In-situ growth of polymeric carbon nitride films with large conjugated structures for efficient photoelectrochemical water splitting

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Abstract: We present successful growth of high quality carbon nitride based copolymer (CNBC) films on the FTO substrate through solvothermal approaches with post-annealing. Structural characterizations of the films reveal the polymeric carbon nitride network consisting of tri-s-triazines and s-triazines bridged by different functional groups. The strong bonding between CNBC films and the substrates via covalent linkage ensures intimate contact and smooth interfacial charge transport. As such, the CNBC films exhibit excellent photoelectrochemical performance, which is attributed to strong visible light harvesting, excellent conductivity, and efficient charge separation and transport. Our studies provide a general solvothermal-based strategy for in-situ growing metal-free films on substrates for efficient photoelectrochemical water splitting.

Keywords: Photoelectrochemical reaction, Graphitic carbon nitride, Solar fuels.

1. Introduction

Previously, most g-C_3N_4 based electrodes presents limited PEC efficiencies due to its intrinsic drawbacks, such as poor conductivity, limited visible-light absorption up to 450 nm, and weak interfaces between the pasted bulk g-C_3N_4 layer and the conducting substrate. In this work, we developed a facile solvothermal method to grow a carbon nitride based copolymer (CNBC) film on different substrates. The solvothermal process allows for covalent linkage of molecular precursors onto the substrate surface, giving strong and intimate interfacial contact. The obtained CNBC film upon post-heating exhibits enlarged conjugating structures between *s*-triazine and tri-s-triazine, resulting in improved conductivity. As a result, the obtained electrodes with *in-situ* grown CNBC films showed greatly enhanced photocurrent density.

2. Experimental

For growth of CNBC film, the pretreated FTO glasses were fixed on a Teflon holder and placed in a 20 ml Teflon-lined autoclave containing 15 ml solution of acetonitrile with 164 mg precursors (cyanuric chloride and cyanuric acid) dissolved inside. Subsequently, the autoclave was sealed and maintained at 200 ^oC for 20 hours. After reaction, the carbon nitride coated FTO glass was obtained (denoted as CNBC-U/FTO), washed and annealed at 450 ^oC under Ar flow to obtain the CNBC/FTO film.

3. Results and discussion

The un-annealed film (CNBC-U) on FTO glass has ~375 nm thickness (Fig. 1A). After annealing at 450 ^oC, the obtained CNBC film became more compact with reduced thickness to 125 nm, suggesting that the heat treatment led to further condensation and polymerization of CNBC-U film. The XRD pattern of the obtained CNBC-U powder (Fig. 1B) shows a broad diffraction peak at 26.8^o, corresponding to the stacking of the conjugated hexatomic heterocyclic system. After annealing at 450 ^oC in Ar, the CNBC sample shows increased intensity of the peak at 26.8^o due to further condensation of the carbon nitride matrix.

Fig. 1C shows the chopped J-V curves under simulated solar irradiation (AM 1.5). Comparing to the reference g-C_3N_4/FTO, the CNBC-U/FTO photoanode presented much larger photocurrent density. The post-annealing leads to further increased photocurrent density for CNBC/FTO. When the applied bias is set as 1.23 V (vs SHE), the anodic photocurrent of CNBC/FTO is 8.4 times of that of g-C_3N_4/FTO reference (Fig. 1D). The impedance plots (Fig. 1E) show that in the dark, the radii of the semicircles for g-C_3N_4, CNBC-U/FTO, and CNBC/FTO are very large with increasing order of CNBC/FTO < g-C_3N_4 < CNBC-U/FTO, suggesting the CNBC film has comparably lower resistance. The light irradiation leads to decreased semicircles radii with increasing order of CNBC/FTO < CNBC-U/FTO < g-C_3N_4, which is consistent with

the photocurrent intensity. The results indicate more effective generation and transport of photogenerated charge carriers in CNBC films.

