# Photochemical Reaction Patterns on Heterostructures of ZnO on **Periodically Poled Lithium Niobate**

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Supporting Information

ABSTRACT: The internal electric field in LiNbO3 provides a driving force for heterogeneous photocatalytic reactions, where photoexcited holes or electrons can participate in redox reactions on positive (+c) and negative (-c) domain surfaces and at the domain boundaries. One method to characterize the surface chemical reactivity is to measure photoinduced Ag deposition by immersing the LiNbO<sub>3</sub> in an aqueous AgNO<sub>3</sub> solution and illuminating with above bandgap light. Reduction of Ag<sup>+</sup> ions leads to the formation of Ag nanoparticles at the surface, and a high density of Ag nanoparticles indicates enhanced surface photochemical reactions. In this study, an n-type semiconducting ZnO layer is deposited on periodically poled LiNbO<sub>3</sub> (PPLN) to modulate the surface electronic properties and impact the surface redox reactions. After plasma enhanced atomic layer deposition (PEALD) of 1, 2, 4, and 10 nm ZnO thin films on PPLN substrates, the substrates were immersed in aqueous AgNO3 and illuminated with above band gap UV light. The Ag nanoparticle density increased for 1 and 2 nm ZnO/PPLN heterostructures, indicating an enhanced electron density at the ZnO/PPLN surface. However, increasing the ZnO thickness beyond 2 nm resulted in a decrease in the Ag nanoparticle density. The increase in nanoparticle density is related



to the photoexcited charge density at the ZnO/PPLN interface and the presence of a weakly adsorbed Stern layer at the ZnO surface. The decrease in the nanoparticle density for thicker ZnO is attributed to photoexcited electron screening in the ZnO layer that suppresses electron flow from the LiNbO<sub>3</sub> to ZnO surface.

KEYWORDS: heterostructure, PPLN, lithium niobate, ZnO, photoinduced, AFM, PFM, PEALD

## INTRODUCTION

Photochemical redox reactions have been used for various processes such as splitting water into H<sub>2</sub> and O<sub>2</sub>,<sup>1,2</sup> converting CO<sub>2</sub> and water into fuel,<sup>3</sup> and removing organic and inorganic compounds from contaminated water.<sup>4,5</sup> For photocatalytic processes involving semiconductors or oxides, above band gap light excites electrons and holes, which can transport to the surface and react with chemical species provided that the redox potential of the reacting species is within the semiconductor or oxide bandgap.<sup>1,2,6</sup> The redox reaction rate is controlled by the number of carriers available at the surface, which is influenced by the recombination and generation rates. The recombination rate is affected by bulk defects and surface states, while the generation rate is controlled by the absorption of light near the surface of the photocatalyst.

A recent review discusses mechanisms where the internal electric field in ferroelectrics can separate photoinduced charge carriers and enhance the efficiency of photocatalytic processes. Materials such as LiNbO<sub>3</sub> and BaTiO<sub>3</sub> are among the group of ferroelectrics with wide bandgaps that can exhibit an internal electric field and enable photocatalytic processes. The internal field near the surface arises from a partially unscreened surface polarization bound charge and can lead to separation of the photoexcited carriers. Consequently, surface photochemical reactions display enhanced efficiency for these materials.<sup>2,6</sup> Specifically, enhanced reduction efficiency has been shown on

(+c) LiNbO<sub>3</sub> and BaTiO<sub>3</sub> domain surfaces for photoinduced metal nanoparticle deposition.<sup>7–</sup>

Lithium niobate (LiNbO<sub>3</sub>) has previously been explored for photochemical efficiency in bulk, powder, and nanowire forms.<sup>2,3,6,9-11</sup> The polarity patterns of periodically poled, single crystal LiNbO3 surfaces have been used for photochemical reactions, where the reduction and oxidation reactions are spatially separated on the different polarity domains.<sup>2,3,6</sup> However, to improve the LiNbO<sub>3</sub> photochemical reaction efficiency, recent efforts have employed multiphase LiNbO<sub>3</sub> nanowires,<sup>9</sup> multicrystalline powders (LiNbO<sub>3</sub> and LiNb<sub>3</sub>O<sub>3</sub>),<sup>10</sup> Fe doped LiNbO<sub>3</sub>,<sup>6</sup> and Ag loaded LiNbO<sub>3</sub>.<sup>12</sup> Another method to improve the photochemical reaction efficiency is to use a semiconductor and ferroelectric heterostructure. Burbure et al. prepared TiO<sub>2</sub>/BaTiO<sub>3</sub> heterostructures that led to an enhancement of the photochemical reaction efficiency. They demonstrated two phenomena: (i) photoinduced charge transfer from BaTiO<sub>3</sub> to the TiO<sub>2</sub> surface<sup>13</sup> and (ii) Ag<sup>+</sup> reduction that reflects the BaTiO<sub>3</sub> polarity pattern irrespective of TiO<sub>2</sub> crystal orientation.<sup>14</sup> The results indicated that the BaTiO<sub>3</sub> electric field controls the surface reactions of  $TiO_2/$ BaTiO<sub>3</sub> heterostructures. Here, we investigate ZnO and



