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Ce³⁺/Eu²⁺ Doped Al₂O₃ Coatings Formed by Plasma Electrolytic Oxidation of Aluminum: Photoluminescence Enhancement by Ce³⁺ → Eu²⁺ Energy Transfer

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Abstract: Plasma electrolytic oxidation (PEO) of aluminum in electrolytes containing CeO₂ and Eu₂O₃ powders in various concentrations was used for creating Al₂O₃ coatings doped with Ce³⁺ and Eu²⁺ ions. Phase and chemical composition, surface morphology, photoluminescence (PL) properties and energy transfer from Ce³⁺ to Eu²⁺ were investigated. When excited by middle ultraviolet radiation, Al₂O₃:Ce³⁺/Eu²⁺ coatings exhibited intense and broad emission PL bands in the ultraviolet/visible spectral range, attributed to the characteristic electric dipole 4f⁰5d¹ → 4f¹ transition of Ce³⁺ (centered at about 345 nm) and 4f⁶5d¹ → 4f⁷ transition of Eu²⁺ (centered at about 405 and 500 nm). Due to the overlap between the PL emission of Al₂O₃:Ce³⁺ and the PL excitation of Al₂O₃:Eu²⁺, energy transfer from Ce³⁺ sensitizer to the Eu²⁺ activator occurs. The energy transfer is identified as an electric dipole–dipole interaction. The critical distance between Eu²⁺ and Ce³⁺ ions in Al₂O₃ was estimated to be 8.6 Å by the spectral overlap method.

Keywords: plasma electrolytic oxidation; Al₂O₃; energy transfer; photoluminescence; Ce³⁺/Eu²⁺

1. Introduction

Ce³⁺ and Eu²⁺ ions have found widespread use as activators in luminescent materials because their parity allows 4f¹ → 4f⁰5d¹ and 4f⁷ → 4f⁶5d¹ electric dipole transitions, respectively. Outer orbitals at 5d states of Ce³⁺ and Eu²⁺ ions are sensitive to crystal-field splitting and nephelauxetic effects [1,2], therefore, energy positions of excitation and emission bands of these ions can be tuned by changing the host matrix. Ce³⁺ ion also acts as an effective sensitizer due to its effective absorption [3]. Numerous studies demonstrated the importance and methods for enhancing the photoluminescence (PL) via an efficient energy transfer (e.g., [4,5]). The energy transfer from the Ce³⁺ sensitizer to the Eu²⁺ activator has been reported for some Ce³⁺/Eu²⁺ doped host lattices because of the spectral overlap between Ce³⁺ emission band and Eu²⁺ excitation band [6–9]. The aim of this work is to investigate PL properties of Ce³⁺/Eu²⁺ doped Al₂O₃ coatings created by plasma electrolytic oxidation (PEO) of pure aluminum and an energy transfer from Ce³⁺ to Eu²⁺ ions.

Recent investigations have shown that PEO process of aluminum is capable of preparation of Ce³⁺ and Eu²⁺ doped Al₂O₃ coatings in electrolyte enriched with CeO₂ and Eu₂O₃ particles, respectively [10,11]. As ionic radii of Al³⁺ (0.53 Å), and Eu³⁺ (0.95 Å) and Ce⁴⁺ (0.97 Å) [12] significantly differ, the substitution of Al³⁺ by either Eu³⁺ or Ce⁴⁺ produces oxygen vacancies that in turn distort the crystal lattice. The excess O^{2−} ions give their electrons to the lattice (2O^{2−} − 4e[−] → O₂), which are then captured by Ce⁴⁺ and Eu³⁺, leading to their reduction to Ce³⁺ and Eu²⁺, respectively [13].

Thus, the interactions of CeO_2 or Eu_2O_3 particles and Al_2O_3 coatings via the PEO process cause the reduction of Ce^{4+} to Ce^{3+} ions and Eu^{3+} to Eu^{2+} ions, enabling their efficient incorporation into Al_2O_3 . Our assumption was that $\text{Al}_2\text{O}_3\text{:Ce}^{3+}/\text{Eu}^{2+}$ coatings could be formed if the PEO of aluminum is performed with an electrolyte containing CeO_2 and Eu_2O_3 particles.

