

## Abstract

Since the industrial revolution, the extensive usage of fossil fuel has resulted in a continuous increase of atmospheric concentration of carbon dioxide, generating a global temperature rise with a catastrophic effect on global weather. Therefore, the sequestration of carbon dioxide and the conversion of carbon dioxide into reusable carbon feedstock have received a world wide attention of scientific community. Photocatalytic reduction of carbon dioxide, capable of turning carbon dioxide into useful commodities such as methane, methanol, carbon monoxide, etc., offers a particularly appealing advantage by tapping the solar radiation as the energy source of reactions.

In this thesis, we report a photoreduction study of carbon dioxide on semiconducting, core-shell heterojunctions fabricated with nanostructured materials of cuprous oxide (core) and titanium oxide (shell). Two cuprous oxide structures are adopted for the anticipated difference in photoreductivity: the cubic structure terminated with (100) face, and the rhombic dodecahedron (r.d.) terminated with (110) face. The techniques such as secondary electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) are employed to characterize the heterojunction. Additionally, a rather unique, operando research technique, i.e. ambient pressure XPS (APXPS), is also used to track the change of reaction species on the photocatalyst surfaces. APXPS C 1s spectra show the  $\text{Cu}_2\text{O}(\text{r.d.})\text{-TiO}_2$  is more reactive than  $\text{Cu}_2\text{O}(\text{cube})\text{-TiO}_2$ , as evidenced by a larger production of carbon species such as formate, carbonyl, carbon dioxide, aliphatic carbons on the surface. After prolong photocatalytic reactions, the chemical identity of accumulated surface species evolved into gas phase can be revealed with a quadrupole mass spectrometer by running the so-called temperature programmed reaction spectroscopy (TPRS) experiments. The production of methane and methanol at  $\sim 400$  K is clearly noted.

The energy diagram relevant to the performance of photocatalysis is also obtained by XPS. The heterojunction of  $\text{Cu}_2\text{O}(\text{cube})\text{-TiO}_2$  has smaller valence and conduction band offsets than its counterpart of  $\text{Cu}_2\text{O}(\text{r.d.})\text{-TiO}_2$ . The larger conduction band offset of  $\text{Cu}_2\text{O}(\text{r.d.})\text{-TiO}_2$  facilitates a better charge carrier separation, with electrons and holes ended up being more accumulated on  $\text{TiO}_2$  and  $\text{Cu}_2\text{O}$ , respectively. It is argued that the larger band offset found for  $\text{Cu}_2\text{O}(\text{r.d.})\text{-TiO}_2$  plays an important role in enhancing its photoreduction capability.