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ferroelectric lithium niobate (LiNbO<sub>3</sub>) to form a semiconductor/ferroelectric heterostructure. The band gap of ZnO is 3.4 eV, which is less than the 3.9 eV bandgap of LiNbO<sub>3</sub>. It has a much smaller spontaneous polarization of 0.05  $C/m^2$ ,<sup>15</sup> which can be neglected compared to the 0.71  $C/m^2$ spontaneous polarization of LiNbO<sub>3</sub>.<sup>16</sup> The oxide heterostructures can serve two purposes: (i) reduction of defect states at the ferroelectric surface<sup>18</sup> and (ii) enhancement of the photoexcited charge separation process.<sup>14,13</sup>

In LiNbO<sub>3</sub>, the positive polarization charge terminated surface is termed a +c domain, and the negative polarization charge terminated surface is termed a -c domain. In general, the polarization surface bound charge can be screened by free carriers, ionized impurities, defects (internal screening), charged adsorbed species, and/or surface states (external screening).<sup>19,20</sup> As shown in Figure 1, the polarization bound



Figure 1. Schematic of screening charges and band bending of ferroelectric LiNbO<sub>3</sub> for (a) -c domains and (b) +c domains. In LiNbO<sub>3</sub>, the surface is externally screened with oppositely charged adsorbed species, including those in a Stern layer.

charge at LiNbO<sub>3</sub> surfaces is predominantly screened by external charges due to the low density of charged defects and low internal carrier concentration  $(10^{12} \text{ cm}^{-3})$ .<sup>17,19</sup> The internal electric field, which arises from partial screening of the polarization bound charge, influences the photoinduced charge carrier density at the surface by displacing electrons toward the +c domain surface and holes toward the -c domain surface.

Among oxides, ZnO is a promising candidate as an electron transport layer due to its relatively high mobility and optical transparency. Wide band gap ZnO thin films have been used for numerous applications in electronic and optical devices and have been more recently considered as photocatalysts and charge transfer layers in photovoltaic heterostructures.<sup>2–4,24</sup> ZnO thin films and nanostructures can be used as efficient photocatalysts and are, in some cases, preferred over TiO<sub>2</sub> due to a higher absorption coefficient.<sup>5</sup> Despite the wide band gap, ZnO is typically an n-type semiconductor with a high internal carrier concentration  $(1 \times 10^{16} \text{ to } 1 \times 10^{18} \text{ cm}^{-3})$ .<sup>21,22</sup> The n-type character of ZnO, which is still an area of research, has been attributed to a number of effects, including interstitial hydrogen, impurities, and oxygen vacancies.<sup>22</sup>

Photoinduced nanopattern formation on periodically poled lithium niobate (PPLN) is a photocatalytic process that has shown Ag nanowire formation and preferred Ag nanoparticle deposition on domain boundaries and +c domain surfaces.<sup>7,8,11,23</sup> Ag nanoparticle deposition is enabled by photo-excited electrons that reduce Ag<sup>+</sup> ions. Shown in Figure 2 are the reduction potential of Ag<sup>+</sup> to Ag, the oxidation potential of OH<sup>-</sup> and H<sub>2</sub>O, and the bandgap positions of +c LiNbO<sub>3</sub>,<sup>17</sup> –c LiNbO<sub>3</sub><sup>17</sup> and ZnO.<sup>24</sup> The structure and pattern of the



**Figure 2.** Redox potentials of  $H_2O$ , hydroxyl ion (OH<sup>-</sup>), and Ag<sup>+</sup> vs normal hydrogen electrode (NHE) with respect to the band gaps of LiNbO<sub>3</sub> – c and +c domain and ZnO. The conduction band (CB) and valence band (VB) positions were determined relative to the vacuum level.

photoinduced nanoparticle deposition on periodically poled ferroelectric materials is influenced by the availability of photoexcited charge carriers at the surface.<sup>6,8,17</sup> This study addresses how the n-type carrier concentration and thickness of ZnO affects photoexcited electron transport from LiNbO<sub>3</sub>, as evidenced by the observed Ag nanoparticle pattern and density. The variation in the Ag nanoparticle pattern with the ZnO thickness provides insight into the charge transfer processes in ZnO/PPLN heterostructures and the photocatalytic redox reactions at the surface.

