## Solar Fuel Production from CO<sub>2</sub> and H<sub>2</sub>O by Brookite-Containing Mixed-Phase TiO<sub>2</sub> Photocatalysts

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Photocatalytic reduction of CO<sub>2</sub> to fuels (CO, methane, methanol, etc) by sunlight is potentially a promising sustainable energy technology that not only reduces greenhouse gas emissions but also produces renewable fuels. TiO<sub>2</sub> has been widely used as a photocatalyst due to its low cost, high stability, and non-toxicity. TiO<sub>2</sub> naturally occurs as three polymorphs: anatase, brookite and rutile. Among them, only TiO<sub>2</sub> anatase, rutile or anatase-rutile mixed phase (P25) have been studied for CO<sub>2</sub> photoreduction. Brookite phase is much less studied as a photocatalyst and has not been studied for CO<sub>2</sub> photoreduction so far. In this work, brookite containing mixed-phase (e.g., anatase-brookite, anatase-brookite-rutile) TiO<sub>2</sub> nanocrystals have been synthesized through a hydrothermal method with a good control in brookite phase fraction. The catalysts were well characterized by UV-vis, XRD, SEM, TEM, BET, and FTIR analysis. The experiments of photocatalytic CO<sub>2</sub> reduction with water vapor using the prepared catalysts were conducted under simulated sunlight irradiation. CO and CH<sub>4</sub> were the major reduction products measured by a gas chromatograph (GC) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). Mixed-phase anatase-brookite TiO<sub>2</sub> demonstrated higher catalytic activity than single phase anatase or brookite. Mechanistic studies including the effects of surface defect sites and interfacial charge transfer between different crystal phases were also investigated.