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Room Temperature Reduction of Carbon Dioxide to Carbon Monoxide Initiated by Localized Surface Plasmon Resonance of Aluminum

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To tackle the issue of global warming, one of the options being considered is to convert CO_2 into fuels using renewable energies, such as photochemical conversion of CO_2, which could displace fossil use and therefore achieve net emission reduction. [1] However, the current approaches of photocatalytic CO_2 conversion suffer from one or multiple of the following drawbacks: 1) the efficiency is far too low for practical large-scale applications; 2) the reaction conditions require elevated temperature or extreme pressure; 3) the need to use precious metal as the catalyst. [2] Overall, the considerable challenge faced by current methods is the development of efficient catalysts based on cheap and earth-abundant elements rather than expensive precious metals, as well as mild reaction conditions to operate. Both of which will contribute to the scalability of the conversion process in order to make any reasonable contribution to the CO_2 emission reduction.

Here we propose the conversion of CO_2 into CO at room temperature at low CO_2 partial pressure using earth-abundant elements: Al and carbon. [3] Al nanoparticle was chosen as a localized surface plasmon resonance (LSPR) source due to its low cost and broadband LSPR response in the UV range. Figure 1A shows an annular dark field (ADF) image of Al nanoparticles dispersed on carbon films. A typical LSPR spectrum is acquired by placing the electron beam close to the nanoparticle (aloof mode), as shown in Figure 1B-C. Electron energy-loss spectra (EELS) imaging is used to acquire both elemental and LSPR maps from the same Al nanoparticle, as shown in Figure 1D. The elemental and LSPR composite maps show that Al nanoparticles have an Al/Al_2O_3 core-shell structure, and the loss probability of the energy associated with the LSPR is located within the vicinity of the nanoparticle surface. By taking advantage of the LSPR of Al, we show that carbon gasification also occurs only with the vicinity of the Al nanoparticle surface in a CO_2 environment, as shown in Figure 2A-B. The reaction rate is measured from the carbon consumption rate using energy-filtered transmission electron microscopy (EFTEM) as a function of the number of particles (Figure 2C), electron flux (Figure 2D), and CO_2 pressures (Figure 2E). The result shows that the reaction rate is linearly proportional to the number of particles and electron flux, while plateaus at a CO_2 pressure of 25 Pa or higher. The temperature of the particle is measured using the bulk plasmon peak of Al during the reaction and is found to be near room temperature (Figure 2F). Our approach has allowed us to demonstrate a direct LSPR initiated reverse Boudouard reaction ($CO_2+C \rightarrow 2CO$) with a high turnover rate at room temperature and low CO_2 partial pressure. The low cost and ease of implementation of our approach increase its scalability and paves the way to store solar energy in the production of carbon fuels effectively. [4]

References:

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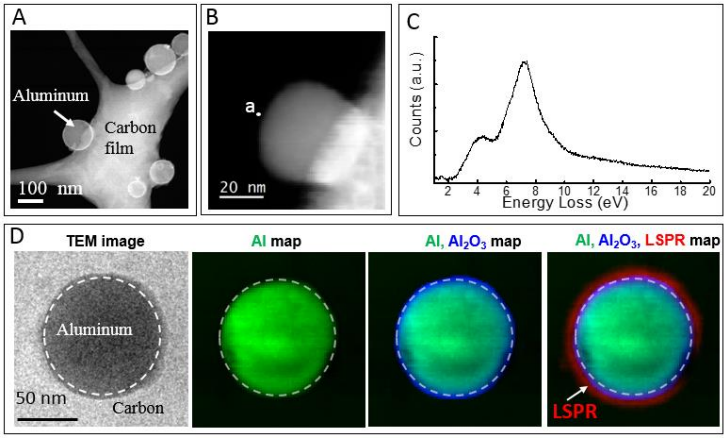

Figure 1. A, ADF image of Al nanoparticles deposited on carbon firm. B, ADF image of an Al nanoparticle. C, EEL spectrum acquired from point a in B. D, TEM image, as well as elemental and LSPR maps showing an Al/Al_2O_3 core-shell structure, as well as the distribution of LSPR within proximity of the nanoparticle. The dashed white line outlines the shape of the Al core.

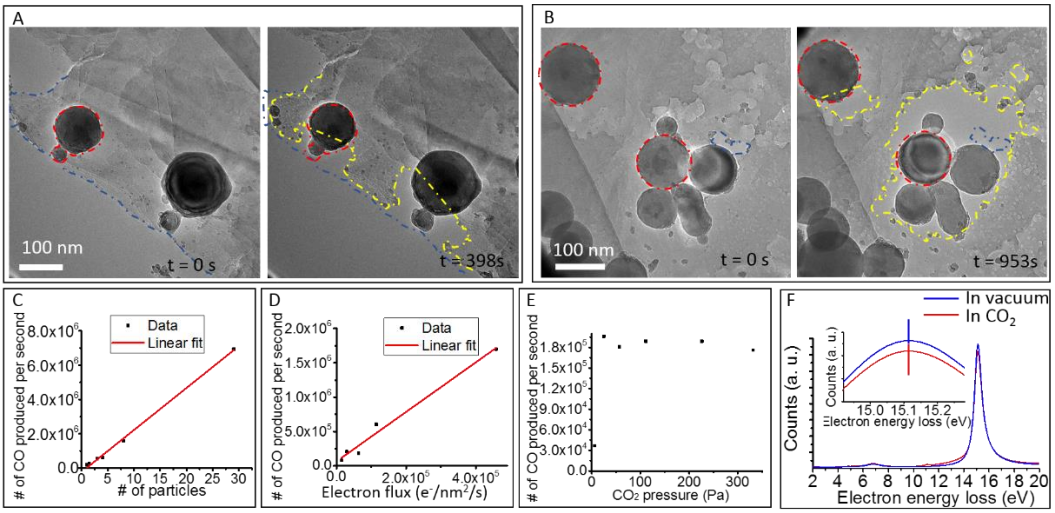

Figure 2. A-B, time-resolved TEM images showing the effect of the electron beam irradiation in a CO_2 environment on graphite near Al nanoparticles. With the presence of Al nanoparticle, gasification of carbon is found to be dominant within the proximity of the Al nanoparticle surface. C-E, the production rate of CO derived from the carbon consumption rate measurements as a function of the number of particles (C), electron flux (D), and CO_2 pressures (E). The result shows that the reaction rate is linearly proportional to the number of particles and electron flux, while plateaus at a CO_2 pressure of 25 Pa or higher. F, Temperature measured during the reaction through the bulk plasmon peak position of a single Al particle confirms the reaction temperature to be near room temperature.

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