Synthesis of 2D perovskite oxynitride $Li_2LaTa_2O_6N$ and the photocatalytic performance for CO_2 reduction

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Abstract: A layered oxynitride $Li_2LaTa_2O_6N$ was successfully prepared, and it was tested for photocatalytic CO_2 reduction reaction for the first time. The 2D perovskite material catalyzed CO_2 reduction into formic acid with high selectivity under visible light irradiation when it was combined with a ruthenium(II) dinuclear complex as CO_2 reduction moiety. The activity, interestingly, was higher than 3D perovskite oxynitride materials such as $CaTaO_2N$ and $LaTaON_2$. The result suggested that numerous potential of layered oxynitride material as a visible light responsive photocatalyst.

Keywords: CO_2 reduction, photocatalyst, layered perovskite

1. Introduction

Photocatalytic CO_2 conversion into valuable organic compounds has drawn considerable attention as a solution for fossil fuel depletion and serious environmental problems.[1] Heterogeneous semiconductor materials have been intensively investigated as potential photocatalysts. Among them, layered compounds have been regarded as particularly interesting materials because of the manipulation of layered structure. For example, ion-exchange and intercalation can result in unique photocatalytic performances, which cannot be accomplished using bulk-type particle photocatalysts.[2] However, most of them are metal oxides that have difficulty in utilizing visible light. Oxynitrides have been applied as visible-light-responsive photocatalysts so far.[3] Nevertheless, the number of layered oxynitride is very limited because of the difficulty in synthesis. For example, $Li_2LaTa_2O_6N$ was reported as layered perovskite oxynitride, by-product such as $LaTaON_2$ can be easily formed.[4]

Here, we present a successful synthesis of 2D perovskite oxynitride $Li_2LaTa_2O_6N$ and the photocatalytic activity for CO_2 reduction. The photocatalytic performance of 2D material is discussed by comparison with 3D perovskite oxynitrides (i.e., $CaTaO_2N$ and $LaTaON_2$).

2. Experimental

$Li_2LaTa_2O_6N$ was synthesized from an amorphous oxide prepared by the polymerized complex method, followed by heating at 1173 K for 10 h under NH_3 flow (20 mL min^{-1}). A 10 % excess amount of Li from stoichiometry was added to compensate the loss during the calcination. The obtained material was characterized by means of X–ray diffraction (XRD), scanning electron microscope (SEM), high-angle annular dark field scanning transmission electron microscope (HAADF–STEM), diffuse reflectance spectroscopy (DRS), time-resolved infra-red (IR) absorption spectroscopy, and electrochemical measurement.

The $Li_2LaTa_2O_6N$ was combined with Ru(II) dinuclear complex as a CO_2 reduction moiety[5] by stirring in acetonitrile(MeCN) solution containing the RuRu complex, followed by filtration and drying. The resulting hybrid photocatalyst was suspended in CO_2 saturated acetonitrile (MeCN) and triethanolamine (TEOA) mixture solution, followed by visible light irradiation ($\lambda \geq 400$ nm).

3. Results and discussion

Figure 1 shows a XRD pattern of the prepared $Li_2LaTa_2O_6N$ along with the corresponding reference pattern.[4] The use of stoichiometric precursor (i.e., no excess Li) caused by-product formations such as $LaTaON_2$, as reported previously.[4] On the other hand, an addition of 10% excess Li suppressed the by-products formations, resulting in a successful formation of $Li_2LaTa_2O_6N$. The prepared $Li_2LaTa_2O_6N$ was also characterized by HAADF–STEM in order to obtain atomic resolution images. As shown in Figure 2, a parallel stripe pattern was observed. A magnified image revealed that the bright lines were comprised of numerous dots and the alignment was in good agreement with the atomic configuration of La^{3+} and Ta^{5+} in perovskite slab, which is expected from crystal structure of $Li_2LaTa_2O_6N$, strongly indicating successful $Li_2LaTa_2O_6N$ formation. The obtained material colored yellow from white after nitridation. The band gap energy estimated from DRS measurement was approximately 2.5 eV.

