifted to a higher negative potential with increasing the concentration of the mixed ions (Supplemental Materials Figure S4).

For the stability of CV profiles, we observed that the CV volume was decreased after electrodeposition by the amperometry, compared with the initial CV, attributed to deposition of the Ln (III) ions present in the electrolyte (Supplemental Materials Figure S5a). In other words, the concentration of the Ln (III) ions in the electrolyte was decreased. It was observed that the CV volume was gradually decreased with increasing the CV cycles (Supplemental Materials Figure S5b), attributed to the deposition process as mentioned above. The CV volume of the electrodeposited material was also gradually decreased (Supplemental Materials Figure S5c). The film became gradually removed from the surface and hydrogen bubble was created by a hydrogen evolution reaction and some were trapped on the surface (Supplemental Materials Figure S5d).

Figure 2 shows the SEM images of the electrodeposited mixed Ln + Eu over TiNS-SiTpy electrodes. It was clearly seen that thick overlayers were formed on the electrode, compared with the electrode before deposition (Figure 2a,a1). Optical microscope images (Figure 2n1 and the Supplemental Materials Figure S6) clearly showed electrodeposited overlayers. The corresponding photos (Supplemental Materials Figure S6) of the electrodeposited electrodes showed a clear discrimination between the undeposited and deposited areas. For electrodeposited La + Eu, nanowire morphology was observed, while others showed stacked films and particulate morphologies. From Ce + Eu to Gd + Eu (from Figure 2c to Figure 2h), stacked film morphology was observed. On the other hand, particulate morphology started to appear from Tb + Eu (Figure 2i). Similar behavior (morphology change from film to particle with increasing the atomic number) was also observed for the electrodeposition on plain Ti electrodes [28]. Electrodeposition was also performed with TiNS electrodes in a 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte. The corresponding SEM and the optical microscope images are provided in the Supplemental Materials Figure S6a,b. Similar morphological change and clear deposition of the Ln elements were observed.



**Figure 2.** SEM (scanning electron microscope) images (**a**–**n**) of electrodeposited mixed Ln over TiNS-SiTpy electrodes in a 5 mM Eu (III) + 5 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte at an applied potential observed in the corresponding CV, and selected optical microscope images ( $300 \times$ ) for TiNS-SiTpy (**a**1) and electrodeposited mixed Yb + Eu on a nanospike electrode (**n**1), and insets show the magnified image of the corresponding SEM image.

Characterization of the electrodeposited samples was performed by EDXS to examine and confirm the presence of Ln elements and other elements such as oxygen and carbon. Figure 3a shows the EDXS profiles of electrodeposited Ln on TiNS-SiTpy electrodes prepared in a 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte. Figure 3b showed the EDXS profiles of electrodeposited Eu (red line), Eu + Gd (pink line) and Eu + Tb (green shaded line) on TiNS-SiTpy electrodes in a 5 mM Eu (III) + 5 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte. It was very clear that the Ln elements were detected based on the Ln M and Ln L signals, whose positions were linearly shifted to a high energy with increasing the atomic number [29]. The EDXS for Pm element was omitted because of radioactivity and prohibition. However, the Pm M and Pm L signal positions could be predicted from Figure 3a. For the La element (atomic no. = 57), La M signals were observed at 0.63 KeV and 0.84 KeV. The La L signals appeared at 4.67 KeV, 4.93 KeV, and 5.38 KeV. For Yb element (atomic no. = 70), Yb M signals were observed at 1.18 KeV and 1.51 KeV. The Yb L signals appeared at 7.41 KeV, 8.39 KeV, and 8.75 KeV. The Ln M and Ln L peak positions are summarized in Table 1.

