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Room Temperature Decoking of Catalyst Nanoparticles Using Localized Surface Plasmon Resonance Energy

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Coking of transition metal (Ni, Co, Fe) catalyst nanoparticles is a persistent problem as it deactivates the catalyst over time for a number of chemical processes, including but not limited to hydrocarbon reforming, cracking, water-gas shift reaction, etc. [1]. Apart from replacing them with more expensive catalysts such as Pt or Pd, reactivation or regeneration of transition metal catalyst is achieved by heating coked product in oxygen to burn off the carbon deposit. We have recently shown that the localized surface plasmon resonance (LSPR) on aluminum (Al) nanoparticles can be used to initiate CO_2 reduction by carbon, through reverse Boudouard reaction (RBR), at room temperature, while using an electron beam to excite LSPR in an environmental scanning transmission electron microscope (ESTEM) [2]. Here we show that RBR can also be used to decoke (or reactivate) Ni catalyst nanoparticles at room temperature.

We chose Ni catalyst as a proof of concept because (a) it is used in multiple industrial processes, (b) we have experience using it for carbon nanofiber (CNF) growth which is an indicator of coking, (c) regrowth of CNFs after removing deposited materials by RBR is symptomatic of catalyst reactivation. We mixed Ni/SiO_2 catalyst powder with Al nanoparticles (40 nm to 160 nm) and loaded them directly on an Au TEM grid. First, the sample was heated to 600 ºC, using a furnace heating holder, before flowing ≈ 2 Pa of C_2H_2 in the ESTEM, equipped with a monochromated FEG and an image corrector, operated at 80 kV. Many CNFs are observed to form as a result of C_2H_2 dissociation catalyzed by Ni particles on the grid and Al nanoparticles (Fig. 1a,c). Next, we introduced ≈ 50 Pa of CO_2 after cooling down the sample to RT and removed CNFs within 20 minutes (Fig. 1b). Note that while the Ni catalyst particles on Al nanoparticles are clean, some CNFs remain away from the Al surface, indicating that electron beam damage is not the primary reason for the removal of CNFs. In addition, frames extracted from high magnification video (Fig. 1d,e,f) confirm that CNF damage starts in the vicinity of an Al nanoparticle (Fig. 1e). We can regrow the CNFs by repeating the growth process outlined above, and both low and high magnification images (Fig. 1c,g) show that Ni nanoparticles are reactivated for C_2H_2 dissociation. Consistent results were obtained by repeating the process several times, matching what we achieved in the past to reactivate Co catalyst by heating the sample in O_2 at 900 °C [3].

As expected, various modes of Al surface plasmons are identified in the low-loss region of electron energy-loss spectra (EELS). Several resonant modes: dipole (DP), quadrupole (QP), and hexapole (HP), and an electrostatic mode at the Al/Al_2O_3 interface are indicated in the spectra collected from various sizes of Al particles with a nearly uniform oxide thickness of ≈ 4 nm (Fig. 2a). We use the discontinuous Galerkin time-domain (DGTD) simulation to show the LSP modes at specific electron energy-losses that impose distinct near-field enhancement (Fig. 2b) to drive RBR that damages the CNFs.

Our ESTEM method elucidates the nanoscale mechanisms of ultraviolet (UV) plasmonics for reactivating coked Ni catalyst. The findings support the hypothesis that further research employing UV light sources and optics can be developed as a cheaper alternative, compared to heating in oxygen, for catalyst reactivation at an industry-level application.

