Photocatalytic Conversion of CO_2 into CH_4 and CO over Nitrogen Modified TiO_2

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Abstract:

TiO_2 is a cheaper alternative for photocatalytic conversions allowing for the conversion of CO_2 into CH_4 and CO. Doping TiO_2 with nitrogen compounds, like urea, has been shown to enhance the absorption of TiO_2 from the UV into the visible portion of the spectrum. This study showed that N-TiO_2 treated at 400 °C and 500 °C significantly produced CH_4 and CO.

Introduction:

- TiO_2 is a low-cost, non-toxic, and stable semiconductor that enables efficient light-induced generation and separation of charges, enabling redox reactions with substrates or induce a photocurrent [1]
- If peak absorption of TiO_2 can be shifted into the visible, it could be used to mitigate CO_2 emissions and produce hydrocarbons [3,4]
- TiO_2 absorbs only about 5% of solar radiation (in UV), but with nitrogen doping, this can be possibly shifted into the visible portion of the spectrum [2]
- Using urea to dope TiO_2 has shown promise, but the thermal decomposition of urea is complex and diverse, producing many nitrogen based product, which are influenced by temperature, heating time, atmospheric composition, and pressure [5]

Methods:

1. Nitrogen doped titanium oxide (N-TiO_2) was synthesized using a 3:7 mass ratio of urea to TiO_2 (Fig. 1).
2. Using a kiln (Fig. 2), mixtures were calcined for an hour at four temperatures (300 °C, 400 °C, 500 °C, and 600 °C) to induce a pyrolysis reaction.
3. A Cary UV-Visible Spectrometer was used to collect UV spectrum (Fig. 4).
4. Bandgap energies were calculated (Fig. 5).
5. In-situ carbon dioxide was produced by combining sodium bicarbonate (Sigma Aldrich) and vinegar (Stop & Shop Brand).
6. Each sample of N-TiO_2 was irradiated at three different light conditions for three hours (Fig. 6).
   a. UV LED light (395 nm)
   b. Visible LED light (590 nm)
   c. Natural sunlight (7/20/17 from 11:30 – 2:30 & 7/27/17 from 11:45 – 2:45pm in Durham, NH)
7. Final products were analyzed in a mass spectrometer (Fig. 3, Table 1).

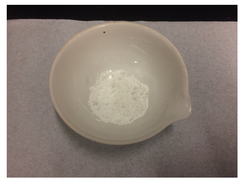

Figure 1.

Figure 2.

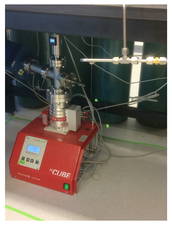

Figure 3.

Results:

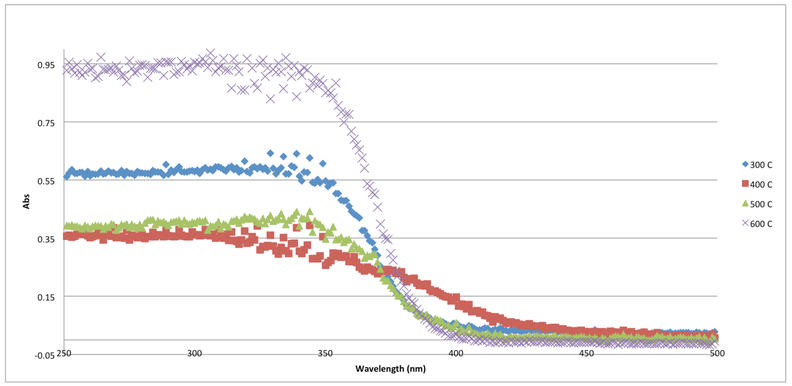

Figure 4. UV spectrum of N-TiO_2 modified at different temperatures.

