Photocatalyst Design for Renewable Hydrogen Production from Biomass and Landfill-Derived Methane

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Incipient Wetness Impregnation

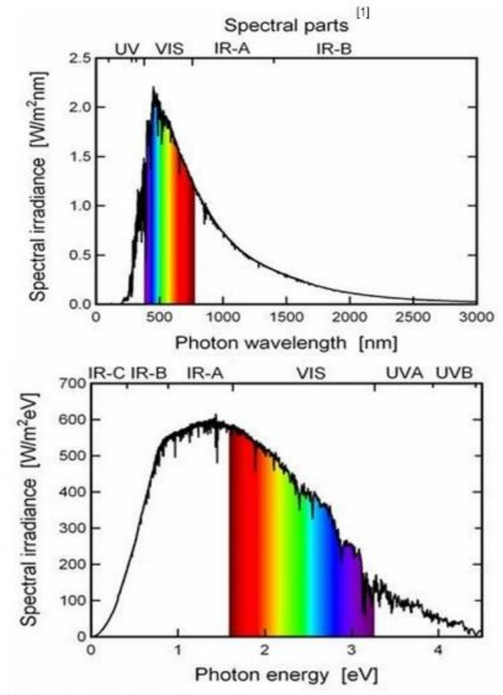
Supporting metals/metal oxides on TiO_2 surface decreases the band gap via a synergistic effect with the Valence (VB) and Conduction (CB) band positions of the TiO_2 and the Fermi level of metal and or the VB/CB position of metal oxide

Annealing

High Temperature High Pressure (HPHT) Annealing produces Ti^{3+} Centers, Oxygen vacancies, and defects that effect the reactivity and BGE of metal oxide semiconductor catalysts

Flame Synthesis Carbon Doping

Carbon doping via low pressure flame synthesis stabilizes defects in the crystal lattice which is hypothesized to increase the photocatalytic activity of metal oxide semiconductors



[1] C. Gueymard. *Solar Energy* (2004) 423

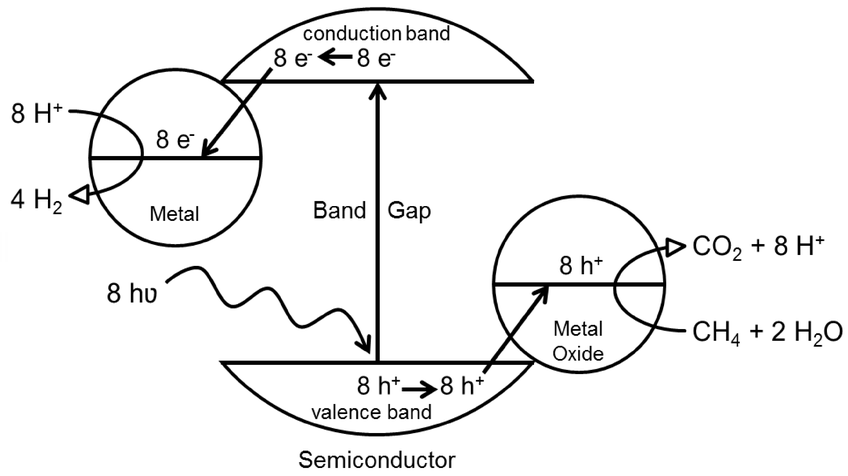
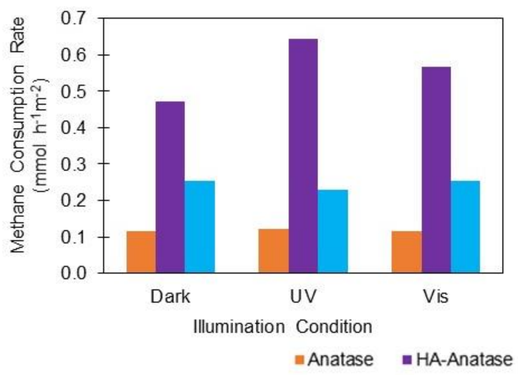
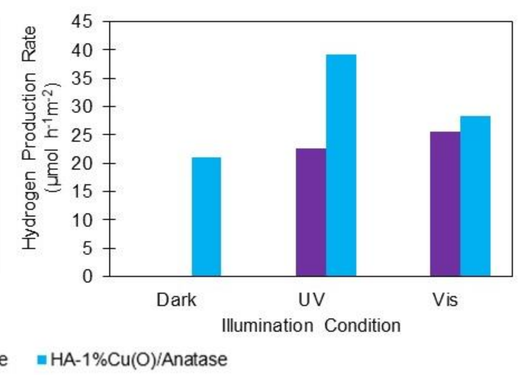


Figure: MSR on a semiconductor photocatalyst with supported metal and metal oxide nanoparticles.