Plasma enhanced atomic layer deposition (PEALD) is a submonolayer deposition process that can achieve uniform, conformal ZnO thin films.<sup>25</sup> In this study, ZnO/PPLN heterostructures were prepared with various ZnO thicknesses (1, 2, 4, and 10 nm) using a PEALD process. To understand the photochemical reactivity of the ZnO/PPLN heterostructures, photoinduced deposition was carried out by illuminating the heterostructures with 254 nm (4.9 eV) and 350 nm (3.5 eV) UV light, which are above and below the band gap of LiNbO<sub>3</sub>.

#### EXPERIMENTAL SECTION

PEALD ZnO on PPLN. This study employs plasma enhanced atomic layer deposition of ZnO thin films on periodically poled LiNbO3 polished substrates which were purchased from Crystal Technologies. The  $6 \times 4 \times 0.5$  mm LiNbO<sub>3</sub> substrates were double side polished with an approximately 20  $\mu$ m period, lithographically patterned polarity grating, and c-axis surfaces with periodically arranged +c and -c domains separated by 180° domain boundaries. An ultrasonic chemical (acetone and methanol) clean and an O2 plasma for 10 s was used to prepare the PPLN surfaces prior to PEALD to remove the surface adsorbed impurities that can act as reactive sites for PEALD nucleation. In addition, the initial plasma treatment provides a surface with reactivity similar to that after each growth cycle. The ZnO thin films of different thicknesses (1, 2, 4, and 10 nm) were deposited at 130 °C using dimethyl zinc (DMZ) as the precursor and oxygen plasma as the reactant with 0.35 and 8 s exposures, respectively. The precursor and plasma steps were separated by 40 s  $N_2$  purge steps. The observed  $\bar{P}EALD\ Zn\bar{O}$  growth rate was determined to be ~2.1 Å/cycle using Rutherford backscattering spectrometry (RBS). The submonolayer, two-step atomic layer deposition requires reactive sites to initiate the reaction of the chemical precursor molecules at the substrate surface.<sup>2</sup>

**PFM of PPLN and ZnO/PPLN.** Piezo force microscopy (PFM) can be used to image the polarity domains of ferroelectric substrates. PFM detects the signal from the LiNbO<sub>3</sub> surface as it expands or contracts due to the converse piezoelectric effect induced by the applied potential. The LiNbO<sub>3</sub> domain expands or contracts if the applied electric field ( $E_{ap}$ ) is parallel or antiparallel to the spontaneous

polarization  $(P_s)$ , respectively (Figure 3). The direction of the ferroelectric polarization points toward or away from the surface in



**Figure 3.** Schematic of the piezoelectric effect in LiNbO<sub>3</sub> with an applied tip voltage  $(V_{ac})$ . The LiNbO<sub>3</sub> –c and +c domains expand (a) or contract (b) with the applied electric field that aligns parallel or antiparallel to the spontaneous polarization, respectively.

alternate +c and -c domains, respectively. An Asylum research molecular force probe (MFP) 3D was used to image the domains in an ambient environment. PFM was performed before and after ZnO deposition with conductive (Pt/Ir coated Si) tip probes (PPP-EFM, Nanosensors) of radius  $30 \pm 10$  nm, spring constant of k = 0.5-9.5 N/m, resonance frequency between 45 and 115 kHz, and resistivity of 0.01–0.02  $\Omega$  cm. The periodic structure of PPLN is evident in the PFM phase image shown in Figure 4, where the color contrast represents the opposite polarity domains. After ZnO deposition on PPLN, a higher tip voltage ( $V_{ac}$ ) was required to image the domains. The tip voltage used for PPLN and (1–10 nm) ZnO on PPLN was between ~250 and 1600 mV. For each sample, the tip voltage was adjusted to obtain the same cantilever signal (~11 mV) at resonance. This signal is directly related to the material oscillation amplitude.