2. Materials and Methods

Pure aluminum foil (99.9%) with 0.25 mm thickness was used as a substrate in PEO. Before PEO, the substrate was cut into plates ($25 \times 10 \text{ mm}^2$), cleaned ultrasonically in acetone and ethanol, rinsed with distilled water, dried in a warm air stream and sealed with insulation resin leaving a working area of $\sim 15 \times 10 \text{ mm}^2$. PEO was carried out in a double-walled glass cell, with water cooling. The temperature of the electrolyte was kept at the constant (20 ± 1) °C during the PEO. Aluminum samples were used as an anode while the cathode was a cylinder of stainless steel. An aqueous solution of 0.1 M H_3BO_3 + 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ was employed as a supporting electrolyte. CeO_2 and Eu_2O_3 particles in different concentrations were added to the electrolyte. The magnetic stirrer allowed for the homogeneous particle distribution in the glass cell. The coatings were formed using a constant current density regime of 150 mA/cm^2 for 10 min. Following PEO, the samples were rinsed in distilled water and dried in warm air.

The surface morphology of formed coatings was examined by scanning electron microscope (SEM, Tokyo, Japan) JEOL 840A and surface elemental distribution were determined by the integrated energy-dispersive x-ray spectroscopy (EDS, Oxford, UK). Phase composition of created PEO coatings was analyzed by X-ray diffraction (XRD, Tokyo, Japan), using a Rigaku Ultima IV diffractometer over a scanning range of 20° – 80° with a 0.05° step size and $2^\circ/\text{min}$ scanning speed. The Kratos AXIS Supra photoelectron spectrometer using a monochromatic Al K_α source with the energy of 1486.6 eV was used for obtaining the X-ray photoelectron spectra (XPS). The base pressure in the analysis chamber was 5×10^{-8} Pa.

Room temperature PL spectral measurements were acquired by a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer (Edison, NJ, USA), with a 450 W xenon lamp as the excitation source, coupled to a double grating monochromator in a wavelength range 220–600 nm. A 290–850 nm double grating monochromator and a side-on Hamamatsu 928P photomultiplier tube (PMT) allowed for recording of the PL emission spectra. The spectra were corrected for the spectral distribution of the excitation lamp and the measuring system's spectral response.

3. Results and Discussion

3.1. PEO Coatings' Morphology, Phase and Chemical Composition

PEO is a high-voltage anodizing process of some metals (Al, Mg, Ta, Ti, etc.) and their alloys, combined with the plasma formation, as indicated by the presence of micro-discharges on the metal surface, and followed by the gas evolution [14]. High pressure ($\sim 10^2$ MPa) and temperature (10^3 K to 10^4 K) at the micro-discharge sites induce numerous processes (electrochemical, thermodynamical, and plasma-chemical) responsible for structural, compositional, and morphological modifications of the obtained oxide coatings. The PEO formed oxide coatings usually have crystalline phases with constituents originating from both the electrolyte and the metal. During the PEO of aluminum, Al_2O_3 layer grows at the oxide/electrolyte and aluminum/oxide interfaces as a consequence of a strong electric field ($\sim 10^7$ V/cm) induced relocation of $\text{O}^{2-}/\text{OH}^-$ and Al^{3+} ions across the oxide [15]. Moreover, melted aluminum and electrolyte components get drawn into the micro-discharge channels. From the channels, the oxidized aluminum gets ejected to the coating surface contacting the electrolyte. In that manner, the coating thickness increases around the channels. During the PEO, the electrophoretic effect drives CeO_2 and Eu_2O_3 particles towards the anode. Local temperature at the micro-discharge sites is higher than the melting points of CeO_2 and Eu_2O_3 particles (~ 2400 °C), enabling the molten particles to react with Al_2O_3 and form Ce and Eu ions doped Al_2O_3 coatings.

SEM images of coating surfaces, formed in supporting electrolyte by PEO, with the addition of CeO_2 and Eu_2O_3 particles in various concentrations, are shown in Figure 1a. PEO coating displays a porous morphology with pores of varying diameter and shape, which appear at the sites of the micro-discharge channels because of the gas evolution erupting the molten oxide material during the PEO process [16]. The surface morphology of the formed coatings does not significantly change with the addition of CeO_2 and Eu_2O_3 particles in supporting electrolyte. Elemental mapping by EDS shows that the main constituents of the coatings are uniformly distributed O, Ce, and Eu from the electrolyte and Al from the substrate (Figure 1b).

