Controlled Carbon Nitride Growth on Surfaces for Hydrogen Evolution Electrodes**

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Methods

*Synthesis of CM-C₃N₄:* the CM complexes were prepared by using 1:1 molar ratio of Cynauric acid and Melamine (1gr total weight) in 40ml of water. The complexes were then mixed for 4 hours using automatic shaker, after which the white CM complexes were precipitated by filtration of the solutions. The white powders were washed several times with water. The resulting powders were dried at 60°C in a vacuum oven. For the films preparation, a CM (thin layer) powder was placed between two substrates. The electrodes were deposited into a ceramic crucible and calcined at 550°C under nitrogen condition with a heating rate of 2.3°C per minute. After the heating, the electrodes were cleaned by a strong airstream.

*Electrode preparation:* commercial 100nm TiO₂ and 50nm ZnO pastes were prepared by mixing 1g of metal oxide in 8.5ml of tripinol, and 15ml of ethanol. First, the metal oxide was added to the 15ml of ethanol and sonicated for 1 min. second the 8.5ml of tripinol and 10ml of 10% ethyl cellulose in ethanol were slowly added. After that the solution was stirred at 70 °C until the volume was ~8.5ml. The commercial 18nm TiO₂ paste was purchased from Dyesol (DSL 18NR-T). The electrodes were prepared by the doctor blade technique on fluorine-doped tin oxide (FTO) and sintered at 550 °C for 45 min. For the deposition C₃N₄-FTO electrodes the FTO was immersed into water for two hours in order to increase FTO hydrophilic properties. The thickness of the TiO₂ electrodes were ~5.5 microns and the C₃N₄ layer on FTO was ~60nm.

*Characterization:* X-ray diffraction-patterns were measured on a Bruker D8 Advance instrument using Cu- Kα radiation. The reference anatase TiO₂ pattern was taken from NIST data base (pattern number 95-900-8216). Elemental analysis was accomplished as combustion analysis using a Vario Micro device. SEM images were obtained on a LEO 1550-Gemini. Energy dispersive X-ray (EDX) analyses and investigations of the morphology by scanning electron microscopy (SEM), were performed on a JEOL (JSM – 7500 F) device equipped with an Oxford Instruments X-MAX 80mm² detector. FT-IR spectra for
the characterization of the compounds were recorded on a Varian1000 FT-IR spectrometer. Optical absorbance spectra were measured using a Varian spectrophotometer equipped with an integrating sphere. The emission spectra were recorded on LS-50B, Perkin Elmer instrument. The excitation wavelength is 350nm. The thickness of the electrodes were determined by "Dektat 3ST" profilometer. Electrochemical tests were performed in 0.1 M phosphate buffer solution (mixing 30.5 ml of 0.2M dibasic sodium phosphate with 19.5 ml monobasic sodium phosphate and dilute it 10 times) and 0.1 M KOH in a standard three - electrode setup with an Ag / AgCl reference electrode and a platinum counter electrode using Gamry Reference 600 potentiostate (Gamry Instruments). Cyclic voltammetry was carried out at a scan rate of 25 mV/s. Linear sweep voltammetry (LSV) measurements were carried out at a scan rate of 10mv/s. All measurements were referred to the Reversible Hydrogen Electrode (RHE) by using the relationship: 

\[ V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 + pH(0.059) \]

The Tafel plots were extracted from the anodic scan. we have determined the series resistance (Rs) associated to each system from the high frequency limit of a measured impedance spectra, finding that Rs of non-metallic electrocatalysts are one order of magnitude higher (ca. 40 Ω cm² and 78 Ω cm² for the TiO₂ and FTO films, respectively) than that reported for the Ni electrode (lower than 1 Ω cm²). According to this, the overpotentials have been corrected with respect to the ohmic drop.

Figure S1. SEM images of the C₃N₄ deposited on 50nm ZnO particles
Figure S2. SEM images of C₃N₄ powder that was prepared from cyanuric acid-melamine (CM) complex in water without the presence of glass (a) and with (b).

Figure S3. X-ray diffraction patterns (a) and FTIR spectra of the cyanuric acid-melamine (CM) complex which was prepared in the presence of glass.

Figure S4. Energy-dispersive X-ray (EDX) spectra of C₃N₄-FTO (a) C₃N₄-glass (b) C₃N₄-TiO₂ (c) C₃N₄-ZnO (d)
Figure S5. X-ray diffraction patterns of TiO$_2$ and C$_3$N$_4$ on TiO$_2$.

Figure S6. X-ray diffraction patterns of C$_3$N$_4$-TiO$_2$ and TiN (black line, pattern number 00-038-1420) and TiC (red line, pattern number 04-004-2919).

Figure S7. Pictures of TiO$_2$ before and after sensitization with C$_3$N$_4$.

Figure S8. 30 times magnification of C$_3$N$_4$-FTO and C$_3$N$_4$-FTO emission spectra.
Figure S9. Tafel plots for (a) FTO, FTO-C₃N₄ and (b) TiO₂, TiO₂-C₃N₄ at pH 13.1 (KOH 0,1M). Results for smooth Ni electrochemically deposited onto FTO are included for comparison.

Figure S10. Cyclic voltammetry measurement of C₃N₄-FTO in 0.1 Kpi buffer solution (a) and 0.1M KOH solution (b). The black and the red curves stand for the fifth and the fiftieth scans respectively. The scan rate was 25mV/s.

Figure S11. Cyclic voltammetry measurement of C₃N₄-TiO₂ in 0.1 Kpi buffer solution (a) and 0.1M KOH solution (b). The black and the red curves stand for the fifth and the fiftieth scans respectively. The scan rate was 25mV/s.
Figure S12. Cyclic voltammetry measurement of C$_3$N$_4$-TiO$_2$ in 0.1M KOH solution of C$_3$N$_4$ on FTO (a) and TiO$_2$ (b). The black and the red curves stand for the fifth and the five hundredth scans respectively. The scan rate was 25mV/s.

Figure S13. Linear sweep voltammetry measurement of C$_3$N$_4$ on 18nm commercial TiO$_2$ in 0.1M KOH solution. The black and the red curves stand for before and after 500 cyclic voltammetry measurements, respectively. The scan rate was 10mV/s.

Figure S14. Energy diagram showing the band alignment of the substrate and C$_3$N$_4$ catalyst.
Scheme S1. Illustration of proposed carbon nitride structure.