The electric field strength experienced by the ferroelectric material is affected by the top surface layer thickness<sup>26</sup> (*d*) and the presence of free carriers. For the case of a dielectric top layer, the electric field strength is inversely related to the thickness; however, for metals, the free carriers can completely screen the applied electric field. Consequently, a semiconductor layer can reduce the applied electric field strength through an increase in thickness or through the free carrier concentration. For a dielectric between the PFM tip and surface, the electric field ( $E_{ap}$ ) near the ferroelectric surface<sup>26</sup> is given as

$$E_{\rm ap} \propto \frac{V_{\rm ac}}{d} \tag{1}$$

where  $V_{ac}$  is the applied oscillating tip voltage and *d* is the distance from the tip to the ferroelectric surface. It is evident from eq 1 that, with an increase in the distance between the tip and ferroelectric

surface, the electric field strength experienced by the ferroelectric material decreases if  $V_{\rm ac}$  is kept constant. The ZnO thickness increases the distance between the PFM tip and PPLN surface, and a higher tip voltage is required to obtain the same displacement.

Photoinduced Ag Nanoparticle Deposition on PPLN and ZnO/PPLN. To establish the surface reactivity and charge transfer processes, Ag nanoparticle deposition was carried out on the ZnO/ PPLN heterostructures and compared with the well-studied photoinduced deposition of Ag nanopatterns on bare PPLN.<sup>7,8,11,23</sup> Prior to photoinduced deposition, the PPLN or ZnO/PPLN substrates were sonicated in methanol for 1 min and dried with N<sub>2</sub> gas. The cleaned sample surfaces were covered with a 35  $\mu$ L droplet of a 0.00001 M AgNO<sub>3</sub> solution and illuminated with 254 nm (4.9 eV) or 350 nm (3.5 eV) UV light of intensity ~1100  $\mu$ W/cm<sup>2</sup> for 8 min. The illumination was obtained using a 100 W Hg lamp with line filters. After UV illumination, the samples were immersed in deionized water for 1 min followed by a N<sub>2</sub> blow dry. The photoinduced Ag nanoparticle pattern was obtained using AFM in tapping mode with nonconducting Si probes of spring constant k = 13-77 N/m and resonance frequency of ~200-400 kHz

Electron Microscopy. An FEI Nova 200 NanoLab was employed to prepare specimens for transmission electron microscopy (TEM) using a focused ion beam (FIB). The 1 and 2 nm ZnO/PPLN samples were coated with carbon and Pt layers to prevent charging and surface damage by electron and ion bombardment. The lift-out technique was used to prepare site specific cross sections of the bulk samples. Scanning electron microscope (SEM) images were obtained to record where the TEM specimens were cut relative to the PPLN domains. The specimens were then loaded onto Mo TEM mesh grids. A JEOL ARM200F instrument (200 kV) was employed to acquire high resolution transmission electron microscopy (HRTEM) images of 1 and 2 nm ZnO on PPLN after Ag nanoparticle deposition. On the other hand, an aberration corrected JEOL ARM200F (200 kV) was employed to acquire high angle annular dark field (HAADF) images and spatially locate and determine the thickness of the ZnO layer using energy dispersive X-ray spectroscopy (EDX).

## RESULTS

**Piezoelectric Force Microscopy (PFM) on PPLN and ZnO/PPLN Surfaces.** PFM was used to measure the piezo response of PPLN +c and -c domains. Figure 4a shows a PFM phase scan of PPLN, where the alternate +c and -c domains are shown with color contrast. As shown in Figures 4b–d, the PPLN domain contrast is also evident for 2, 4, and 10 nm PEALD ZnO films on PPLN. However, as the ZnO thickness was increased, a higher tip voltage ( $V_{ac}$ ) was required to achieve



Figure 4. PFM phase image of (a) bare PPLN, (b) 1 nm ZnO/PPLN, (c) 4 nm ZnO/PPLN, and (d) 10 nm ZnO/PPLN. The lower line scan plots show the measured phase vs distance along the indicated red lines in the image. The  $180^{\circ}$  domain boundaries are evident, which separate the alternate opposite polarity domains of PPLN.

the same tip displacement, as shown in Figure 5. The increase in tip voltage with thickness suggests that the screening is due



Figure 5. Tip voltage  $(V_{\rm ac})$  to maintain a constant PFM amplitude vs ZnO thickness.

to the dielectric layer thickness, and the screening effect due to free carriers is not significant.