Figure 1. (a) SEM images of coatings created in supporting electrolyte: (i) Without addition CeO_2 and Eu_2O_3 and with the addition of (ii) 4 g/L CeO_2 , (iii) 4 g/L Eu_2O_3 , (iv) 4 g/L CeO_2 + 4 g/L Eu_2O_3 . (b) Energy-dispersive x-ray spectroscopy (EDS) maps of coating created in supporting electrolyte with the addition of 4 g/L CeO_2 + 4 g/L Eu_2O_3 .

Integrated EDS analysis of all coatings created in the experiment is given in Table 1. The content of Ce and Eu in the coatings increases with increased concentration of CeO_2 and Eu_2O_3 particles in supporting electrolyte, respectively.

Table 1. EDS analysis of plasma electrolytic oxidation (PEO) coatings coalesced in supporting electrolyte with different concentrations of added CeO_2 and Eu_2O_3 powders.

Concentration of Particles in Supporting Electrolyte	Atomic (%)			
	O	Al	Ce	Eu
4 g/L CeO_2	65.25	34.62	0.13	-
4 g/L Eu_2O_3	65.19	34.55	-	0.26
4 g/L CeO_2 + 0.5 g/L Eu_2O_3	64.89	34.95	0.10	0.06
4 g/L CeO_2 + 1 g/L Eu_2O_3	64.73	35.06	0.11	0.09
4 g/L CeO_2 + 2 g/L Eu_2O_3	64.39	35.35	0.11	0.16
4 g/L CeO_2 + 4 g/L Eu_2O_3	64.79	34.82	0.12	0.27
0 g/L CeO_2 + 0.5 g/L Eu_2O_3	64.95	34.98	-	0.07
4 g/L CeO_2 + 0.5 g/L Eu_2O_3	64.90	34.94	0.10	0.06
8 g/L CeO_2 + 0.5 g/L Eu_2O_3	64.99	34.73	0.21	0.07
12 g/L CeO_2 + 0.5 g/L Eu_2O_3	64.97	34.65	0.32	0.06

XRD patterns of created coatings are presented in Figure 2. Diffraction peaks corresponding to the gamma phase of Al_2O_3 (reference ICDD card No. 10-0425) and Al substrate (reference ICDD card No. 89-4037) are observed in XRD patterns. Obviously, the formation of gamma Al_2O_3 during the PEO is favored by the rapid solidification of molten alumina due to the contact with surrounding low-temperature electrolyte [17]. We were not able to detect any peaks corresponding to CeO_2 or Eu_2O_3 particles as well as any other Ce or Eu species, probably due to low concentration of incorporated Ce and Eu elements into Al_2O_3 coatings (Table 1).

Figure 2. (a) XRD patterns of coatings created in 0.1 M H_3BO_3 + 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ + 4 g/L CeO_2 with the addition Eu_2O_3 in different concentrations, (b) XRD patterns of coatings formed in 0.1 M H_3BO_3 + 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ + 0.5 g/L Eu_2O_3 with the addition CeO_2 in different concentrations.

For further investigation of the chemical nature and oxidation state of Ce and Eu in created coatings, we recorded a high-resolution Ce 3d and Eu 3d core-level spectra of Ce and Eu doped Al_2O_3 coating created in supporting electrolyte with the addition of 4 g/L CeO_2 + 4 g/L Eu_2O_3 particles (Figure 3). The peak deconvolution of the high-resolution XPS peaks of Ce 3d shows that the level of Ce ion is composed of four Gaussian peaks, i.e., two pairs of doublets ($3d_{5/2}$ at 881.5 eV and 885.3 eV, $3d_{3/2}$ at 899.5 eV and 903.9 eV), characteristic for Ce^{3+} oxidation state [18]. The Eu 3d core level spectrum consists of two doublets: (i) The Eu $3d_{5/2}$ (at 1135.3 eV) and Eu $3d_{3/2}$ (at 1165.3 eV) peaks, attributed to Eu^{3+} oxidation state, and (ii) at lower binding energies at ca. 1125.1 eV and 1155.2 eV, from the Eu^{2+} oxidation state [19]. These results indicate that interaction between CeO_2 and Eu_2O_3 particles with Al_2O_3 , under environmental conditions set by PEO, causes the reduction of Ce^{4+} ions to Ce^{3+} ions and the reduction of some of Eu^{3+} to Eu^{2+} ions in Al_2O_3 host (e.g., [10,11] and references therein).

