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Supplementary information

Catalytic effect of laser-combined atmospheric pressure plasma in lowering the reduction temperature of hematite

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EXPERIMENTAL SETUP

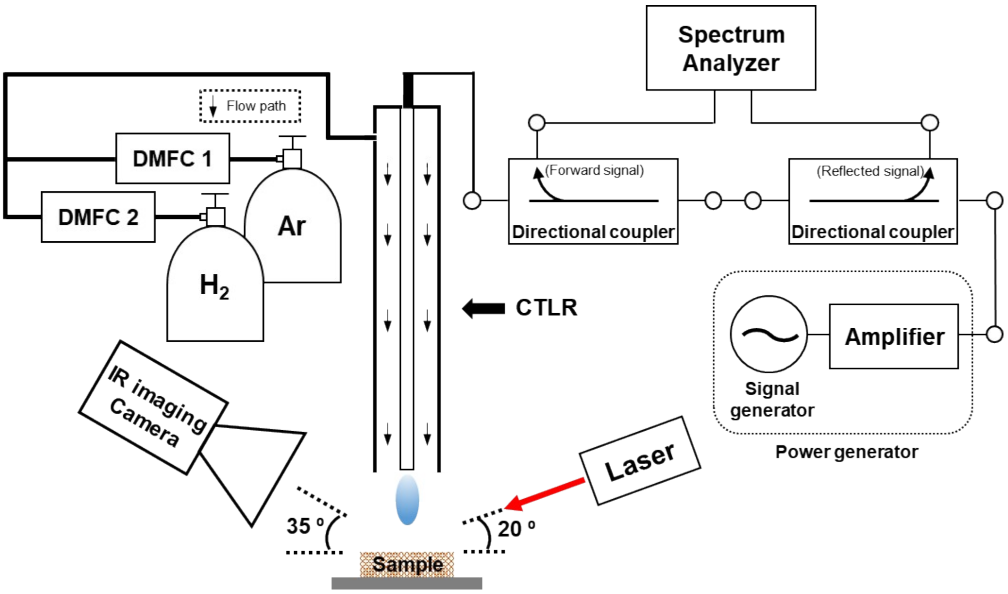

Fig S1. Experimental schematic diagram.

Figure S1 shows the experimental schematic diagram of the microwave CTLR plasma system combined with a laser. We use argon as a carrier gas and hydrogen as a feed gas to boost the generation of radical hydrogen species. The system consists of the CTLR electrode, digital mass flow controllers (VIC-D200 Series, MFC KOREA), and a microwave source. In the microwave source, a power generator (2.45GHz ISM BAND SSPA, KRF) with a signal generator and an amplifier is used to drive a plasma. The net input power coupled to the plasma is measured using a spectrum analyzer (E4408B, Agilent) with two directional couplers (ZUDC20-183+, Mini-Circuits) guiding the forward and reflected signals. The compact laser operating in a continuous wave with 808 nm and 1.5 W controls the surface temperature of a sample, and the laser path angle to the sample plane is 20 degrees.

The sample used in the experiments is hematite in the form of powder (particle size < 5 µm, purity 99 %) (310050-500G, Sigma-Aldrich). We prepare the sample by compacting the powder in an aluminum plate with a shallow recess in the middle to prevent its dispersion by the gas flow. During the treatment of the sample, we monitor the surface temperature of the sample using an IR imaging camera (P620, FLIR) with a notch filter to block the laser light. The camera angle to the sample plane is 35 degrees. Since the emissivity data for hematite powder is not available, we set the emissivity of 0.95 as a reasonable value.[1,2] After the treatment, we analyze the oxidation state of the sample using an X-Ray diffractometer (RINT 2000, Rigaku), a Raman spectrometer (FEX-MD, NOST), Scanning Electron Microscope (SU6600 ,Hitachi), and X-ray Photoelectron Spectrometer (ESCALAB 250, Thermo Scientific).

The flow rates of individual gases are critical in obtaining high-density plasma while maintaining the stability of the plasma plume for a given microwave input power. For instance, too little argon flow will result in a small plasma plume size, while too much argon flow will result in an unsteady turbulent flow. On the other hand, too much hydrogen flow will lead to a small plasma volume. For a nominal input power level of 15 W, we achieve a stable plasma plume with an argon flow rate of about 2 standard liter per minute (SLM), and an hydrogen flow rate of about 10 standard cubic centimeters per minute (SCCM).

