catalysts

MDPI

Supplementary Information

Tailoring g-C_3N_4 with Lanthanum and Cobalt Oxides for Enhanced Photoelectrochemical and Photocatalytic Activity.

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1. Post Measurements Analysis

1.1. XRD Analysis:

In the post-PEC sample analysis, we scratched the used La_2O_3-CoO-g-C_3N_4 photoanode and re-characterized it by XRD and SEM. XRD analysis will help investigate the stability, structural, compositional, and morphological changes in the photocatalyst in a photoelectrochemical process. The XRD pattern recorded is presented in SI. Fig. 1(supplementary information). Multiple La oxide, hydroxide, and Co oxides phases are detected. In the post electrochemical XRD, it is evident that La_2O_3 CoO and g C_3N_4 peaks appeared significantly at their specified 2θ positions, as shown in figure S1, which supports the stability of the La_2O_3-CoO-g-C_3N_4 photocatalyst. However, after the water-splitting process, some new peaks of low to moderate intensity are significantly observed, which are distinguished by different colors for La $(OH)_3$ and Co_3O_4, respectively. It happened because of electrolyte interaction with the photocatalyst under visible light and electrochemical reactions. La$(OH)_3$ can be recognized by its 2θ positions at 14.5°, 26.2°, 27.8°, 30°, 42°, 53.8°and 71.4° respectively. These 2θ values correspond to the following hkl miller indices, originating from the reflection (100), (110), (101), (200), (210), (112), and (302), respectively. This post-XRD pattern is well aligned with the standard PDF card number # 36-1481 for hexagonal $P6_3$ La$(OH)_3$. On the other hand, due to the PEC process, some low-intensity XRD peaks from Co_3O_4 are also observed. These can be seen at 2θ values 10.8°, 15.8°, 17.2°, 24.1°, 30°, and 33.7° respectively in Figure S1. Their corresponding hkl miller indices are (111), (220), (311),(331),(333), and (440). These peaks are in accordance with the PDF card Number 01-078-1969, a cubic phase Co_3O_4. In the XRD pattern of post electrochemical measurement sample, high-intensity peaks of La_2O_3-CoO-g-C_3N_4 photocatalyst are also found. It is worth noting that during the PEC water splitting process, some of La_2O_3 changed to La $(OH)_3$ hexagonal phase, and CoO oxides transformed into various cobalt oxide phases like $Co^{(+2)}$ $Co^{(+3)}$ in Co_3O_4. This can be another reason for enhanced PEC activity of La_2O_3-CoO-g-C_3N_4 where mixed phases of La and valance states of cobalt-metal such as Co^{2+} and Co^{3+} coexists. It is also due to the combined effect of the metal oxide's impregnation with g-C_3N_4 arising from the chemical coupling effects of La and Co oxides and g-C_3N_4 support. Such behavior of Co oxides with g-C_3N_4 towards enhanced photocatalytic activity is already reported in the literature. In summary, the differences in the XRD analysis (SI. Fig. 1) illustrated that the crystal structure of the La_2O_3-CoO-g-C_3N_4 photocatalysts did not change greatly even after the photocatalytic reaction. Therefore, La_2O_3-CoO-g-C_3N_4 can be regarded as stable photocatalysts for PEC water splitting reactions.

