

Structure-Activity Evolution of AgNbO3 via Exsolution

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Significance and Relevance

Exsolution is a technique of industrial significance which facilitates the formation of stable catalyst heterostructures. Using a model perovskite, AgNbO₃, this work expands understanding of how the structure-activity relationship develops for photocatalytic dye degradation during exsolution. Using an array of characterization techniques, focusing on both the labile Ag⁺ cations and static Nb⁵⁺ cations, a picture is being built of the structural development during thermal exsolution.

| Preferred and 2 nd choice for the topic: | Photocatalysis and photoelectrocatalytic approaches, so energy utilization | olar |
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| | Fundamental advances in understanding catalysis | |

Preferred presentation: Poster

Introduction and Motivations

Exsolution is an excellent approach to designing highly active and stable perovskite photocatalyst heterostructures.¹ Under reduction conditions, labile metal cations are drawn from the bulk to the perovskite surface where they coalesce to form nanoparticles (NPs). These NPs are strongly embedded within the surface, improving their stability compared to standard deposition techniques. For AgNbO₃, exsolution leads to Ag NP formation.² In photocatalysis, Ag NPs are known to act as plasmonic co-catalysts, enhancing light interaction and charge carrier lifetime of semiconductor photocatalysts.³ The effect of Ag-exsolution on AgNbO₃ photocatalytic activity is multi-modal, through: perovskite surface reforming, changing bulk structure, and Ag NP co-catalyst formation.

Materials and Methods

AgNbO₃ synthesized by grinding Ag₂O and Nb₂O₅ in a 1:1 molar ratio, then calcining under O₂ at 900 °C for 5 hrs. The perovskite was exsolved under 5% H_2/N_2 at 400 °C for 15, 30, or 45 mins. Product characterizations: XRD, UV-vis DRS, SEM, STEM-EDX, TPR, TRPL, XPS.

Photocatalytic degradation of Rhodamine B dye (40 mL, 5 mg L⁻¹) using AgNbO₃ (40 mg) was performed under irradiation of a 500 W UV lamp for 3 hrs. Dye concentration was determined from the relative absorption (λ_{RhB} = 554 nm) using UV-vis spectroscopy.

Results and Discussion

AgNbO₃ was successfully exsolved to form a Ag/AgNbO₃ heterostructure. Under reduction using 5% H₂ at 400 °C, Ag⁺ cations were removed from the perovskite bulk and formed Ag⁰ NPs on the surface. SEM images of samples which underwent 0, 15, 30, and 45 mins of exsolution clearly show an increase in the surface coverage of NPs. Initially, NPs formed at grain boundaries and in surface ridges, then arose in areas of lower surface energy, and eventually covered the entire perovskite surface. UV-vis DRS data confirms the NP's Ag⁰ composition from characteristic absorption peaks in the 400-600 nm region which increase in intensity alongside exsolution time. XRD, XPS and STEM-EDX analyses reinforce this conclusion.

The fate of the Nb⁵⁺ cations has been less clear. XRD analysis cannot identify any changes to the perovskite structure, however curious shifting in the Nb 3d XPS indicates the Nb coordination number may be changing from 6-to-5-to-6 as the structure is exsolved. To probe the Nb changes



further, *in-situ* XAS analysis is being pursued; this technique will also allow for a kinetic assessment of Ag⁺ movement through the perovskite structure. Understanding the Nb coordination environment will give a fuller picture on the bulk structure evolution.

Dye degradation tests of the photocatalyst series revealed a volcano trend between photocatalytic performance and extent of exsolution (Fig. 1). Considering just the Ag^0 formation, the initial increase in Ag^0 surface coverage (0 to 30 mins) likely improved catalytic performance because the NPs were acting as plasmonic co-catalysts. The steep drop in activity after 30 mins could be explained by an over-production of Ag^0 NPs blocking the $AgNbO_3$ surface from light absorption and blocking active sites from dye-interaction. Changes to the perovskite structure will also have contributed to the catalytic activity. During reduction, oxygen vacancy formation is expected which can aid performance in small numbers – by acting as electron sinks which delay electron-hole recombination – but in large numbers can be detrimental to fast charge carrier movement. The role Nb plays is under investigation and is the final part needed for full comprehension of the structure-activity relationship.



Figure 1. Graph showing effect of exsolution time on AgNbO₃ photocatalytic dye degradation of Rhodamine B and on Ag NP surface coverage (indicated by UV-vis DRS Ag (λ_{Ag} : 400-600 nm)).

References

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