Methane Consumption Rate at 700 °C



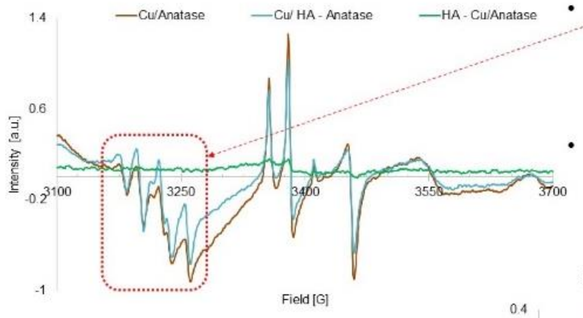
Hydrogen Production Rate at 700 °C



Anatase ■ HA-Anatase ■ HA-1%Cu(O)/Anatase

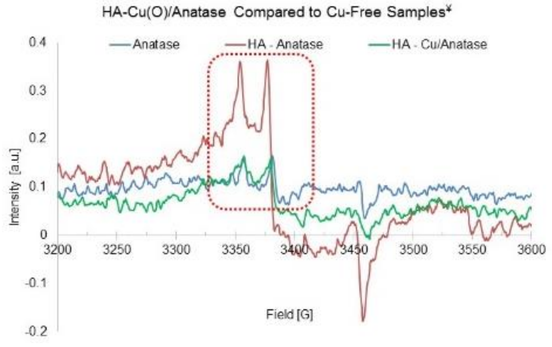
EPR Analysis of Copper Supported on HA-Anatase

HA-Cu(O)/Anatase Compared to Cu Modified Samples



- Copper(II) Oxide (Cu^{2+}) Hyperfine
  - Cu(O)/Anatase
  - Cu(O)/HA-Anatase
  - Not seen in HA-Cu(O)/Anatase
    - Indicating Cu^{2+} was reduced during annealing
- Ti^{3+} Center
  - All treated samples
  - Not seen in untreated Anatase

HA-Cu(O)/Anatase Compared to Cu-Free Samples*

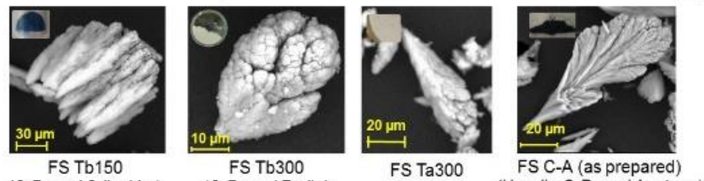


- Hydrogen annealing post supporting copper (Cu/HA-Anatase)
  - Reduction of the Copper(II) Oxide to Copper Metal
    - Lack of hyperfine for Cu^{2+}
  - A decreased reduction (Ti^{3+}) of the titanium of the support

Low Pressure Flame Synthesized TiO_2

Low Pressure Flame Spray Pyrolysis was a synthesis method to synthesize various polymorphs of carbon-doped TiO_2 from Titanium isoproproxide precursor.

Pre-mixed gases fed into the chamber, maintained at a 20 torr during the synthesis.

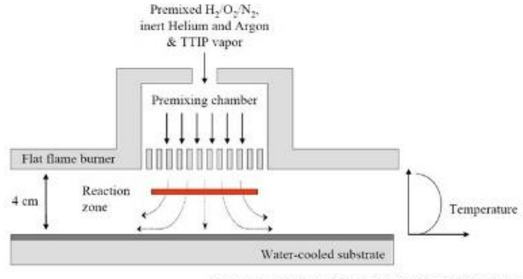


FS Tb150 (C-Doped Srilankite) | FS Tb300 (C-Doped Rutile) | FS Ta300 (Anatase) | FS C-A (as prepared) (Heavily C-Doped Anatase)

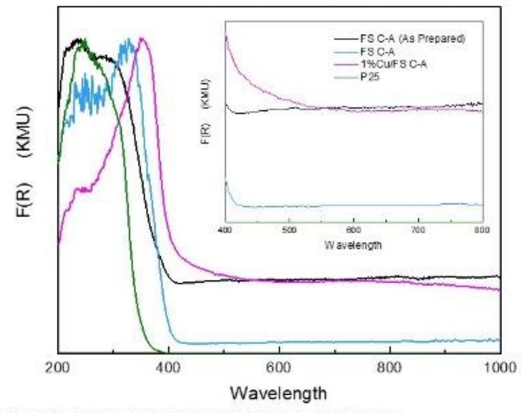
Sample	Tauc$^{1/2}$ BGE [eV]	dR_∞/dt BGE [eV]
FS Tb150	3.35	3.42, 3.63
FS Tb300	3.46	3.34, 3.04
FS Ta300	3.27	3.29, 3.57
FS C-A (as prepared)	2.75	3.27*
FS C-A (Calcined)	2.95	3.07, 3.17
1%Cu(O)/FSCA	2.78	3.19, 2.83

* Low intensity of derivative peak

1%Cu/FS C-A has a small BGE, 2.75 eV, and the absorbance of in the visible spectrum was greater than pure TiO_2 (P25) indicating that 1%Cu/FS C-A could potentially be a good visible-light-active photocatalyst.



Normalized Kubelka-Munk



Synthesis performed in Laboratory of Dr. Stephen Tse, Mechanical and Aerospace Engineering Department at Rutgers. Training and first set of samples provided by Hadi Halim