Photoinduced Ag Nanoparticle Deposition on PPLN and ZnO/PPLN. The resultant Ag nanoparticle patterns on PPLN and ZnO/PPLN heterostructures after photoinduced deposition are shown in Figures 6, 7, and 8. Two control experiments were conducted to exclude the possibility of unexpected surface reactions. In the first control experiment, the 2 nm ZnO on PPLN heterostructure was immersed in a 35  $\mu$ L of a AgNO<sub>3</sub> solution in the absence of UV light. The AFM scan in Figure 6a showed a smooth surface with an absence of Ag nanoparticles, which ruled out the possibility of direct reaction of ZnO with AgNO3 in water. In the second control experiment, photoinduced Ag nanoparticle deposition using 350 nm (3.5 eV) UV light illumination was performed on 2 nm ZnO/PPLN to analyze the contribution of electrons photoexcited in the ZnO. In this case, the photon energy is above the ZnO bandgap but below the LiNbO3 bandgap. The AFM image in Figure 6b shows sparse Ag nanoparticles irrespective of the +c and -c LiNbO3 domains. This indicates the contribution of ZnO photoexcited electrons is negligible in Ag nanoparticle pattern formation for 2 nm ZnO thickness.

The photoinduced Ag nanoparticle formations on PPLN and 1, 2, 4, or 10 nm ZnO/PPLN were conducted under similar



**Figure 7.** AFM scans of photoinduced Ag nanoparticle patterns using UV light of 254 nm for (a) bare PPLN, (b) 1 nm ZnO/PPLN, and (c) 2 nm ZnO/PPLN. The width and height profile across the domain boundary separating +c and -c domains display the size of the Ag nanoparticles on (d) bare PPLN, (e) 1 nm ZnO/PPLN, and (f) 2 nm ZnO/PPLN.

conditions of exposure time, intensity, and  $AgNO_3$  concentration. Two UV wavelengths (254 and 350 nm) were used for  $Ag^+$  photoreduction, where the energy of 254 nm UV light (4.9 eV) is above the LiNbO<sub>3</sub> bandgap, and that of 350 nm UV light (3.5 eV) is below the LiNbO<sub>3</sub> bandgap but above the ZnO bandgap. Photoinduced Ag nanoparticle deposition was performed on all ZnO thicknesses and bare LiNbO<sub>3</sub> with 254 nm UV light as shown in Figures 7a-c and Figures 8a-b. In addition, as shown in Figures 8c-d, Ag<sup>+</sup> photoreduction was also performed using 350 nm UV light on the 4 and 10 nm/PPLN. While UV illumination tends to reduce band bending due to photovoltage effects, the observation of preferred deposition on the 1 and 2 nm ZnO/PPLN heterostructures indicates that effect does not dominate the internal field.



Figure 6. AFM scan of Ag nanopatterns on 2 nm ZnO/PPLN (a) with no UV light illumination and (b) with 350 nm (3.5 eV) UV light illumination.



**Figure 8.** AFM scans ( $5 \times 5 \mu m$ ) of photoinduced Ag nanoparticle patterns using 254 nm UV light on (a) 4 nm ZnO/PPLN and (b) 10 nm ZnO/PPLN, and 350 nm UV light on (c) 4 nm ZnO/PPLN and (d) 10 nm ZnO/PPLN.

The Ag nanoparticle patterns on the PPLN and ZnO/PPLN samples are summarized below.

Pattern of Ag Nanoparticles on +c and -c Domains. The AFM image in Figure 7a shows that the deposition of Ag nanoparticles is spatially enhanced on PPLN +c domains compared to -c domains. For the 1 nm ZnO on PPLN structures, an increased density of nanoparticles was observed on both domains. Figure 7b indicates a higher density of Ag nanoparticles was maintained on the +c domain surface compared to that maintained on the -c surface. As the ZnO thickness increases to 2 nm, the nanoparticle density further increases on the -c domain and appears to be comparable to that on the +c domain. There is a notable change in the Ag nanoparticle pattern for ZnO films ≥4 nm, as is evident in Figures 8a-d. In this case, large agglomerated clusters were observed which were not evidently correlated with the domains.

Ag Nanoparticles at Domain Boundaries. Preferential Ag nanoparticle deposition was observed along the domain boundaries on PPLN and on 1 and 2 nm ZnO/PPLN heterostructures. Figure 7b indicates that for 1 nm ZnO on PPLN, the domain boundary nanoparticles are larger in size and have a higher density. The height vs width profiles of the AFM topography image shows the domain boundary width for 1 nm ZnO/PPLN is ~2 times (2.2  $\mu$ m) larger than on bare PPLN (1  $\mu$ m), as shown in Figures 7e and d, respectively. In the AFM scan of the 2 nm ZnO/PPLN, the domain boundary nanoparticle density and width appears to be reduced compared to that of PPLN.

