Plasma assisted NH_3 synthesis over plasmonic titanium oxynitride/titania thin films

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Highlights

- NH_3 synthesis from a N_2/H_2 mixture over an oxynitride/titania coating was studied in a micro DBD reactor with a discharge gap of 0.5 mm at room temperature and ambient pressure. A high-voltage pyramid-shaped electrode was used to strengthen plasma and increase conversion.
- The oxynitride/titania coating was deposited onto the ground electrode. The coatings were synthesized by nitridation of titania with a NH_3/N_2 mixture at temperatures in the 650-850°C range. The N- content increased with nitridation temperatures.
- The optimal N_2/H_2 mixture to get the maximum ammonia yield shifted from the stoichiometric (1:3) to equimolar (1:1) over the oxynitride catalyst.

1. Introduction

Ammonia (NH_3) is a crucial chemical feedstock to produce fertilizers, pesticides and many other chemicals.[1] The Haber-Bosch process for NH_3 synthesis suffers from the requirements of high pressure in the range of 150-250 bar and high temperature up to 450°C as well as the Fe-based catalysts.[2] Non-thermal plasma (NTP) has attracted growing interest for NH_3 production from N_2 and H_2 at ambient pressure and temperature.[3] Especially dielectric barrier discharge (DBD) reactors provide stable discharge and they are scalable from small laboratory reactors to large industrial plants with megawatt input power. Previous results demonstrate that pyramid-shaped micro-tip electrodes can excite more nitrogen molecules than the traditional flat electrodes. The pyramid electrodes show 58% more nitrogen oxides yield efficiency at 32% less energy cost.[4]

Alternative materials to noble metals such as transition metal nitrides and oxynitrides allow for controllable dispersion behavior, improved absorption, and catalysis at room temperature. In this work, titanium oxynitrides supported on mica were synthesized for application in a dielectric barrier discharge (DBD) reactor with a pyramid-shape electrode. This approach allows synergy between vibrationally excited species generated by plasma and catalyst surface vibrationally excited states (plasmons).

2. Methods

The titanium oxynitride (TON) catalysts were obtained by reducing the titania nanopowder with a 50 vol.% NH_3/N_2 mixture at 650, 750 or 850 °C for 5 h at a heating rate of 5 K min^{-1} (sample codes: TON-650, TON-750, and TON-850, respectively). Then the TON powder was suspended in a water/methanol solution and brush coated onto a mica plate with a diameter of 25 mm. The coated mica plate was sealed to the ground electrode providing a dielectric layer in the reactor. The catalysts were characterized by XRD, XPS, SEM, and UV-VIS spectroscopy. The plasma assisted catalytic tests were performed in a parallel-plate micro-DBD plasma reactor. 160 regular pyramids with 1 mm^2 base 1 mm height in a periodic pattern on a Titanium coin was used as high-voltage electrode as shown in Figure 1(b). There are no infinitely sharp points that exist in reality and achieving extreme sharpness at atmospheric pressure is highly susceptible to damage as described elsewhere.[4] At a discharge gap of 0.5 mm, the N_2/H_2 mixture with a total flowrate of 80 ml/min monitored by a set of MFCs was flowing through in the reactor to synthesize NH_3. The ammonia was monitored by an FTIR spectrometer (Shimadzu). The plasma was created by a power generator (G2000, Redline Technology). The voltage was measured by a high voltage probe (100 MΩ, 3.0 pF) connected to an oscilloscope (Picoscope). A 400 pF external capacitor was connected in this circuit to measure the charge.

3. Results and discussion

With the increasing nitridation temperature, a vivid color change was observed (Figure 1(a)). The XRD patterns of nitridated samples indicated that anatase was the dominant crystalline phase in TON-650. The oxynitride phase was also detected. The anatase phase was converted to rutile in TON-850. The total N content increased from 5.3 to 52.8 at%. UV-VIS spectra showed strong absorption (Figure 1(c)). The absorption increased in the entire visible range with the increasing N content demonstrating plasmonic effect. At the same time, the absorbance in the UV region decreased.

The NH_3 yield is improved compared to that over non-coated electrode (Fig. 1(d)). While the best NH_3 yield is obtained with the appearance of the TON-850 when the N_2 concentration is 65%. The N_2 concentration for highest NH_3 yield of each sample is increased, which is beneficial for NH_3 synthesis since the N_2 is cheaper, more abundant and more accessible than the H_2. We also find that the N-doping content of TON samples is increased after plasma reaction which means that part N_2 is consumed for the further nitridation for the catalyst's coatings which might the main reason for the N_2 concentration increasing for best NH_3 yields.

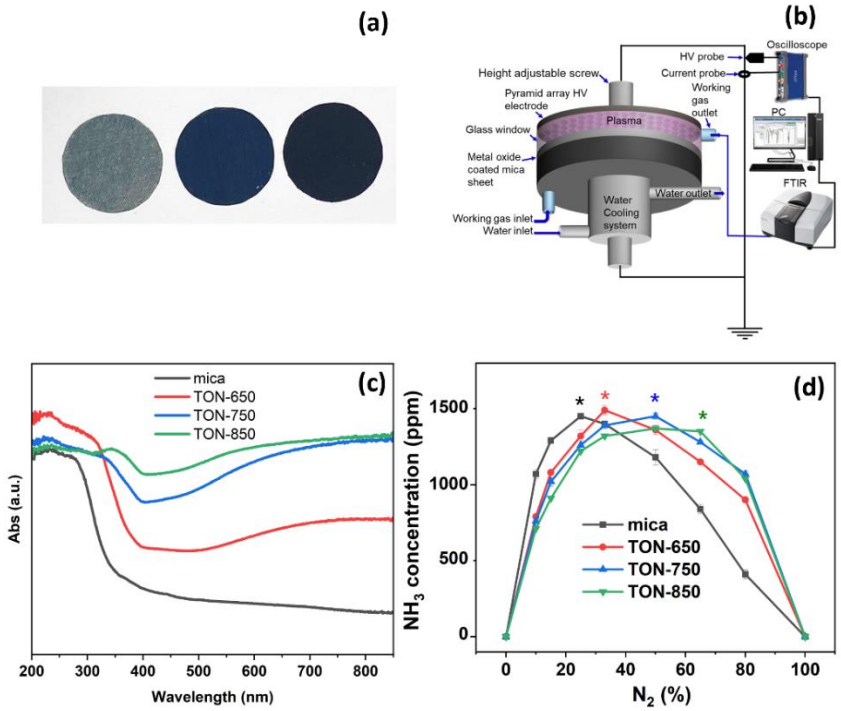

Figure 1. (a) optical images of TON-650, TON-750, TON-850. (b) Schematic view of reactor and (c) UV-vis spectra and (d) the NH_3 concentration of mica, TON-650, TON-750 and TON-850.

4. Conclusions

Plasma assisted the NH_3 synthesis over plasmonic titanium oxynitride films has been studied in a parallel-plate micro-DBD reactor with a pyramid-shape electrode. With increasing reduction temperature under NH_3/N_2, the N-doping content is increased in the coatings. The optimal N_2/H_2 mixture to get the maximum ammonia yield shifted from the stoichiometric (1:3) to equimolar (1:1) over the oxynitride catalyst.

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Keywords
Non-thermal plasma, Pyramid-shape electrode, Ammonia synthesis, Titanium oxynitride