The several other peaks at 0.26 keV, 0.39 KeV, and 0.52 KeV were attributed to C K, N K, and O K signals, respectively [29]. The Ti K<sub> $\alpha$ </sub> and Ti K<sub> $\beta$ </sub> signals (from the Ti support) were observed at 4.5 KeV and 4.93 KeV, respectively. A Cl K signal was also significantly observed at 2.63 KeV, attributed to trapped or complexed ClO<sub>4</sub> ion. The presence of ClO<sub>4</sub> ion was also confirmed by FT-IR spectroscopy below. For the EDXS of mixed Eu + Gd (pink line) and Eu + Tb (green shaded line) on TiNS-SiTpy electrodes (Figure 3b), mixed Ln L and Ln M signals were observed, indicating that two Ln elements were co-electrodeposited. The elemental atomic % ratios of Gd/Eu and Tb/Eu were estimated to be 5.66%/ 6.34% and 8.41%/10.96%, respectively (Supplemental Materials, Table S1). The co-deposition was also confirmed by XPS data, discussed below. EDXS elemental mapping images were obtained for the three selected samples (Supplemental Materials Figure S7). On the basis of the data, it was concluded that Gd and Eu (or Tb and Eu) were both uniformly deposited on the electrodes.

Complex formation and major functional groups were examined by taking FT-IR spectra of the electrodeposited samples. Figure 4a,b show the transmittance FT-IR spectra of electrodeposited Ln and mixed Eu + Gd (pink line) and Eu + Tb (green line) on TiNS-SiTpy electrodes, respectively. All the FT-IR profiles were observed to be very similar, indicating that all the electrodeposited materials had a similar metal complex. A strong and broad peak was commonly observed at 3590 cm<sup>-1</sup>, attributed to a stretching vibration of OH group. The corresponding bending vibration appeared at 1640 cm<sup>-1</sup>. Two strong peaks were observed between 1200 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> (shaded areas) and assigned to stretchings of both  $CO_3^{2-}$  and  $NO_3^{-}$  groups [30,31]. A strong peak was also observed at 1080 cm<sup>-1</sup>, assigned to the vibration of  $CIO_4^{2-}$  ion [32]. A broad peak around 600 cm<sup>-1</sup> was plausibly due to a Ln-O vibrational mode [33,34]. On the basis of the FT-IR data, it was concluded that the electrodeposited materials had OH/H<sub>2</sub>O,  $CO_3^{2-}$ ,  $NO_3^{-}$ , and  $CIO_4^{2-}$  groups with Ln-O bondings. The deduced complex was further discussed below, with the aid of XRD data.



**Figure 3.** EDXS (energy dispersive X-ray spectroscopy) profiles of electrodeposited Ln (**a**) and electrodeposited Eu (**b**, red line), Eu + Gd (**b**, pink line), and Eu + Tb (**b**, green shaded line) on TiNS-SiTpy electrodes. Si K signal was due to Si substrate for mounting electrodeposited materials.

Ln	Ln M (KeV)	Ln L (KeV)
La	0.63, 0.84	4.67, 4.93, 5.38
Ce	0.67, 0.88	4.87, 5.27, 5.61
Pr	0.71, 0.92	5.03, 5.49, 5.85
Nd	0.75, 0.99	5.23, 5.72, 6.09
Sm	0.82, 1.09	5.64, 6.2, 6.57
Eu	0.88, 1.15	5.83, 6.47, 6.84
Gd	0.92, 1.20	6.05, 6.72, 7.11
Tb	0.95, 1.25	6.25, 6.97, 7.36
Dy	1.01, 1.31	6.49, 7.26, 7.63
Но	1.05, 1.36	6.72, 7.51, 7.88
Er	1.09, 1.42	6.93, 7.79, 8.17

**Table 1.** EDXS (energy dispersive X-ray spectroscopy) Ln M and Ln L peak positions (KeV taken in 0.01 keV step).



**Figure 4.** Transmittance FT-IR (Fourier-transform infrared) spectra of electrodeposited Ln (**a**) and electrodeposited Eu (**b**, red line), Eu + Gd (**b**, pink line), and Eu + Tb (**b**, green line) on TiNS-SiTpy electrodes.