**Crystallinity and Thickness of ZnO on PPLN.** The TEM specimens of Ag nanoparticle covered 1 and 2 nm ZnO/PPLN samples were prepared with a domain boundary at the center, as shown in Figure 9. The crystal structure and thickness of the PEALD ZnO thin films are indicated in the TEM images in Figure 10. The 2 nm ZnO films exhibit an amorphous structure between the PPLN surface and Ag nanoparticles, as shown in Figures 10b–d; however, the thicker ZnO films exhibit a crystalline structure.<sup>25</sup> Due to the amorphous structure, the ZnO cannot be differentiated from the amorphous carbon

![](_page_4_Picture_7.jpeg)

**Figure 9.** SEM image of the location of the TEM specimen relative to PPLN domains. Light and dark gray parallel stripes indicate the PPLN +c and -c.

![](_page_4_Figure_9.jpeg)

Figure 10. TEM images of the photoinduced deposition of Ag nanoparticles on 1 nm ZnO/PPLN (a and b) and for 2 nm ZnO/PPLN (c and d). The 1 and 2 nm ZnO films are sandwiched between Ag nanoparticles and the  $LiNbO_3$  substrates in panels b and d, respectively.

protective layer. As shown in Figures 10a–d, the large particle clusters appear to correspond to domain boundary Ag nanoparticles on the 1 and 2 nm ZnO/PPLN. From the TEM images, the height of the nanoparticles at the domain boundaries and domain surfaces on both heterostructures is within the range (7–15 nm) measured using AFM (Figures 7e and f). EDX scans and HAADF images were performed on the same 2 nm ZnO/PPLN sample, and the results are shown in Figures 11a and b. The EDX scan shows the Zn K peak, confirming ZnO on the surface. As shown in Figure 11b, the HAADF image and normalized EDX Zn K-shell peak intensities from the same sample confirm the preserved ZnO layer. The EDX line scans were performed across the interface to spatially locate the ZnO layer in the 2 nm ZnO/PPLN sample. The line scans were acquired with the electron beam

30 µm

![](_page_5_Figure_2.jpeg)

Figure 11. EDX spectra (a) from the ZnO surface layer and the LiNbO<sub>3</sub> substrate of 2 nm ZnO/PPLN indicates that the Zn signal is detected only on the surface. The Mo and Pt impurities were introduced during the focused ion beam TEM specimen preparation. HAADF image (b) of the 2 nm ZnO/PPLN sample and normalized EDX Zn K-peak intensities in each area.

rastering over a rectangular area (approximately 1 nm wide and 15 nm long) as shown in Figure 11b. The normalized Zn Kpeak intensity to background intensity for each spectrum is also plotted in Figure 11b. Areas 2 and 3 show the highest normalized intensities, indicating the ZnO layer is located within 2.5 nm of the PPLN substrate.

# DISCUSSION

The reactions that occur during Ag nanoparticle pattern formation on periodically poled LiNbO<sub>3</sub> are illustrated in Figure 12. The photoelectrons excited near the LiNbO<sub>3</sub> surface

![](_page_5_Figure_7.jpeg)

**Figure 12.** Schematic of photoinduced redox reaction on LiNbO<sub>3</sub> – c and +c domain surfaces with UV light ( $\lambda = 254$  nm, E = 4.2 eV) illumination above the band gap of LiNbO<sub>3</sub>. Favorable oxidation and reduction reactions are shown for the –c and +c domain surfaces.

drift toward or away from the surface under the influence of the internal electric field and/or diffuse in all directions due to the thermal energies. The available electrons at the surface reduce  $Ag^+$  to Ag, which nucleates to form nanoparticles. The photoexcited holes oxidize water molecules to •OH radicals and H<sup>+</sup> ions and hydroxyl ions (OH<sup>-</sup>) to •OH radicals.<sup>6</sup> Prior work from our group has noted that the Stern layer can limit the concentration of  $Ag^+$  ions near the surface, which can lead to a reduced density of randomly deposited nanoparticles.<sup>8</sup>