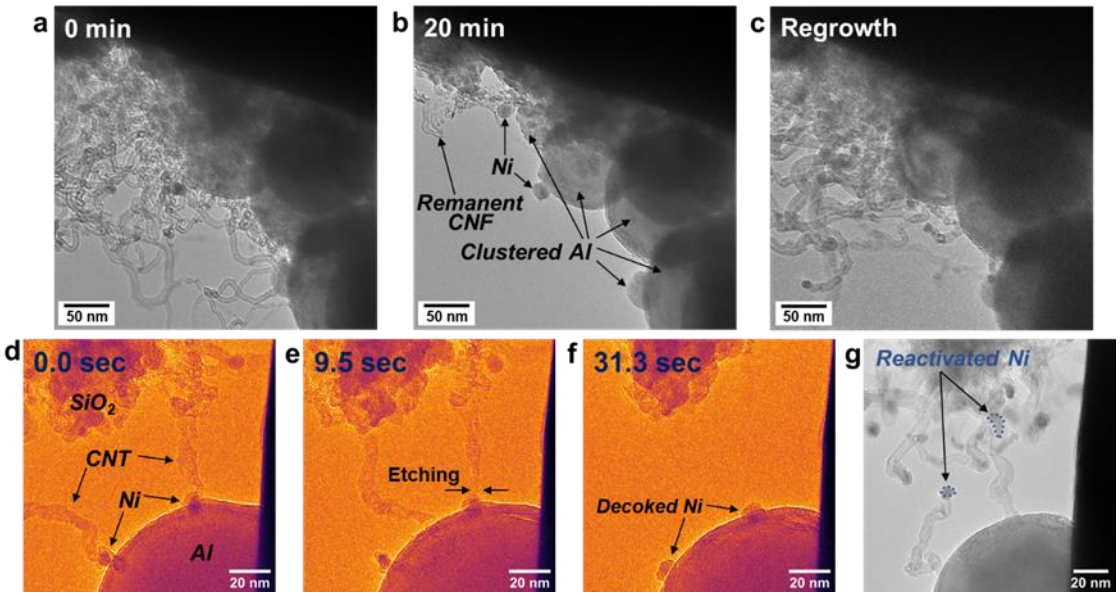

Figure 1. TEM images of **a,** an overview of CNFs formed on Ni catalysts, a source of deactivation. **b,** removal of CNFs by coupling a parallel electron beam (0.13 A/cm^2) to the LSP modes on a cluster of Al in a CO_2 environment. **c,** Regrowth of CNFs. **d-f,** False-color images extracted from an in-situ video showing the LSP field-driven CNF etching from individual Ni nanoparticles, starting near Al in CO_2. **g,** Regrowth of CNFs from the reactivated Ni catalysts.

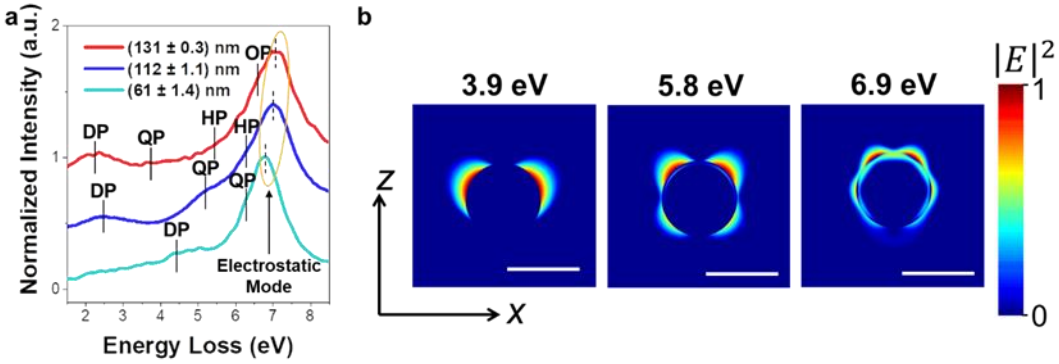

Figure 2. a, Low-loss EELS showing spectral features associated with the LSP modes (DP, QP, and HP) of Al and the electrostatic mode at the Al/Al_2O_3 interface (dashed lines). **b,** DGTD simulation displaying the field enhancement of DP, QP, and HP of a 100-nm Al nanoparticle. Scale bars are 100 nm.

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