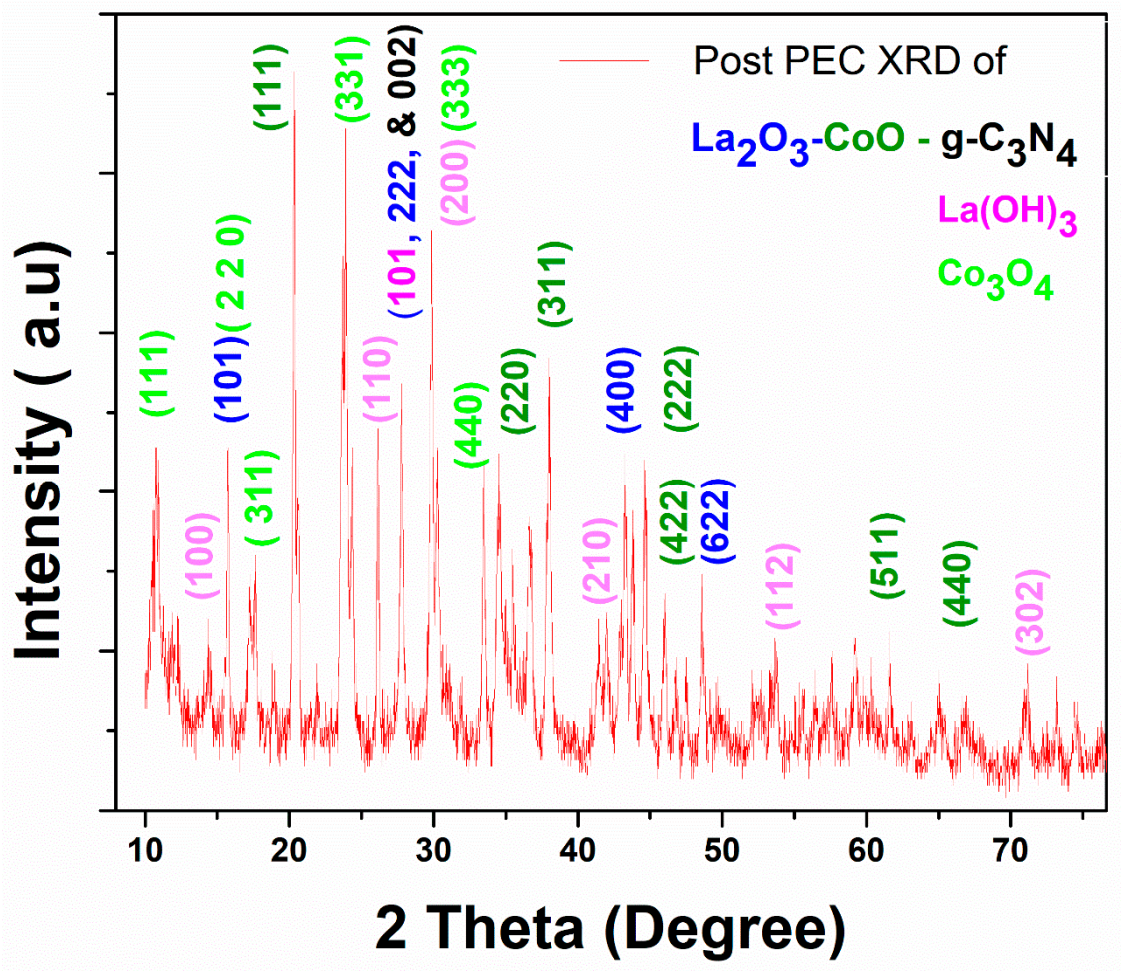

Figure S1. The Post PEC measurements XRD spectrum of La_2O_3-CoO-g-C_3N_4.

1.2. FE-SEM/EDX Analysis:

The post photoelectrochemical measurement analysis presents a comparative view of the surface topography of La_2O_3-CoO-g-C_3N_4 photocatalyst prepared by hydrothermal process. The figure (SI Figure 2 a and b) describes the agglomeration of La and Co oxide nanoparticles over the g-C_3N_4. The fresh sample as of figure 2 (a & d) comprises of nanoflakes of g-C_3N_4 which after the PEC water splitting reaction have been converted into rods with chunks or agglomerations of La and Co oxide nanoparticles. The XRD data (figure 1 and S1 fig1) showed significant peaks of La_2O_3-CoO-g-C_3N_4 at its specified 2θ positions with significant intensities in both pre and post-PEC measurements and augmented the stability of the La_2O_3-CoO-g-C_3N_4 photocatalyst. Furthermore, the EDX elemental analysis of the used La_2O_3-CoO-g-C_3N_4 photocatalyst showed La, Co, O, N, and C at their relative KeV values. The post-measurement EDX analysis is compared with its pre-analysis, and it is concluded that all the key elements are present in comparable atomic intensities and are in good agreement with each other with respect of energy/electronic transitions. Thus La_2O_3-CoO-g-C_3N_4, even after the water-splitting process, signifies homogenous distribution of these elements on the surface. That resulted in enhanced PEC activity.

