

Synthesis, Characterization, and Variable Range Hopping Transport of Pyrite (FeS₂) Nanorods, Nanobelts and Nanoplates

Miguel Cabán-Acevedo, Dong Liang, Kit S. Chew, John P. DeGrave, Nicholas S. Kaiser and Song Jin*

Department of Chemistry, University of Wisconsin–Madison, 1101 University Avenue, Madison,
Wisconsin 53706, United States

AUTHOR EMAIL ADDRESS: jin@chem.wisc.edu

I. Thermal dynamics of pyrite formation and decomposition

Table S1. List of the free energy of formation ($\Delta_f G$, in kJ/mol) for the various chemical species involved in the formation and decomposition of iron pyrite.

Chemical Species	Free Energy of Formation ($\Delta_f G$) / kJ/mol				
	600 K	700 K	773 K	800 K	900 K
FeCl ₂ (g)	-169.969	-174.514	-177.625	-178.914	-183.147
Cl ₂ (g)	0	0	0	0	0
FeBr ₂ (g)	-110.827	-116.982	-121.325	-122.995	-128.842
Br ₂ (g)	0	0	0	0	0
S ₂ (g)	35.511	22.562	14.256	10.033	0
FeS ₂ (s)	-143.86	-137.074	-131.035	-129.946	-120.367
Fe _{0.877} S (s)	-107.356	-107.403	-107.364	-107.335	-106.047

Notes:

1) Values for 600 K, 700 K, 800 K, and 900 K are taken from: Chase, M. W. J., NIST-JANAF Thermochemical Tables. 4th ed.; American Institute of Physics: Woodbury, New York, 1998. The values for 698 K were taken from 700 K as approximations and the values for 773 K were linearly extrapolated from the tabulated values. Value for Fe_{0.877}S (s) at 773 K was calculated by averaging the values for 600–800 K.

2) There are many forms of “sulfur” vapor species available but most other possible forms of gaseous sulfur have similar free energy of formation to S₂(g), except only for atomic S vapor, which is too unfavorable to be realistic. Using these alternative values for various solid or gaseous sulfur do not

significantly change the values of the free energy of reactions considered in the main text, certainly not their qualitative trend.

II. Calculation of electrolyte gate and back gate capacitance of the FET device in Figure 5(c)

The electrolyte gate capacitance C_g is derived by using a parallel plate capacitor model $C_g = \epsilon\epsilon_0 S/t$ where ϵ is the dielectric constant of PEO (~ 10), ϵ_0 is the vacuum permittivity, S is the area surrounded by electrolyte, t is the thickness of capacitor. We choose Debye length of the electrolyte ($\lambda_D = 1$ nm) as the thickness of capacitor. Taking into account the total area $S = (2d+w)L$ surrounded by electrolyte, where d , w , L are the thickness, width, and length of the device, respectively. The general expression for the capacitance of electrolyte gating for pyrite NRs, NBs and nanoplates is then $C_g = \epsilon\epsilon_0(2d + w)/\lambda_D$.

Based on the similar model, the back gate capacitance is calculated using $C_g = \epsilon\epsilon_0 S/d$ in which ϵ_0 is vacuum permittivity, $\epsilon=3.9$ is the dielectric constant of SiO₂ layer. $S = 1 \mu\text{m} \times 2.74 \mu\text{m}$ is the area that the NR in contact with the substrate. $d = 600$ nm is the thickness of dielectric silicon oxide layer. So the capacitance for this back-gated pyrite NB is calculated to be 1.58×10^{-16} F.

III. Field effect and variable range hopping transport in pyrite nanoplates

Pyrite nanoplates FET devices show similar back gating effect to pyrite nanorods and nanobelts. Figure S1 shows a typical back gated FET measurement of a single pyrite nanoplate. Temperature dependent electrical measurement of pyrite nanoplates also reveals Mott variable range hopping transport from 50 – 220 K and thermal activation of carriers from 300 – 400 K, as shown in Figure S2.

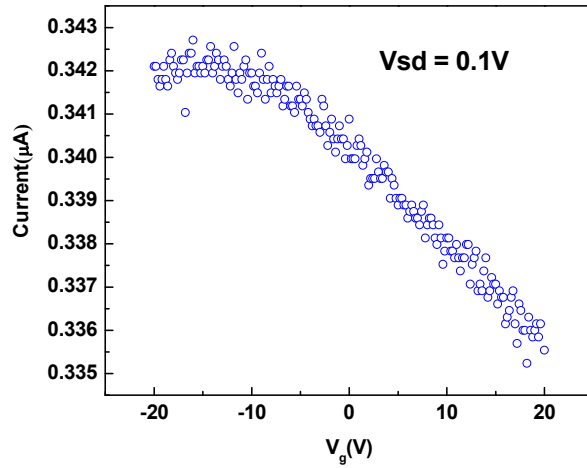


Figure S1. Back gating of a typical pyrite nanoplate.

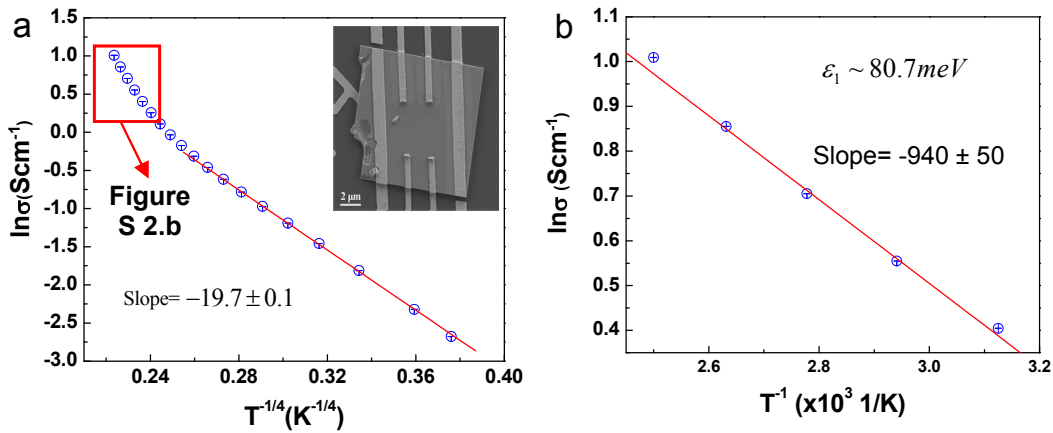


Figure S2. Logarithm conductivity ($\ln \sigma$) as a function of temperature (T) from 50 K to 400 K for a nanoplate device. (a) The linear dependence in the $\ln \sigma$ vs. $T^{-1/4}$ from 50 K to 220 K suggests Mott variable range hopping. Inset shows the SEM image of the nanoplate device. (b) $\ln \sigma$ vs. T^{-1} . Activation energy of about 80.7 meV was obtained from the linear fitting.