**Improved catalyst designs for photocatalytic water splitting**

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**Introduction**

The sun light is the original source of the fossil and renewable energy resources on the global and is potentially sufficient to support the sustainability of the human society. Photocatalytic water splitting to produce hydrogen and oxygen has been considered as one of the most promising technologies to provide sustainable and clean fuel for the future and has been intensively explored in recent years. However, most of the reported catalytic materials are still inefficient because of fast recombination of charge carriers. Semiconductor combination and cocatalyst loading are effective methods for improving photocatalytic activity via formation of heterojunction structure enhancing the charge separation in the solid phases.

**Design of catalysts**

Band engineering is a commonly used approach used for improving the photocatalysts. the separation of photogenerated charges is another key issue. Clearly, the photogenerated charges must be efficiently separated to avoid bulk/surface charge recombination and must be transferred to the separated active sites of water splitting.

In this work, we find carbon fibers (CFs) are useful conductors for transporting charge carriers between the phases. SiC has a narrow-band-gap and more negative conduction and valence bands than those of TiO$_2$. When SiC is loaded on TiO$_2$, the photogenerated electrons of SiC can move to TiO$_2$ while holes of TiO$_2$ can travel back to SiC. The photocatalysts NiO$_x$ and IrO$_x$ are loaded on TiO$_2$ and SiC, respectively. We find these different phases play very important roles in the efficient separation of charge carriers. Further, a composite photocathode, NiO/CdS@ZnO gives very good performance. The fast recombination of charge carriers in these systems is prohibited.

We developed a solid solution catalyst, In-Ni-Ta-O-N, which splits water under visible light into 2:1 H$_2$ and O$_2$. We find efficient separation of charge carriers in the solid solution too. NiO and In$_2$O$_3$ nanodots exist on the surface acting as H$_2$ and O$_2$ evolution sites, respectively.

**Results and Discussion**

In the CuO/CFs/TiO$_2$ composite, electrons first jump to CF and then to CuO particles. CF serves as an electron acceptor and transporter to further lengthen the lifetime of the photogenerated charge carriers from TiO$_2$ nanoparticles. The activities of the CuO/CFs/P25 photocatalysts are shown in Fig. 1. The catalysts have high photocatalytic hydrogen production activities in aqueous solutions containing ethanol (10 vol%) as sacrificial reagent. The activity of CuO/CFs/P25 with 1 wt% CF is about 45 times (2000 µmol•h$^{-1}$•g$^{-1}$) higher than pure P25.1

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**Figure 1.** The CFs loading content courses of H$_2$ evolution under Xe light irradiation.

TiO$_2$ itself has a limited activity for the photocatalytic water splitting, because it only absorbs a small ratio of the photo energy at the UV end of the spectrum. SiC has a negative conduction and valence band (VB), as well as a much narrower band gap, and compensates the disadvantage of TiO$_2$. When the two materials are properly combined, their Fermi levels align. SiC uses the abundant visible light to produce exited electrons, which flow into TiO$_2$. Holes of TiO$_2$ transfer back to SiC. SiC-TiO$_2$ is more active than TiO$_2$. NiO$_x$ is a good electron collector. If NiO$_x$ is loaded on the surface of TiO$_2$ in the SiC-TiO$_2$ composite, the excited electrons flow from TiO$_2$ into NiO$_x$ smoothly due to the consecutive potential gradients between the phases. IrO$_x$ is usually taken as an oxidation cocatalyst because of its high capacity for hole capture. NiO$_x$/SiC shows a low activity (0.45 µmol for 5 h), but IrO$_x$/SiC presents a higher activity (49 µmol for 5 h) than that of the SiC(1 wt%)-TiO$_2$ (34 µmol for 5 h). This result tells us that consuming the photo-excited holes rather than electrons in SiC can efficiently help to separate the electron-hole pairs. The sample IrO$_x$/SiC(1 wt%)-NiO$_x$/TiO$_2$ has an activity two orders of magnitude higher than the other samples. In IrO$_x$/SiC(1 wt%)-NiO$_x$/TiO$_2$, the electrons with high energy from both the conduction band and valence band of SiC transfer back to TiO$_2$, while the holes in the valence bands transfer back from TiO$_2$ into SiC simultaneously.2
Figure 2. (a) Photocatalytic H₂ evolution rate from an aqueous solution contains ethanol. (b) An efficient separation of charge carriers takes place in the IrO₂/SiC-NiOₓ/TiO₂ composite.

The oxide In-Ni-Ta-O is totally inactive under visible light for overall water splitting. The partially nitridized material becomes active. Without Ni, the nitrogen oxide has no activity. The activity shows a peak with the suitable Ni content. The ratio of H₂/O₂ in all the tests perfectly keeps 2.0. It is noted that the activity of the optimized In-Ni-Ta-O-N material is higher than that of the GaN:ZnO catalyst without loading a cocatalyst (RuO₂ or Rh₂O₃).

Figure 3 illustrates the plots of photo stimulated voltage (J-V) of the composite electrode materials under AM 1.5 illumination are presented in. The inset shows the three-electrode configuration used. The bare ZnO nanorods produce a photocurrent density of 140 µA/cm² at -0.6 V, versus the Ag/AgCl reference electrode, in a 0.25 M Na₂S and 0.35 M Na₂SO₃ electrolyte. A CdS coating layer improves the photocurrent response in the low potential range, viz. from -1 V to -0.7 V, and the photocurrent density of the shell/core structured CdS@ZnO reaches 294 µA/cm² at -0.6 V. When NiO is deposited on the CdS@ZnO, the photocurrent density increases to 950 µA/cm² at -0.6 V, which is 6.78 times of increase. It is noted that no photocurrent is recorded when NiO is directly deposited on the ZnO nanorods.

Figure 3. The photoelectrochemical response for the bare ZnO nanorods and the composite photoelectrodes.

Significance
This work describes 4 designs of photo catalysts and electrodes for the splitting of water. Overall water splitting under visible light irradiation was achieved. These designs utilizes the synergistic and the interface effect of the semiconductor phases and forms composite materials. A well design and fabrication of the contacts between phases enhances the activity for 1-3 orders of magnitudes. An efficient separation of the charge carriers is the key for these catalysts.

References