In this research, we observe that ZnO on PPLN results in a change of the Ag nanoparticle density and spatial distribution, indicating a change in the photoexcited electron availability at the surface. We note that the size of Ag nanoparticles and their separation is much larger than the structural variations of the ZnO thin films, suggesting that the film structure is not relevant for the transitions identified here. For 1 nm ZnO/PPLN heterostructures, the overall Ag nanoparticle deposition is enhanced, and the selectivity is maintained. As the ZnO layer is increased to 2 nm, the Ag nanoparticle density on the -c domain surface becomes comparable to that on the +c domain surface. However, for ZnO thicknesses  $\geq$ 4 nm, the reduction process changes completely. Here, agglomerated Ag clusters form on the surface with no apparent relationship to the LiNbO<sub>3</sub> domains and domain boundaries, and the role of the LiNbO<sub>3</sub> domains and domain boundaries is no longer evident.

We considered the effect of absorption of the UV light due to the increasing ZnO thickness. The absorption coefficient ( $\alpha$ ) for ZnO at 350 and 254 nm is ~200000 cm<sup>-1.27</sup> Therefore, even for 10 nm-thick ZnO films, less than 20% of the incident light would be absorbed, suggesting that the light absorbed in the LiNbO<sub>3</sub> is not significantly reduced by the absorption in the ZnO.

To understand the variation in  $Ag^+$  reduction and the transport of photoexcited electrons from PPLN to the ZnO surface, we have considered the effects of the following three attributes: (i) the band alignment and band bending, (ii) the Stern layer, and (iii) screening due to photoexcited carriers in the ZnO.

Band Alignment and Band Bending of ZnO/LiNbO3. The favorable flow of photoexcited electrons and holes from one material to the other can be understood by the band alignment diagrams at the interface of a heterojunction.<sup>2,28-30</sup> For oxide materials, the band alignment is often described by alignment of the charge neutrality levels of the constituents, which can be reasonably represented by the measured Fermi levels. The reported Fermi level positions of ZnO and LiNbO3 are  $0.3^{32}$  and  $0.9 \text{ eV}^{33}$  below the conduction band minimum, respectively. On the basis of these values, alignment schematics of the ZnO/LiNbO3 heterostructures have been constructed in Figure 13. As noted in Figure 1, the LiNbO3 surface exhibits band bending due to partial internal screening. The internal screening by charged defects results in band bending and an electric field. However, with the deposition of ZnO on -c and +c LiNO<sub>3</sub> domain surfaces, the screening scenario changes as

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![](_page_6_Figure_2.jpeg)

**Figure 13.** Schematics showing the band relations and band bending for (a) -c and +c LiNbO<sub>3</sub> domains and (b) 1, (c) 2, (d) 4, and (e) 10 nm ZnO on -c and +c LiNbO<sub>3</sub> domains. The band bending in -c and +c LiNbO<sub>3</sub> domains is due to partial internal screening. As the ZnO thickness increases, the screening charge increases, reducing the LiNbO<sub>3</sub> band bending. Thus, the LiNbO<sub>3</sub> internal electric field decreases with the increase in ZnO thickness, and electron diffusion dominates electron drift.

the free carriers and defects of the ZnO contribute to screen the  $LiNbO_3$  bound charge, as shown in Figure 13b.

The screening effect has been observed in other systems. Schwinkendorf et al. and Cagain et al. studied the accumulation of an electron sheet layer in ZnO at the ZnO/BaTiO<sub>3</sub> +c domain interface for field effect transistors and the ZnO/lead zirconate titatnate (PZT) +c domain interface for capacitor structures.<sup>34,35</sup> With an increase in the ZnO thickness, the ZnO free carrier and defect areal density increases and contributes to a further reduction of the LiNbO<sub>3</sub> band bending, as indicated in Figures 13b–e. Consequently, the internal electric field strength decreases, and electron diffusion dominates electron drift. The diffusion process results in the loss of selective deposition on the positive domains and domain boundaries.

Stern Layer. The presence of a partially screened polarization charge will lead to the formation of a Stern layer at the surface of polar materials. The high ZnO electron carrier concentration  $(1 \times 10^{-18} \text{ cm}^{-3})^{21,22}$  apparently contributes to screening of the LiNbO3 polarization bound charge. Consequently, the more effective screening alters the Stern layer composition compared to that for bare LiNbO3. The Stern layer can affect the Ag<sup>+</sup> ion transport to the surface<sup>8</sup> and thus can affect the Ag nanopattern on the ZnO/PPLN heterostructures. For an AgNO3 aqueous solution, the Stern layer consists of Ag<sup>+</sup>, NO<sup>3-</sup>, OH<sup>-</sup>, and dipole water molecules, which can form a densely packed layer to screen the surface charge.<sup>8,36</sup> The dense layer results in a barrier for Ag<sup>+</sup> ions to reach the surface. With an increase in the ZnO thickness, the polarization screening is expected to be more efficient, leading to a less dense Stern layer. The existence of a weak Stern layer on ZnO/ PPLN heterostructures can enhance the reaction rate and thus increase the density of Ag nanoparticles on both +c and -c domain surfaces and domain boundaries.