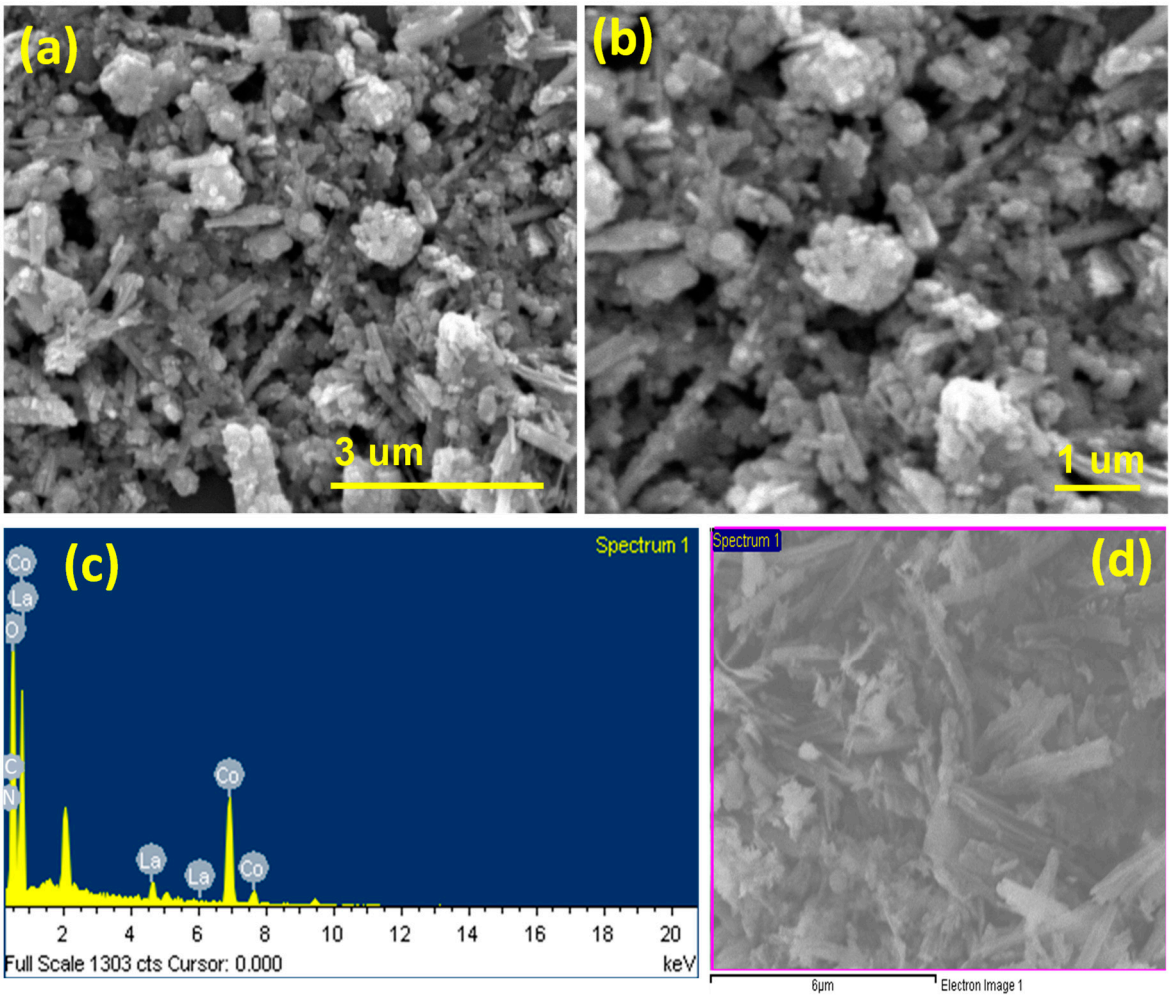

Figure S2. The surface morphology in post-PEC measurements of La_2O_3-CoO-g-C_3N_4 (**a**,**b**). Figure S2 (**c**,**d**) shows the EDX spectrum and corresponding micrograph.