The excellent PEC performance of the CNBC/FTO sample could be attributed to the enhanced charge transport in the conjugated carbon nitride network (Fig. 1F), intimate contact between CNBC and FTO allowing for effective interfacial charge transfer, and the enhanced visible light harvesting of CNBC. In particular, the post annealing leads to creation of carbodiimide (N=C=N) bridges that greatly enlarge the conjugation system of s-triazines and tri-s-triazines, giving better conductivity. [1,2]

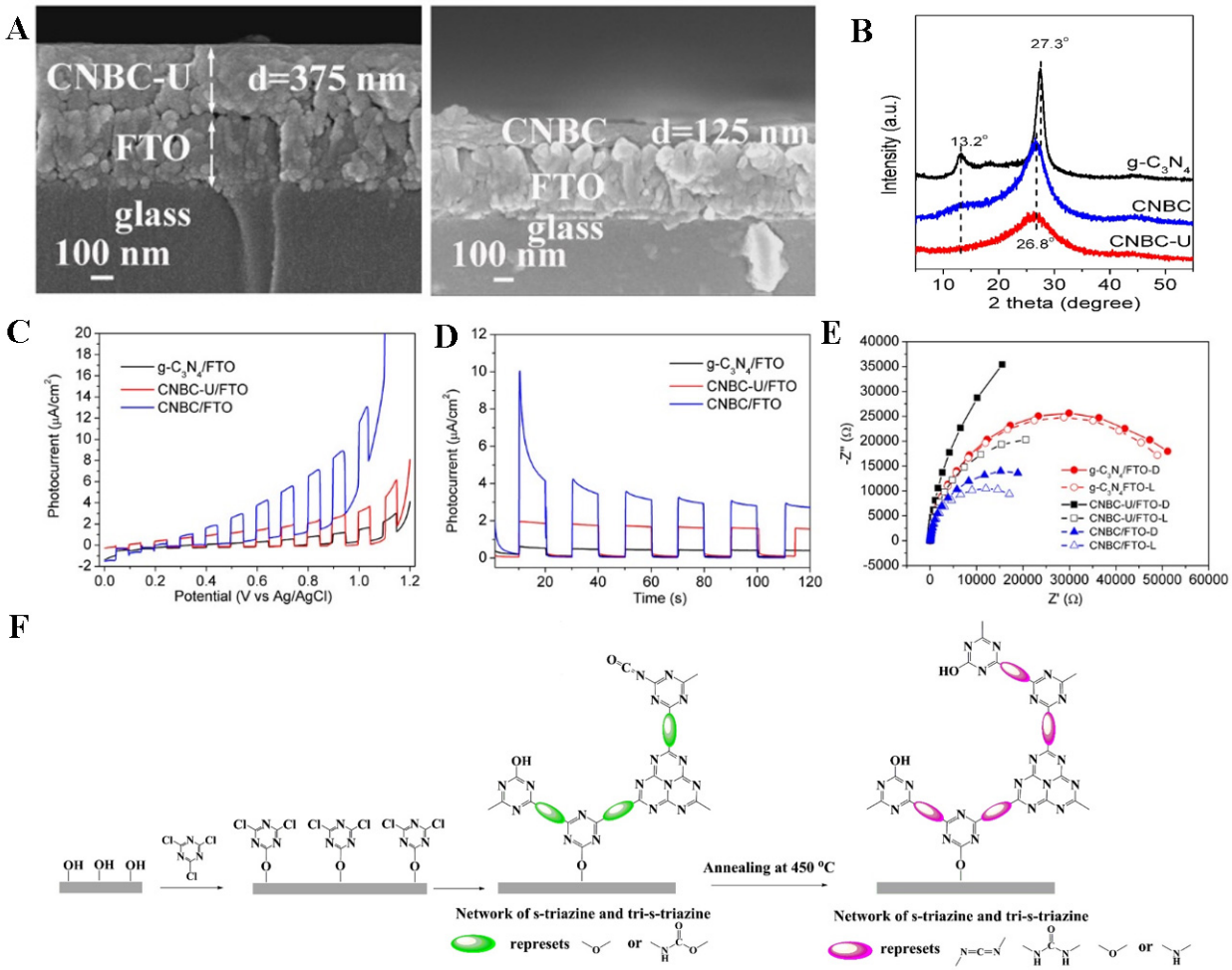

Figure 1. (A) SEM, (B) XRD, (C, D) photocurrent and (E) impedance of the prepares samples. (F) Scheme of CNBC structure.

4. Conclusions

In conclusion, we have developed a facile solvothermal method to in-situ grow novel CNBC thin films on FTO. The strong bonding between CNBC films and the substrates via covalent linkage ensures intimate contact and smooth interfacial charge transport. The obtained CNBC films exhibit excellent PEC performance. This work provides a general guide of solvothermal methods for in-situ growing metal-free films on various substrates for efficient PEC water splitting.

References

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