Due to the reduced Stern layer effect, minimal ZnO carrier concentration screening, and the internal electric field at the domain surfaces and boundaries, the photoinduced deposition is increased for 1 nm ZnO on PPLN. However, as the ZnO thickness is increased to 2 nm, the electric field strength decreases; the Ag nanoparticle size decreases, and the selectivity is lost.

Photo Induced Screening. For ZnO/LiNbO3 heterostructures, photoexcited electrons in the ZnO layer can contribute to photoinduced reactions and screening. The 254 nm UV light used to illuminate ZnO/PPLN excites carriers in both ZnO and PPLN, and the 350 nm UV light excites carriers only in ZnO. As discussed above, the silver nanoparticle pattern is controlled by the photoexcited carriers at LiNbO3 surfaces for 1 and 2 nm ZnO on PPLN. For  $\geq$ 4 nm ZnO/LiNbO<sub>3</sub>, the random pattern of large Ag nanoparticle clusters indicates the Ag cluster formation is independent of the PPLN domains. The large cluster formation is evident on the 4 nm ZnO/PPLN sample surface when photoinduced Ag deposition was performed using 3.5 eV UV illumination. However, with the illumination of 4.9 eV UV on 4 nm ZnO/PPLN, the presence of small Ag nanoparticles is observed in addition to the clusters. This indicates that the density of small particles is due to photoexcited electrons from the PPLN which transport to the ZnO surface and reduce Ag<sup>+</sup> ions. In contrast, for 10 nm ZnO/ PPLN, the absence of small nanoparticles indicates a negligible concentration of photoexcited electrons from the PPLN. We propose that the large Ag clusters are due to electrons excited in the ZnO, and these electrons screen the electron transport from the PPLN.

We note that the PFM images of ZnO/PPLN heterostructures were not screened by the ZnO carrier concentration as the domains were displayed for all thicknesses. However, unlike the PFM measurements, during the photoinduced Ag deposition process, the sample surfaces were illuminated with UV light, which photoexcites carriers in the ZnO and enhances the free carrier concentration.

# CONCLUSIONS

The Ag nanoparticle patterns formed on ZnO/PPLN heterostructures were examined to understand the effect of

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PEALD ZnO thin films on photoexcited electron transfer and photochemical reactions. AFM was employed to characterize the Ag nanopatterns on PPLN and ZnO/PPLN heterostructures. TEM was used to verify crystal structures and ZnO thicknesses, and EDX was used for elemental detection to locate the ZnO thin film. We provide evidence that 1-2 nm ZnO thin films on both +c and -c PPLN domains change the composition of the Stern layer. We suggest that a weak Stern layer forms at the ZnO/PPLN surface as the PPLN polarization bound charge is screened by the ZnO free carriers and defects. Thus, the Ag<sup>+</sup> ions will be more readily accessible to the photoinduced electrons to form Ag nanoparticles.

The electron diffusion process dominates over electric field assisted electron drift on -c domain surfaces covered with 1 and 2 nm ZnO, which enables an increase in the density of Ag nanoparticles. The band alignment of ZnO and LiNbO3 is appropriate for electron transfer from LiNbO<sub>3</sub> to ZnO, which also contributes to enhancing the reaction rate at the surface. However, the thicker (≥4 nm) ZnO films evidently impede charge migration from LiNbO3 to the ZnO surface irrespective of domain surface polarity. We suggest that screening by photoexcited charge carriers in the ZnO creates this effect. This study provides evidence that a limited thickness (<4 nm) of ZnO on PPLN can increase the photoinduced reaction rate on +c and -c domain surfaces and at the domain boundaries. A more extensive study could establish how the band gap and band alignment of different metal oxide/PPLN heterostructures would affect the photochemical spatial dependence and efficiency.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06060.

TEM, AFM, and PFM images (PDF)

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#### Notes

The authors declare no competing financial interest.

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