Figure 3. (a) High-resolution XPS spectrum of Ce 3d, (b) high-resolution Eu 3d XPS spectrum of coating created with the addition of 4 g/L CeO_2 + 4 g/L Eu_2O_3 to the supporting electrolyte.

3.2. PL of $\text{Al}_2\text{O}_3:\text{Ce}^{3+}$ and $\text{Al}_2\text{O}_3:\text{Eu}^{2+}$ Coatings

The PL excitation and emission spectra of Ce^{3+} and Eu^{2+} singly doped Al_2O_3 coatings are presented in Figure 4. The PL excitation spectrum of $\text{Al}_2\text{O}_3:\text{Ce}^{3+}$ coating (Figure 4a) exhibited the broad band in the range from 250 to 340 nm and peaked at about 285 nm, corresponding to the direct excitation from the Ce^{3+} ground state 4f to the field-splitting levels of 5d state [20]. The corresponding PL emission

spectrum excited at 285 nm shows one broad emission band peaked at about 340 nm, attributed to the transitions of 5d excited state to the $^2F_{7/2}$ and $^2F_{5/2}$ ground states [20].

Figure 4. Photoluminescence (PL) excitation and emission spectra of: (a) $\text{Al}_2\text{O}_3:\text{Ce}^{3+}$, (b) $\text{Al}_2\text{O}_3:\text{Eu}^{2+}$, created in supporting electrolyte with the addition of 4 g/L CeO_2 and 4 g/L Eu_2O_3 , respectively.

Figure 4b presents PL excitation and emission spectra of Al_2O_3 coating doped with Eu ions. The PL spectra show the characteristic Eu^{2+} broad band excitation and emission [21]. Although XPS indicates that Eu incorporated into Al_2O_3 is also in the 3+ oxidation state, typical f-f transitions of Eu^{3+} ions have not been identified in PL excitation and emission spectra, not even under the 395 nm excitation corresponding to the $^7F_0 \rightarrow ^5L_6$ transition of Eu^{3+} . The PL excitation spectrum shows a large absorption band ranging from 250 to 330 nm, with center at 260 nm, attributed to the $4f^65d^1$ multiplet excited states of Eu^{2+} ions. Under the excitation of 260 nm the PL emission spectrum shows two distinct bands reaching maxima at about 405 and 500 nm, caused by the $4f^65d^1 \rightarrow 4f^7$ ($^8S_{7/2}$) transition of Eu^{2+} ions. This transition is structurally sensitive to the local environment around the Eu^{2+} in Al_2O_3 [21]. The gamma Al_2O_3 has two different sites for Al^{3+} ions. The appearance of two emission bands for a single transition of Eu^{2+} in $\text{Al}_2\text{O}_3:\text{Eu}^{2+}$ is thus attributed to the Eu^{2+} substituting the Al^{3+} ions at both crystallographic sites.