The crystal phase of the electrodeposited materials was examined by taking XRD. In Figure 5a, a TiNS-SiTpy electrode (before electrodeposition) shows XRD diffraction peaks at  $2\theta = 35^{\circ}$ ,  $39^{\circ}$ ,  $40.0^{\circ}$ ,  $53.0^{\circ}$ , and  $63^{\circ}$ , attributed to the (010), (002), (011), (012), and (110) crystal planes of hexagonal Ti (JCPDS 98-004-4872), respectively [28]. The XRD patterns were the same as those of bare TiNS. For the XRD patterns of electrodeposited Eu (Figure 5b), Eu + Gd (Figure 5c), and Eu + Tb (Figure 5d) on TiNS-SiTpy electrodes, four broad peaks (green shaded regions) were newly and clearly appeared around  $2\theta = 10^{\circ}$ ,  $20^{\circ}$ ,  $29^{\circ}$ , and  $50^{\circ}$ . All the electrodeposited materials showed very similar XRD profiles. In addition, very similar XRD profiles were also reported for electrodeposited Ln (III) species prepared in an unmixed Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte over diverse

electrodes [21–23,28]. These results are in good agreement with the FT-IR profiles that showed very similar for the three samples of electrodeposited Eu, Eu + Gd, and Eu + Tb on TiNS-SiTpy electrodes. On the basis of these similar XRD patterns and the previously reported literature [21–23,30], it was concluded that the electrodeposited materials had a complex of  $Ln_2(OH) \cdot (NO_3)_{y-z}(CO_3)_{y-z}(ClO_4)_z \cdot nH_2O$  complex [21–23,30]. Joo et al. also reported very similar XRD profiles for electrodeposited Ln materials on Ni and carbon sheet substrates and assigned a similar complex formula [21–23,30]. The crystal planes of the four broad peaks are shown on the corresponding peaks [30].



**Figure 5.** XRD (X-ray diffraction) profiles for bare (**a**, gray line), electrodeposited Eu (**b**, red line), Eu + Gd (**c**, pink line), and Eu + Tb (**d**, green line) on TiNS-SiTpy electrodes. Green shaded areas and star symbol indicate the major XRD peak positions of the complex.

The chemical states of the electrodeposited materials were examined by XPS (Figure 6). For the XPS of electrodeposited Eu (red line), Eu + Gd (pink line), and Eu + Tb (green line) on TiNS-SiTpy electrodes, the survey profiles (Figure 6a) commonly show Eu, Ti, O, and C elements. All the binding energies were not referenced and a charging effect may be slightly involved in the spectra. For the high resolution Eu 3d XPS profiles (Figure 6b), Eu element was commonly detected, as expected, and the Eu  $3d_{3/2}$  and Eu  $3d_{5/2}$  peaks were observed at 1166.2 eV and 1136.5 eV, respectively, with a spin-orbit splitting energy of 29.7 eV, assigned to Eu (III) oxidation state [25,35]. Two smaller peaks around 1157 eV and 1127 eV could be assigned to the Eu  $3d_{3/2}$  and Eu  $3d_{5/2}$  peaks of Eu (II) oxidation sate [25,35]. This indicates that Eu (II)-O species were possibly deposited in the reduction region. The ratio of Eu (III)/Eu (II) peaks was estimated to be  $14 \times$  and  $11 \times$  for electrodeposited Eu (red line) and Eu + Gd (pink line) on the electrodes, respectively. For the Tb 3d XPS profile of electrodeposited Eu + Tb (green line) on TiNS-SiTpy electrode (Figure 6c), the Tb  $3d_{3/2}$  and Tb  $3d_{5/2}$  peaks were observed at 1277.1 eV and 1242.5 eV, respectively, with a spin-orbit splitting energy of 34.6 eV, attributed to Tb (III) oxidation state [21,33,35]. For the Gd 3d XPS profile of electrodeposited Eu + Gd (green line) on TiNS-SiTpy electrode (Figure 6d), the Gd 3d<sub>3/2</sub> and Gd 3d<sub>5/2</sub> peaks were positioned at 1220.4 eV and 1188.1 eV, respectively, with a spin-orbit splitting energy of 32.3 eV, attributed to Gd (III) oxidation state [22,34,35].



