

Nanometer-resolved Operando Photo-Response of Faceted BiVO₄ Semiconductor Nanoparticles

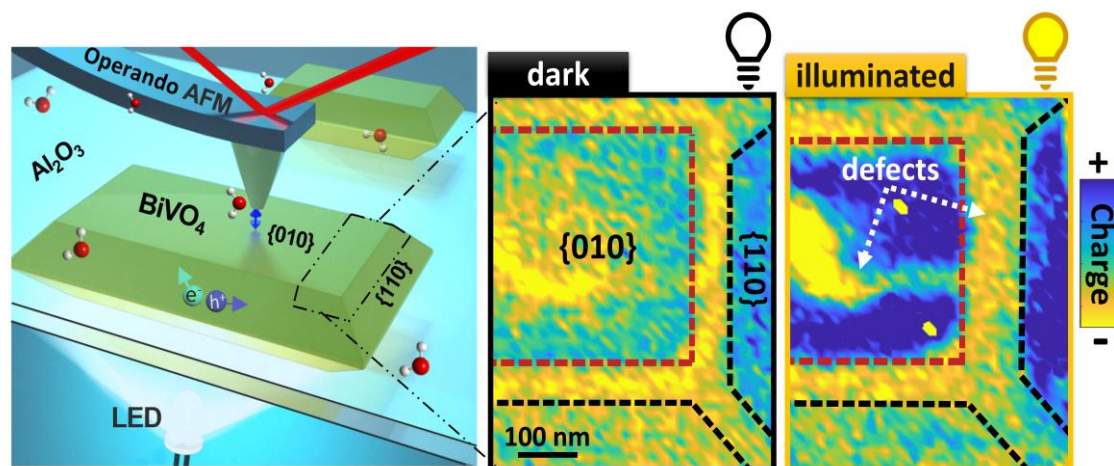
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Photo(electro)catalysis with semiconducting nanoparticles (NPs) is an attractive approach to convert abundant but intermittent renewable electricity into stable chemical fuels. However, our understanding of the microscopic processes governing the performance of the materials has been hampered by the lack of operando characterization techniques with sufficient lateral resolution. Here, using Atomic Force Microscopy we demonstrate that the local surface potentials of NPs of bismuth vanadate (BiVO₄) and their response to illumination differ between adjacent facets and depend strongly on the pH of the ambient electrolyte. The isoelectric points of the dominant {010} basal plane and the adjacent {110} side facets differ by 1.5 pH units. Upon illumination, both facets accumulate positive charges and display a maximum surface photo-response of +55mV, much stronger than reported in the literature for the surface photo voltage of BiVO₄ NPs in air. High resolution AFM images reveal the presence of numerous surface defects ranging from, vacancies of a few atoms, to single unit cell steps, to microfacets of variable orientation and degree of disorder. These defects typically carry a highly localized negative surface charge density and display an opposite photo-response compared to the adjacent facets. Strategies to model and optimize the performance of photocatalyst NPs therefore require an understanding of the distribution of surface defects, including the interaction with the ambient electrolyte [1-2].



- [1] Su, S., Siretanu, I., van den Ende, D., Mei, B., Mul, G., & Mugele, F. Facet-Dependent Surface Charge and Hydration of Semiconducting Nanoparticles at Variable pH. *Advanced Materials*, 33(52), 2106229 (2021).
- [2] Su, S., Siretanu, I., van den Ende, D., Mei, B., Mul, G., & Mugele, F. (2024). Nanometer-Resolved Operando Photo-Response of Faceted BiVO₄ Semiconductor Nanoparticles. *Journal of the American Chemical Society*, 146(3), 2248-2256.