SOLAR-DRIVEN THERMOCHEMICAL CO_2 REDUCTION USING NONSTOICHIOMETRIC PEROVSKITE

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The solar energy is, by far, the most abundant renewable energy source. Thus, our challenge is to capture the vast, yet intermittent solar energy for on-demand usage. To address this issue, we pursue solar thermochemical fuel production using nonstoichiometric perovskite oxides. It relies on the redox reaction in which the nonstoichiometric perovskite strips oxygen atoms from carbon dioxides and water vapors. As a result, syngas, carbon monoxide and hydrogen fuels can be produced, reaching to the thermodynamic efficiency of 13~75% depending on materials and operation condition. Ceria has produced large amount of carbon monoxide and hydrogen in a solar-thermochemical cycle, showing the record solar-fuel conversion efficiency of ~1%. However, the operation temperature is extremely high, over 1500 °C, challenging reactor design. To moderate reaction condition with enhanced fuel productivity, we focus on the structure-thermochemistry relation in the Mn-based perovskite oxides, specifically Sr-doped $LaMnO_{3-\delta}$. Lower thermochemical temperature cycle, 1400-800 °C, was chosen. The hydrogen yield from water vapor increases with increasing the Sr content. It is mainly due to lower redox enthalpy rather than the entropy contribution. Carbon monoxide was also produced from CO_2, with the amount exceeding 5 ml/g. In situ X-ray absorption spectroscopy shows that the mean Mn valence increases from 3.12 to 3.41 while the Mn-O length decreases during CO_2 reduction. These results suggest that Mn redox in the MnO_6 octahedron is a key to improve thermochemical fuel productivity using the nonstoichiometric perovskite compound.