The $Li_2LaTa_2O_6N$ was combined with a ruthenium(II) dinuclear complex (**RuRu'**) as CO_2 reduction moiety, and the hybrid photocatalyst was tested for CO_2 reduction in MeCN and TEOA mixture solution under visible light irradiation. Formic acid was detected as a product with high selectivity (≥ 97%) and the amount was 50 times higher than the amount of employed **RuRu'**, confirming catalytic cycles. Moreover, interestingly, the layered perovskite oxynitiride demonstrated higher activity than $CaTaO_2N$ and $LaTaON_2$, which are simple perovskite oxynitride materials. Electrochemical and time-resolved IR absorption measurements suggested that the negative conduction band potential and relatively long lifetime of electrons were responsible for the high performance. Those results suggested a high potential of 2D perovskite oxynitride material as a visible-light-responsive photocatalyst.

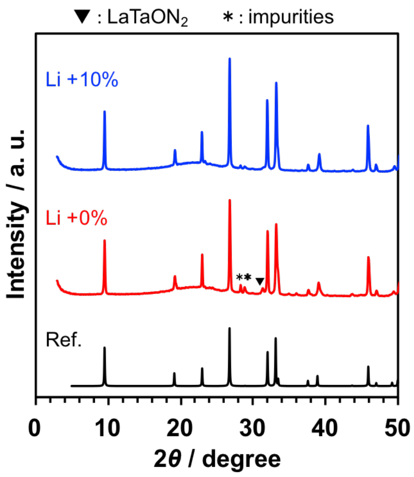

Figure 1. XRD pattern of $Li_2LaTa_2O_6N$ with different amount of Li along with reference pattern.

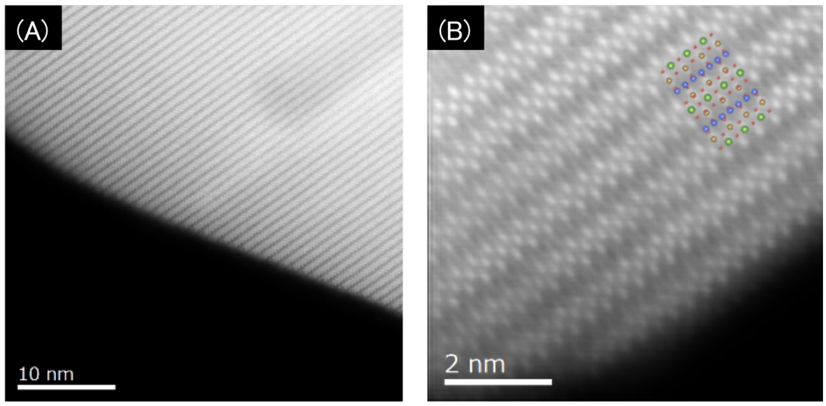

Figure 2. (A) HAADF–STEM image and (B) magnified HAADF–STEM image of $Li_2LaTa_2O_6N$. In Figure 2(B), crystal structure of $Li_2LaTa_2O_6N$ is also shown, where blue marks : Li^+, green marks : La^{3+}, brown marks : Ta^{5+} and red marks : O^{2-}/N^{3-}.

4. Conclusions

A successful synthesis of the 2D perovskite oxynitride $Li_2LaTa_2O_6N$ was achieved by the polymerized complex method, which was confirmed by XRD and HAADF–STEM analysis. The material exhibited photocatalytic CO_2 reduction to formic acid when combined with a Ru(II) dinulclear metal complex. Moreover, interestingly, the performance was higher than 3D perovskite oxynitride materials such as $CaTaO_2N$ and $LaTaON_2$, demonstrating high potential of layered oxynitride compound as a visible light responsive photocatalyst.

References

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