Recent Trends in Artificial Leaves: Atomistic-design and Surface-probing using Selective Two-dimensional Nanomaterials as Examples

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Abstract:

Photocatalytic CO_2 conversion to hydrocarbon fuels, which makes possible simultaneous solar energy harvesting and CO_2 reduction reaction (CO_2RR), is considered a killing-two-birds-with-one-stone approach to solving the energy and environmental problems. However, the development of solar fuels has been hampered by the low photon-to-fuel conversion efficiency of the photocatalysts and lack of the product selectivity. Recent advances in development of integrated nanostructured materials have offered unprecedented opportunity for photocatalytic CO_2RR [***Nanoscale*** *12*, 23301 (2020), invited review article]. Here, four cases in 2D-layered nanomaterials (TMDCs and beyond) with defect engineering (e.g. interstitial, vacancy, *etc.*) for CO_2RR will be illustrated: (i) single-layer [***Nature Comm.*** *11*, 3682 (2020)] to few-layer MoS_2 with vacancies controlled by plasma; (ii) reconstructed edge atoms of monolayer WSe_2 [***Nature Comm.*** *13,* 1256 (2022)]; (iii) the carbon-doped or carbon-implanted SnS_2 nanosheets [***Nature Comm.*** *9,* 169 (2018); ***Nano Energy*** *72*, 104717 (2020)]; and (iv) direct Z-scheme of ZnS/ZIS heterojunctions [***Nano Energy*** *93*, 106809 (2022)].

Ascertaining the function of in-plane intrinsic defects and edge atoms is necessary for developing efficient photocatalysts. A perfect planar layer of TMDC is usually inactive to catalysis, whereas the artificially generated sulfur vacancy clusters have enhanced CO_2 activation with multi-fold increase in CO_2 photoreduction efficiency. Vacancy clusters, as well as reconstructed and imperfect edge configurations enable CO_2 binding to form linear and bent molecules. Nanoscale redox mapping using scanning tunnelling microscope at the TMDC–liquid interface shows layer-dependent redox behavior [***Nature Comm.*** *12*, 1321 (2021)] and also confirms that the edge is the most preferred region for charge transfer [***Nature Comm.*** *13,* 1256 (2022)]. Besides the challenges in materials, to make such energy conversion techniques towards practical solutions, some key questions need to be addressed. For instance: **What are the determining steps for CO_2RR?** Advancements in *in situ* and *operando* synchrotron radiation-based spectroscopies, including X-ray absorption [***Nature Comm.*** *11*, 4233 (2020)] and X-ray photoelectron spectroscopy (XPS), *etc.*, along with various vibrational spectroscopies, such as Raman and Fourier transform infrared spectroscopy (FTIR), have enabled scientists to probe the geometric, bonding and electronic information of the catalyst and obtain atomic insights into the catalytic surfaces and reaction mechanisms [***J. Am. Chem. Soc.*** *142*, 2857 (2020); ***Nano Energy*** 93, 106809 (2022)].