3.3. PL of $\text{Al}_2\text{O}_3:\text{Ce}^{3+}/\text{Eu}^{2+}$ Coatings

Figure 4 shows the spectral overlapping of the Ce^{3+} PL emission to the Eu^{2+} PL excitation in Al_2O_3 between 300 and 400 nm, which indicates that the energy transfer from a sensitizer Ce^{3+} to an activator Eu^{2+} is possible. To verify the energy transfer from Ce^{3+} to Eu^{2+} in $\text{Al}_2\text{O}_3:\text{Ce}^{3+}/\text{Eu}^{2+}$ coatings, the PL emission spectra excited at 260 and 285 nm of coatings formed in supporting electrolyte with the addition of 4 g/L CeO_2 and different concentrations of Eu_2O_3 are shown in Figure 5. The PL emission spectra of $\text{Al}_2\text{O}_3:\text{Ce}^{3+}/\text{Eu}^{2+}$ coatings consist of the emission band peaking at about 345 nm, assigned to the $4f^05d^1 \rightarrow 4f^1$ transition of Ce^{3+} ion, and two emission bands peaking at about 405 and 500 nm, attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion. The intensity of the PL band of Ce^{3+} decreases with the increasing concentration of Eu_2O_3 in supporting electrolyte, i.e., content of incorporated Eu in Al_2O_3 coatings (Table 1), but the intensity of PL bands of Eu^{2+} increases. With the higher Eu^{2+} doping content, the Ce^{3+} emission practically disappears, and only the Eu^{2+} emission remains in the PL spectra of $\text{Al}_2\text{O}_3:\text{Ce}^{3+}/\text{Eu}^{2+}$ coatings. These results indicate that the energy transfer from Ce^{3+} to Eu^{2+} is confirmed. The intensity of PL bands of Eu^{2+} not only increases due to $\text{Ce}^{3+} \rightarrow \text{Eu}^{2+}$ energy transfer, but also due to the increase of the Eu content in the Al_2O_3 coatings.

Figure 5. PL emission spectra of $\text{Al}_2\text{O}_3:\text{Ce}^{3+}/\text{Eu}^{2+}$ coatings formed in supporting electrolyte with the addition of 4 g/L CeO_2 and different concentrations of Eu_2O_3 excited at: (a) 260 nm, (b) 285 nm.

$\text{Ce}^{3+} \rightarrow \text{Eu}^{2+}$ energy transfer in $\text{Al}_2\text{O}_3:\text{Ce}^{3+}/\text{Eu}^{2+}$ coatings created in supporting electrolyte with the addition of 0.5 g/L Eu_2O_3 and different concentrations of CeO_2 is verified as well (Figure 6). The intensity of PL bands originating from Ce^{3+} and Eu^{2+} increases with increasing concentration of CeO_2 in the supporting electrolyte, i.e., content of incorporated Ce^{3+} in Al_2O_3 coatings (Table 1). The intensity of PL bands of Eu^{2+} increases due to $\text{Ce}^{3+} \rightarrow \text{Eu}^{2+}$ energy transfer, but the intensity of the PL band of Ce^{3+} increases due to the increase of the Ce^{3+} content in the Al_2O_3 coatings.

Figure 6. PL emission spectra of $\text{Al}_2\text{O}_3:\text{Ce}^{3+}/\text{Eu}^{2+}$ coatings formed in supporting electrolyte with the addition of 0.5 g/L Eu_2O_3 and different concentrations of CeO_2 excited at: (a) 260 nm, (b) 285 nm.

The energy transfer efficiency (η_T) from Ce^{3+} to Eu^{2+} can be calculated by the formula $\eta_T = 1 - I_S/I_{S0}$, where I_S and I_{S0} are the PL intensities of the Ce^{3+} emissions with and without the presence of Eu^{2+} , respectively [22]. The energy transfer efficiencies from Ce^{3+} to Eu^{2+} are calculated from the spectra in Figure 5 and presented in Figure 7. The energy transfer efficiency increases with increasing Eu^{2+} concentration, indicating that the energy transfer from Ce^{3+} to Eu^{2+} is effective under middle UV excitation. The energy transfer $\text{Ce}^{3+} \rightarrow \text{Eu}^{2+}$ can also be observed via the shortening of the Ce^{3+} emission decay times with the increasing Eu^{2+} concentration, as demonstrated in Ref. [7].

Figure 7. Energy transfer efficiency of Al₂O₃:Ce³⁺/Eu²⁺ coatings created in supporting electrolyte with the addition of 4 g/L CeO₂ and different concentrations of Eu₂O₃.

In order to identify the energy transfer mechanism from a Ce³⁺ sensitizer to an Eu²⁺ activator, the equation of exchange interaction and electric multipolar interactions proposed by Dexter and Reisfeld was used [3]:

$$\frac{I_{S0}}{I_S} \propto C^{\frac{n}{3}}. \quad (1)$$

From Equation (1) the dominant multipolar interaction can be identified, where C is the total concentration of Ce³⁺ and Eu²⁺ ions, and $n = 6, 8, 10$ values correspond to dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions, respectively. In Figure 8, the plots of $C^{n/3}$ vs. I_{S0}/I_S are presented. The best fit is with $n = 6$, i.e., the energy transfer Ce³⁺ → Eu²⁺ is primarily due to the electric dipole–dipole interaction.