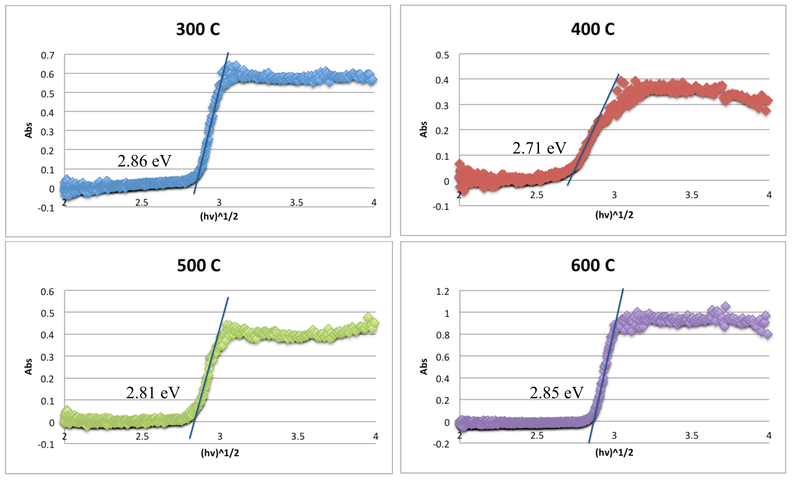

Figure 5. The bandgap energies were calculated from the x-intercept of the linear portion of the plot on a plot of the absorption vs. $(hv)^{1/2}$.

Table 1. Products (CH_4 and CO) distribution over N-TiO_2 samples. Significantly produced (marked YES), and not significantly produced (marked NS).

	UV (395nm)		Visible (590nm)		Sunlight	
Temp of Modification (°C)	CH_4	CO	CH_4	CO	CH_4	CO
300	NS	NS	NS	NS	NS	NS
400	NS	NS	NS	NS	**YES**	**YES**
500	NS	NS	**YES**	**YES**	**YES**	**YES**
600	NS	NS	NS	NS	NS	NS

Discussion:

- Without modification, TiO_2 absorbs better in the UV, with modification, they are suppose to absorb better in the visible [1,3]
- The hypothesis is that with increased temperature modification, the absorption peak would shift more to the visible (Fig. 4) (similar to the study done by [1])
- Bandgap energies decreased (Fig. 5) with nitrogen modification [1] suggesting that Ti^{4+} atoms are not being reduced to a lower oxidation state
- Sample modified at 500 °C absorbed well at 590 nm and in sunlight and sample modified at 400 °C absorbed well in sunlight which leads to significant production of CH_4 and CO (Table 1)

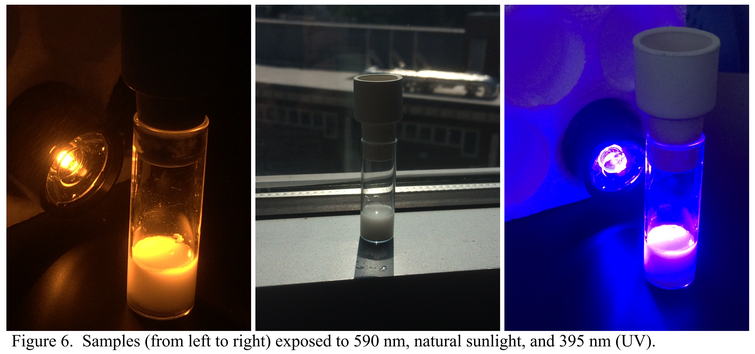

Figure 6. Samples (from left to right) exposed to 590 nm, natural sunlight, and 395 nm (UV).

Summary:

- Nitrogen modified TiO_2 was shown to shift absorption peak into the visible light range
- Bandgap energies were significantly decreased compared with undoped TiO_2 (3.2 eV) [4]
- CH_4 and CO was generated from photocatalytic CO_2 conversion in 3 of the 12 samples (400 °C and 500 °C in sunlight and 500 °C at 590 nm)

References:

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