A new strategy to stabilize carbon nitride photocatalyst for nitrogen reduction

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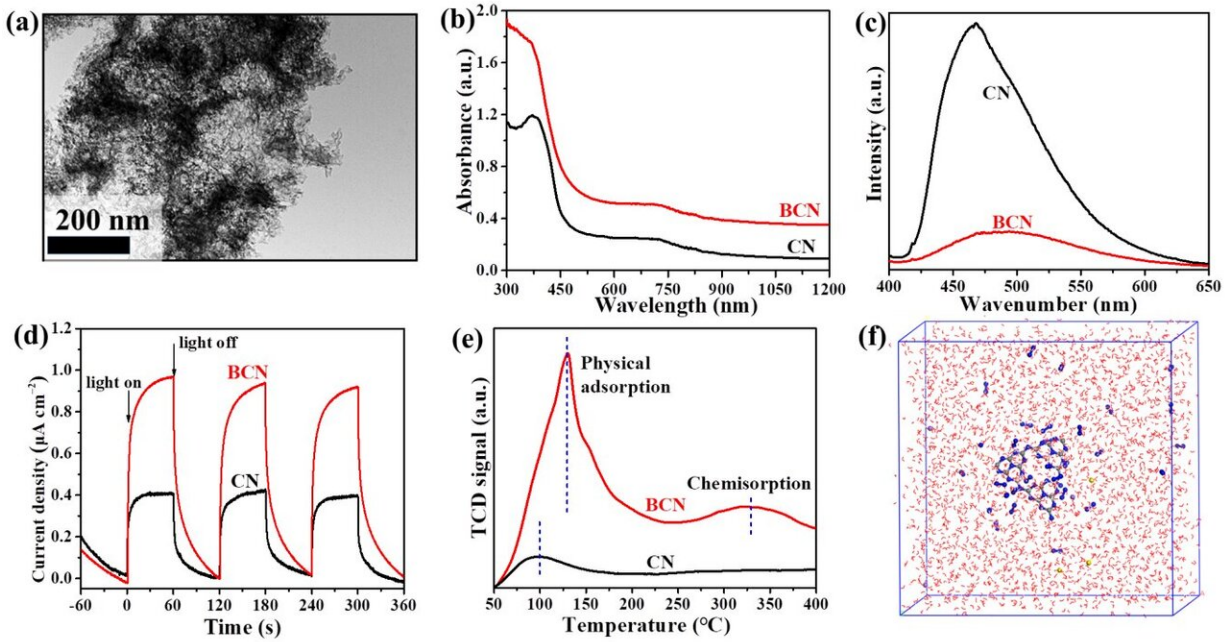

(a) TEM image of BCN; (b) UV-vis diffuse reflectance spectra, (c) steady-state PL spectra, (d) transient photocurrent responses and (e) N2-TPD of CN and BCN; (f) MD simulation snapshots of BCN. Credit: WANG Weikang

Researchers from the Institute of Solid State Physics, Hefei Institutes of Physical Science developed a boron doped carbon nitride nanosheets with B-N-C coordination to stabilize surface exposed active nitrogen atoms and dramatically enhance photocatalytic ammonia synthesis

performance. Their findings were published in *Small*.

It is well known that nitrogen (N_2) accounts for ~78% in our atmospheric environment, which is essential element for almost all life forms including plants and animals on earth.

Up to now, the most mature technology of artificial synthetic ammonia (NH3) is the over century-old Haber-Bosch process, operated under drastic conditions due to the intrinsically inert characteristic of N_2 molecules.

Currently, photocatalytic N_2 reduction has been regarded as a promising means for sustainable NH_3 synthesis at ambient conditions. As a class of metal-free polymer semiconductor photocatalyst, graphitic carbon nitride (g-C_3N_4) possesses many advantages, such as low cost, abundance, superior visible-light activity and high chemical/photochemical stability, exhibiting great potential for photocatalytic nitrogen reduction reaction (NRR).

However, several issues are still existent associated with the NRR using the g-C_3N_4-based photocatalyst. It is an important issue that exposed active nitrogen atoms (e.g., edge or amino N atoms) in g-C_3N_4 could participate in NH3 synthesis during the photocatalytic NRR.

Moreover, the pristine bulk g-C_3N_4 generally possesses relatively low specific surface area, which is adverse to the N_2 adsorption and activation, as well as high recombination rate of photogenerated electrons and holes, resulting in its low photocatalytic efficiency.

Therefore, developing effective strategies to stabilize surface exposed active nitrogen atoms of g-C_3N_4, capable of improving the N_2 adsorption/activation and visible-light utilization, simultaneously effectively inhibiting the recombination of photogenerated carriers in g-

C_3N_4, is critically important and highly needed to achieve high-efficiency g-C_3N_4 based photocatalysts.

Herein, the team synthesized the porous B-doped g-C_3N_4 nanosheets (BCN) by a facile thermal treatment approach using dicyandiamide (DICY) and boron oxide (B2O3) as reactants. The formed B-N-C coordination in BCN not only effectively enhanced the visible-light harvesting and suppressed the recombination of photogenerated carriers in g-C_3N_4, but also acted as the catalytic active site for N_2 adsorption, activation and hydrogenation.

The as-synthesized BCN exhibited high visible-light driven photocatalytic NRR activity, affording an NH_3 yield rate of 313.9 μmol g–1 h–1, nearly 10 times of that for pristine g-C_3N_4.

More information: Weikang Wang et al. Formation of B-N-C Coordination to Stabilize the Exposed Active Nitrogen Atoms in g-C 3 N 4 for Dramatically Enhanced Photocatalytic Ammonia Synthesis Performance, *Small* (2020). DOI: 10.1002/smll.201906880

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