Quantification of XRD patterns using Rietveld Refinement Method

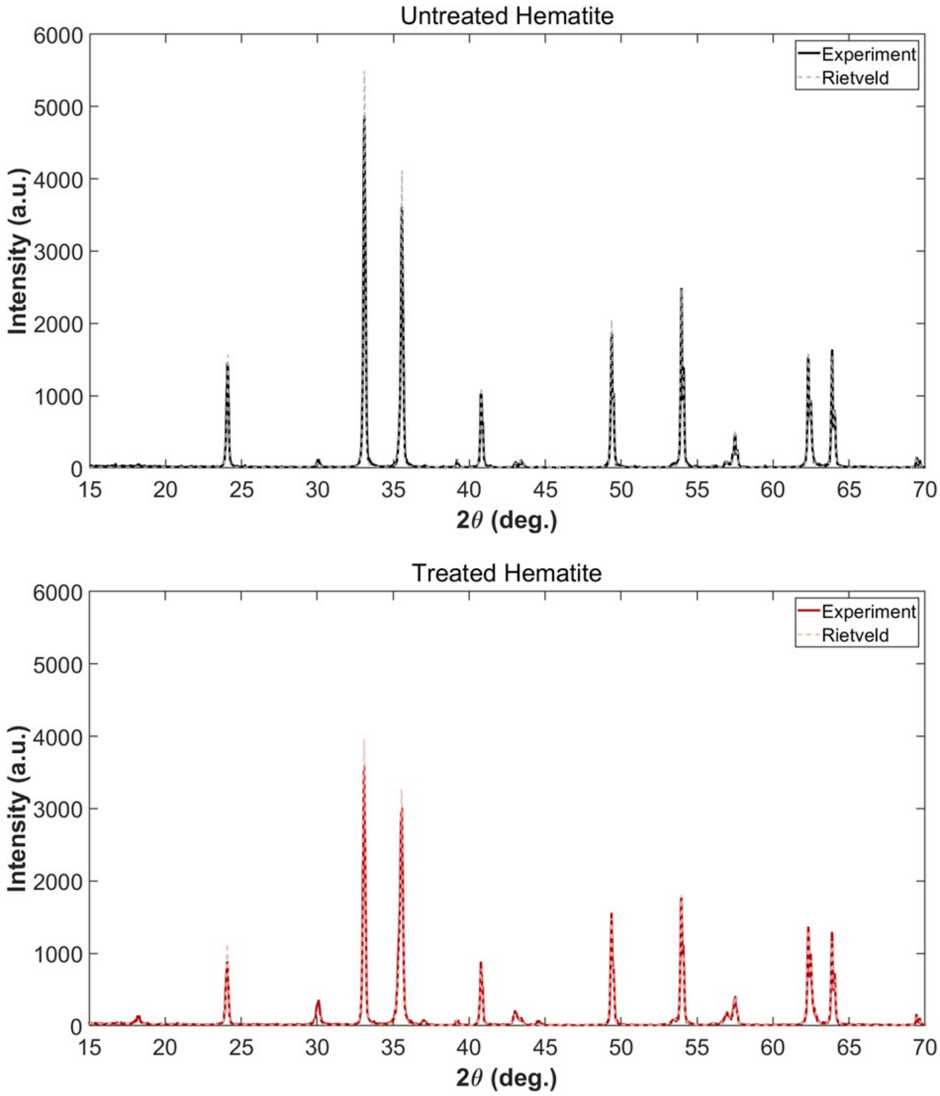

Fig S2. Comparison of XRD patterns and Rietveld refinement data.

	Fe_2O_3				Fe_3O_4				Sig (Goodness-of-fit)
	Volume Fraction	Mass Fraction [Wt. %]	Lattice Parameter [Å]	Density [g/cm³]	Volume Fraction	Mass Fraction [Wt. %]	Lattice Parameter [Å]	Density [g/cm³]	
Reference	**0.9442**	**94.46983 ± 0.7517607**	**a=5.0433 c=13.7721**	**5.2447**	**0.0558**	**5.530165 ± 0.15357354**	**a=8.3991**	**5.1911**	**1.890**
Treated	**0.8141**	**81.55854 ± 1.3648969**	**a=5.0430 c=13.7711**	**5.2456**	**0.1859**	**18.441456 ± 0.0**	**a=8.3968**	**5.1954**	**1.989**

Table S1. The volumetric fraction, mass fraction, lattice parameter, and density conducted with MAUD software and COD (Crystallography Open Database) database.[3]

Figure S2 and Table S1 shows the results of Rietveld refinement method on XRD patterns (**Fig. 3**) using MAUD simulation. The volume fraction of Fe_3O_4 increases from 0.0558 to 0.1859 after laser-combined plasma treatment. The simulation results also revealed that the hematite powder is partially reduced to magnetite after laser-combined plasma treatment.

References

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