Radioytic solvated electron for carbon neutrality

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High-energy radiation (X/γ-rays or accelerated e^-) ionizes and excites water to ensure an initial homogeneous distribution of abundant reactive radicals[1], in which short-lived solvated electron (e_{sol}^-) represents the known strongest reducing species in nature that enable CO_2 activation to form $CO_2^{\bullet-}$ radicals with nearly diffusion-controlled rate ($e_{sol}^- + CO_2 \rightarrow CO_2^{\bullet-}$; $k_1 = 8.2\times10^9\ M^{-1}\,s^{-1}$). This first activation step has been regarded as the most energy-demanding and rate-limiting in precedent CO_2 reduction using photolytic and electrolytic electrons, but can be easily realized via radiolytic aqueous electrons[2]. Using e_{sol}^- chemistry, we have showed a selective and catalyst-free CO_2 conversion to oxalate through fast aqueous $CO_2^{\bullet-}$ dimerization ($CO_2^{\bullet-} + CO_2^{\bullet-} \rightarrow C_2O_4^{2-}$; $k_2 = 1.4\times10^9\ M^{-1}\,s^{-1}$) at ambient conditions. The transformation of $CO_2^{\bullet-}$ radicals to energy-rich fuels has been extended further by controllable intermediates binding with precisely designed catalysts. Besides, using surface-coordinated $CO_2^{\bullet-}$, we developed a strategy for the preparation of antioxidant copper under ambient high-energy irradiation. It is shown that effective adsorption of $CO_2^{\bullet-}$ on copper leads to further formation of bidentate formate multilayers, which hardly degrades surface characteristics but is resistant to chemical attack from a range of highly corrosive solutions such as H_2O_2, NaCl, Na_2S, and NaOH.

In sum, the efficient use of sustainable high-energy radiation as unprecedented energy input for the chemical transformation of CO_2 and water to value-added chemicals holds new promise for a carbon-neutral, sustainable energy economy.

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