Figure 8. Plot of $C^{n/3}$ vs. I_{S0}/I_S for: (a) $n = 6$, (b) $n = 8$, (c) $n = 10$.

The critical transfer distance for electric dipole–dipole interactions equal to [8]:

$$R_C^6 [\text{\AA}] = 6 \cdot \frac{10^3}{L^4} \cdot \frac{\int I(\text{Ce}) \cdot I(\text{Eu}) dE}{\int I(\text{Ce}) dE \cdot \int I(\text{Eu}) dE'} \quad (2)$$

where $I(Ce)$ and $I(Eu)$ are the intensities of Ce^{3+} emission and Eu^{2+} excitation spectra, respectively, and L is the largest energy point at which the spectral overlap occurs. As can be extracted from the graph in Figure 9, that point is equal to 3.985 eV, the term with integrals is equal to 0.3596 eV^{-1} , and thus the critical distance was estimated to be 8.6 Å.

Figure 9. Normalized spectral line-shapes for the Ce^{3+} emission and Eu^{2+} excitation.

3.4. CIE Chromaticity Analysis

The Commission International de l'Eclairage (CIE) 1931 (x,y) coordinates of $Al_2O_3:Ce^{3+}/Eu^{2+}$ coatings created in supporting electrolyte with the addition different concentration of CeO_2 and Eu_2O_3 were estimated by the JOES software, v. 2.8 [23], and the results are presented in Figure 10 and Table 2. From the diagram, the evident is the shift from pure blue towards the white color by increasing Eu^{2+} concentration. There is also a small shift in the same direction by changing the excitation from 260 to 285 nm. The emission color of the samples with constant Eu^{2+} is almost independent on the Ce^{3+} concentration. Thus, the emission color of $Al_2O_3:Ce^{3+}/Eu^{2+}$ can be fine-tuned from pure blue to white by increasing Eu^{2+} concentration.

Figure 10. Commission International de l'Eclairage (CIE) 1931 chromaticity diagram of $Al_2O_3:Ce^{3+}/Eu^{2+}$ coatings doped with various concentrations of CeO_2 and Eu_2O_3 particles and excited at 260 nm. Labels are explained in Table 2.

Table 2. CIE x, y coordinates, color purity and dominant wavelength of $\text{Al}_2\text{O}_3\text{:Ce}^{3+}/\text{Eu}^{2+}$, coatings doped with various concentrations of CeO_2 and Eu_2O_3 particles and excited at 260 and 285 nm.

Label	Concentration of Particles		λ_{ex} (nm)	x	y	Color Purity	$\lambda_{\text{dominant}}$ (nm)
	CeO_2	Eu_2O_3					
a	4	0	260	0.10644	0.08603	1	467
b	4	0.5	260	0.20944	0.18067	0.606957	471
c	4	1	260	0.21295	0.21447	0.501821	477
d	4	2	260	0.24027	0.25217	0.374879	483
e	4	4	260	0.25693	0.27666	0.285429	488
f	0	0.5	260	0.21503	0.19208	0.550572	472
g	8	0.5	260	0.2022	0.17773	0.606957	471
h	12	0.5	260	0.21743	0.19386	0.550572	472

4. Conclusions

In summary, we have successfully prepared Al_2O_3 coatings doped with Ce^{3+} and Eu^{2+} ions by the PEO process and their PL properties have been investigated in detail. PL emission spectra of $\text{Al}_2\text{O}_3\text{:Ce}^{3+}/\text{Eu}^{2+}$ are a sum of PL originating from 5d–4f transitions of Ce^{3+} and Eu^{2+} ions. Due to the spectral overlapping of the Ce^{3+} PL emission with the Eu^{2+} PL excitation in Al_2O_3 , an energy transfer from Ce^{3+} sensitizer to Eu^{2+} activator occurs. The energy transfer mechanism is dominant by electric dipole–dipole interaction.

Author Contributions: S.S. conceptualized the idea; S.S. developed the coating; S.S. developed the methodology; S.S. and A.Ć. performed the experiments, and analyzed data; S.S. and A.Ć. contributed equally in manuscript preparation, editing and submission.

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