Photocatalytic CO_2 reduction over TiO_2NT/g-C_3N_4 based heterostructures

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Significance and Relevance

Photocatalytic reduction of carbon dioxide (CO_2) to produce energy fuels is presented by using a novel TiO_2NT/g-C_3N_4 heterostructure. The heterostructure formation imparts unique characteristics enhancing the CO_2 adsorption and activation efficacy with respect to the bare components. Moreover, composite fabrication is by far the most efficient method to improve charge carrier separation efficiency.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling / Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: Short Oral / Poster

Introduction and Motivations

An attractive approach to addressing two of the main environmental concerns, namely fossil fuel dependency and environmental pollution due to greenhouse gases, is photocatalytic CO_2 reduction, on TiO_2 tubular nanostructures coated with g-C_3N_4. The polymeric carbon nitride (g-C_3N_4) shows great potential for photocatalytic CO_2 reduction because of its suitable conduction band position, which satisfies the thermodynamic condition of most CO_2 reduction reactions.[3] In recent years, investigations on metal-based semiconductors have received broad attention, especially using TiO_2, ZnO, CdS, Cu_2O. Here a hybrid structure has been explored performing the process under mild reaction conditions with an increased conversion yield and controlled selectivity. The nanostructured TiO_2 semiconducting material was developed to improve the visible-light absorption, sustainability and stability of the system and to enhance the photocatalytic performance by suppression of the photogenerated carriers.

Materials and Methods

The tubular-shaped TiO_2 array has been fabricated by anodic oxidation (AO) of a metallic titanium substrate in ethylene glycol electrolyte containing 0.3 wt. % NH_4F, and 2% vol. H_2O. Then, the self-ordered TNTs surface was decorated with graphitic carbon nitride (g-C_3N_4) prepared by a simple thermal heating and condensation method. Typically, the polymeric carbon nitride was prepared by placing 2 g of melamine in a porcelain crucible with the anodized TNTs disc as a cover, then the precursor was heated to 550 °C for 3 h in a muffle furnace at atmospheric pressure in air. [1]

The prepared material has been characterized by chemical–physical, morphological, and structural investigations, then the functional properties of the composite have been studied by electrochemically by chronoamperometry experiments under dark and illuminated conditions and linear sweep voltammetry. Finally, the materials have been tested in the electrocatalytic CO_2 reduction reaction.

Results and Discussion

Aimed at reducing environmental impact, we have developed a new photo-assisted route for electrochemical conversion of CO_2 by using a new composite heterostructure identified as TiO_2NT/g-C_3N_4.

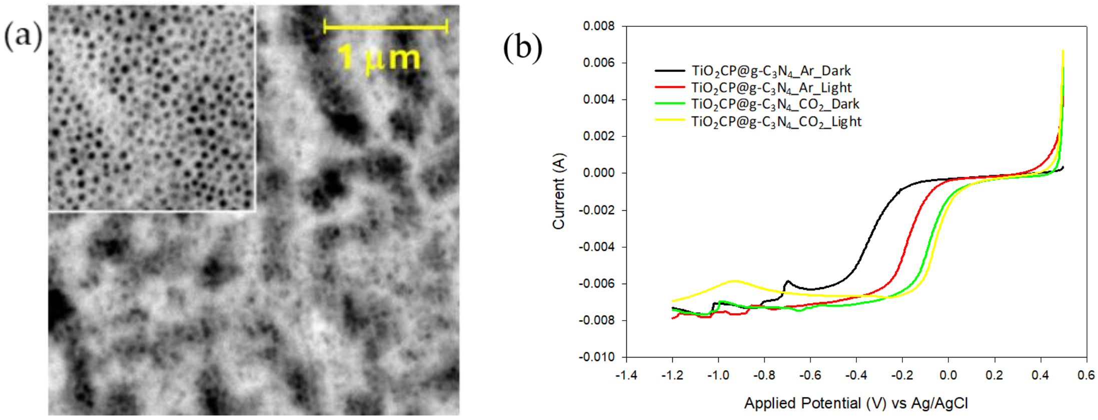

Figure 1a, SEM images of the composite and of bare TiO_2NT array, left side insert. **Figure 1b** reports the LSW curves acquired in 0.5 M Na_2SO_4 under Argon and CO_2 as an example of the electrochemical characterization of the composite.

Figure 1a shows the SEM image of the composite and that of the bare TiO_2NT array in the insert on the left, highlighting a highly ordered and uniform pore structure of the nanotubes which is ideal and beneficial for the adsorption of the polymeric g-C_3N_4. **Figure 1b** reports the linear sweep voltammetry (LSW) curves acquired under Argon and CO_2 evidencing the positive shift (~120mV) of the potential under illumination in the case of CO_2.

XPS measurements have been acquired for investigating the electronic structure of the g-C_3N_4/TNT composite material and to confirm the prepared samples' chemical composition and valence state. For the composite, a shift to a higher binding energy and an increase in the electronic signal have been observed, indicating an interaction between the polymeric moiety and the TiO_2 nanotubes, and an increased electron density on Ti compatible with a charge transfer from the electron-rich g-C_3N_4 surface to the unoccupied orbital of Ti^{4+}.[2] This observation confirms the interaction between the two components and, ultimately, the effective preparation of the heterojunction.

The prepared material has been tested in photo-assisted electrocatalytic reduction of CO_2, serving as cathodic electrode, in a full electrochemical cell employing different solutions (0.1 M $KHCO_3$ and 0.5 M k_2SO_4) as circulating electrolyte and a Pt plate as anode. The reduction products were monitored under potentiostatic electrolysis to confirm the occurrence of CO_2 reduction.

References

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