**Figure 6.** Survey (**a**), Eu 3d (**b**), Tb 3d (**c**), Gd 3d (**d**), O 1s (**e**), Ti 2p (**f**), and C 1s (**g**) XPS spectra for electrodeposited Eu (red line), Eu + Gd (pink line) and Eu + Tb (green line) on TiNS-SiTpy electrodes.

For the Ti 2p XPS profiles (Figure 6f), Ti  $2p_{1/2}$  and Ti  $2p_{3/2}$  XPS peaks were commonly observed at BEs of around 464.9 eV and 459.2 eV, respectively, with a spin-orbit splitting of 5.7 eV. This was attributed to Ti (IV) oxidation state [36,37]. For the O 1s XPS profiles, two broad regions were observed at 531.0 eV and 533.0 eV. The lower BE peak was attributed to the lattice oxygen of Ti-O and/or Ln-O [36,37]. The higher BE peak was assigned to surface/complex species of OH/H<sub>2</sub>O and defects [36,37]. The C 1s peaks commonly showed two broad regions around 290.4 eV and 285.5 eV. The lower BE peak was due to C-C species, while the higher BE peak was plausibly due to C-O species such as carbonates [21,33,35].

Figure 7a displays the photoluminescence (PL) emission spectra of electrodeposited mixed Eu + Ln on TiNS-SiTpy electrodes at an excitation wavelength of 395 nm. The 395 nm light matches the  ${}^{5}L_{6} \leftarrow {}^{7}F_{0}$  (ground state) transition energy of Eu (III) ion. It was quite interesting that the electrodeposited Eu, Eu + Gd, and Eu + Tb samples showed strong emission signals, while other PL emission signals were very weak. Several sharp peaks were observed and attributed to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  transitions [25,38];  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  (578.5 nm),  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  (587.2 nm, 594.6 nm),  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  (612.6 nm, 615.4 nm, 619.2 nm, and 623.1 nm),  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$  (649.3 nm and 653.6 nm), and  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  (686.8 nm, 691.9 nm, 699.4 nm, and

703.4 nm). Several peaks for each  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  transition were attributed to the 2J+1 sublevel splittings under crystal field potential. For the 2D/3D-photoluminescence mapping profiles of the selected electrodeposited Eu (Figure 7b,b1), Eu + Gd (Figure 7c,c1), and Eu + Tb (Figure 7d,d1) samples, the dense regions are mainly at an excitation wavelength of 395 nm, corresponding to the  ${}^{5}L_{6} \leftarrow {}^{7}F_{0}$  transition energy [25]. The  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  transition regions were also quite densely spaced. On the basis of the PL profiles, it could be concluded that characteristic emission of Eu (III) ion was active when Gd (III) and Tb (III) ions were mixed. Furthermore, Gd (III) ion improved the emission of Eu (III) compared with that of electrodeposited Eu.



**Figure 7.** Emission spectra (**a**) of electrodeposited mixed Eu + Ln on TiNS-SiTpy electrodes and the selected 2D/3D-photoluminescence mapping profiles for electrodeposited Eu (**b** and **b1**), Eu + Gd (**c** and **c1**), and Eu + Tb (**d** and **d1**). Inset photos show the corresponding samples under UV light.

Photoluminescence decay kinetics were evaluated for the selected electrodeposited Eu, Eu + Gd and Eu + Tb samples, and the PL decay curves are displayed in Figure 8. The PL emission line was fixed at 610 nm, corresponding to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition. A third-order exponential decay function was used and the consequent fitting parameters are summarized in Table 2. The average lifetimes were measured to be 0.12 µs, 1.32 µs, and 1.03 µs for the Eu, Eu + Gd, and Eu + Tb samples, respectively. The Eu + Gd sample showed the longest lifetime. As a consequent result, the strongest PL emission signal was observed for the Eu + Gd sample shown in Figure 7 above.



**Figure 8.** PL (photoluminescence) decay curves at 610 nm emission line at an excitation wavelength of 374 nm for electrodeposited Eu (red dots), Eu + Gd (pink dots), and Eu + Tb (green dots).

**Table 2.** Fitting parameters of the PL (photoluminescence) decay curves in Figure 8 for electrodeposited Eu, Eu + Gd, and Eu + Tb on TiNS-SiTpy electrodes.

