东北师范大学
Northeast Normal University
School of Physics, 5268 Renmin Street, Changchun 130024, China

Report

on the thesis presented by Blashkov Ilia Vladimirovich, entitiled "Photocatalytic reaction $NO + CO \rightarrow CO_{2ads} + 1/2N_2\uparrow$, activated on zinc oxide by irradiation in the UV and visible spectral ranges" for degree of a Candidate of Sciences in 1.3.8. Condensed Matter Physics – The Saint-Petersburg State University.

ZnO is an important photocatalyst that are particularly suitable for both fundamental and applied studies on defect- and exciton-induced photocatalysis. While extensive research has been conducted, there is rare study concerning the photocatalytic reaction of NO and CO on ZnO, which is practically meaningful for environment and health issues. In the thesis reviewed, the author presents a unique research on investigating the photocatalytic reaction of NO and CO on self-sensitized ZnO by means of mass spectrometry and thermoprogrammable desorption spectroscopy. It is shown that the reaction was proceeded under both UV and visible irradiation (365 nm< λ< 578 nm) at room temperature, with N_2 and CO_2 as the final product. The conditions and features of the reduction reaction of NO to N_2 were revealed. The quantum yield of the N_2 release reaction was maximal in the visible region, which was attributed to the longer lifetime of photoactivated centers than with UV illumination of the illuminated surface. Exciton photoactivation channel was proved to work for the N_2 release reaction over $ZnO/ZnO_{1-x}/O^-$. Therefore, the research presented in the thesis has both theoretical and practical significance for the subject of study.

In the first chapter the thesis begins by offering a comprehensive literature review on the general background of ZnO materials including the preparation, the defective surface and the doping method, and the interaction of O_2, CO, CO_2, NO with ZnO surface. Lastly, reaction of NO and CO over several types of photocatalysts was reviewed in this chapter.

In the second chapter the thesis introduces the technique and methodology of the experiment as well as the characterizations of ZnO samples. Mass spectrometry, TPD, and photocatalytic reactor were introduced in detail. Self-sensitized ZnO samples were prepared by the well-established method, and carefully characterized.

In the third chapter, the thesis reports the results of the study on the interaction of CO, NO and NO + CO mixture with the surface of ZnO, pre-oxidized at 823K, in the dark and under photoactivation irradiation in the UV and visible region. It was revealed that CO was rapidly adsorbed on ZnO with little effect of photoadsorption; NO was reversibly adsorbed on ZnO, with intense photoadsorption to release N_2O; running a mixture of NO + CO on the samples led to rapid adsorption of CO and NO with the release of N_2O which was accelerated by increasing CO concentration due to the reduction effect of CO on ZnO surface. UV or visible irradiation of ZnO in the mixture of CO and NO led to the the release of N_2, with N_2O as intermediate product, and CO_2 adsorbed on ZnO surface.

Tel./Fax: +86 431 85099772
Mobile: +86 13604441281
ORCID ID: 0000-0003-0561-8902
Email: xtzhang@nenu.edu.cn

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The total process is written as $\boldsymbol{NO + CO \rightarrow CO_{2ads} + 1/2N_2\uparrow}$ on ZnO in UV and visible regions, with quantum yield higher in the visible region than in the UV region, following the spectral dependent feature of NO photoadsorption. On the $ZnO/ZnO_{1-x}/O^-$ sample, efficiency and quantum yield of N_2 release were 5-7 times higher with λ=382 nm irradiation than with λ=365 nm, suggesting the exciton-induced photoreaction channel.

Overall, the thesis presents a unique research on the photocatalytic reaction of $\boldsymbol{NO + CO \rightarrow CO_{2ads} + 1/2N_2\uparrow}$ on ZnO in the UV and visible regions. The results of the research have resulted in 2 papers and 4 conferences reports. The main conclusion of the thesis will undoubtedly inspire the research on the photocatalytic removal of NO and CO over oxides, which is critically important subject in environment and health related research fields.

A shortage I can see is the thesis contains several mistakes in typewriting. However, these mistakes do not spoil the positive impression made by the research. I can fairly conclude that the thesis entitiled "**Photocatalytic reaction $\boldsymbol{NO + CO \rightarrow CO_{2ads} + 1/2N_2\uparrow}$, activated on zinc oxide by irradiation in the UV and visible spectral ranges**", by **Blashkov Ilia Vladimirovich**, deserves to be awarded the degree of Candidate of Physical and Mathematical Sciences.

Xintong Zhang
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Dissertation Council Member
Prof. of Materials Physics and Chemistry
School of Physics,
Northeast Normal University,
Email: xtzhang@nenu.edu.cn
Tel. 0086 431 85099772