Parameters *	Eu/TiNS-SiTpy	Eu + Gd/TiNS-SiTpy	Eu + Tb/TiNS-SiTpy	
τ <sub>1</sub> (μs)	0.14601	0.92757	0.37351	
τ <sub>2</sub> (μs)	1.08873	4.52343	1.92062	
τ <sub>3</sub> (μs)	0.00232	0.15218	0.07966	
B <sub>1</sub>	142.7179	529.1066	545.0598	
B <sub>2</sub>	258.5388	225.3185	721.3731	
B <sub>3</sub>	2167.448	441.1102	303.7022	
R <sub>1</sub>	0.05556	0.442569	0.347142	
R <sub>2</sub>	0.100649	0.188467	0.459434	
R <sub>3</sub>	0.84379	0.368965	0.193424	
А	192.6185	412.9804	943.3153	
x <sup>2</sup>	1.04538	1.04873	1.038885	
$\tau_{average}$ (µs)	0.11965 (±0.0366)	1.31918 (±0.163)	1.02747 (±0.0825)	
$KI(t) = A + \sum B_i e^{\frac{-t}{\tau_i}}$ , $R_i = B_i / (\sum_{j=1}^{3} B_j)$ , $\tau_{amerage} = \sum_{j=1}^{3} R_j \cdot \tau_i$ , $R = \text{the relative ratio factor.}$				

\*  $I(t) = A + \sum_{i} B_i e^{\overline{\tau_i}}$ ,  $R_i = B_i / (\sum_{i=1}^{n} B_i)$ ,  $\tau_{average} = \sum_{i=1}^{n} R_i \cdot \tau_i$ , R = the relative ratio factor.

## 4. Conclusions

To further understand the electrochemistry of lanthanide ions, electrochemical tests of cyclic voltammetry and amperometry were performed using TiNS-SiTpy electrodes for Ln (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) ions and mixed Eu (III) + Ln (III) ions in a 0.1 M NaClO<sub>4</sub> electrolyte. Electrodepositions of the single and mixed Ln ions were successfully performed on the functionalized Ti nanospike electrodes. The physicochemical properties of the electrodeposited materials were fully examined by SEM, XRD, EDXS, FT-IR, XPS, PL, and PL decay kinetics. On the basis of XRD and FT-IR profiles, the electrodeposited materials had a similar complex structure of  $Ln_2(OH) \cdot (NO_3)_{V-z}(CO_3)_{V-z}(CIO_4)_z \cdot nH_2O$ . EDXS confirmed the electrodeposited Ln elements, the composition of the mixed Ln elements, and the elements of the functional groups. XPS further confirmed the oxidation states of the Ln elements. PL emission signals were strongly observed for electrodeposited Eu, Eu + Gd, and Eu + Tb samples. The emission signals were assigned to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J(=0,1,2,3,4)}$  transitions of Eu (III) ions. The PL lifetimes were measured to be 0.12  $\mu$ s, 1.32  $\mu$ s, and 1.03  $\mu$ s for the Eu, Eu + Gd, and Eu + Tb samples, respectively. It was observed that Tb and Gd enhanced the PL emission, while other Ln ions negated the emission signal of Eu (III) ions. Tb and Gd additions exhibited longer lifetimes.

The present unique results can provide very useful information on lanthanide (display) material designs, electrochemical application tests, electrochemical recovery for recovery from wastes, and other Ln-related material understanding.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10 .3390/met11060977/s1, Figure S1: Cyclic voltammetry profiles in a 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte over bare TiNS electrodes; Figure S2: Cyclic voltammetry profiles in a 10 mM Ln (III)/0.1 M NaClO<sub>4</sub> electrolyte over TiNS-SiTpy electrodes; Figure S3: Selected superimposed cyclic voltammetry profiles; Figure S4: Selected superimposed cyclic voltammetry profiles; Figure S5: CV profiles and a photo; Figure S6: SEM and the corresponding optical microscope (300×) images; Figure S7: EDXS elemental mapping images; Table S1: EDXS elemental atomic composition ratios (%).

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