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A visible light-sensitive tungsten carbide/tungsten trioxide composite photocatalyst
Photocatalytic Ohmic layered nanocomposite for efficient utilization of visible light photons

Hyun Gyu Kim and Euh Duck Jeong
Korea Basic Science Institute, Busan Centre, Busan 609-735, Korea

Pramod H. Borse, Seongho Jeon, Kijung Yong, and Jae Sung Lee
Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

Wei Li and Se H. Oh
R&D Center, General Motors, Mail Code 480-106-185, 30500 Mound Rd., Warren, Michigan 48090-9055

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The WO$_3$/W/PbBi$_2$Nb$_{1.9}$Ti$_{0.1}$O$_9$ photocatalyst was fabricated by depositing the tungsten clusters over the $p$-type perovskite base material with the chemical vapor deposition method, and later partly oxidizing the surfaces of these clusters to obtain $n$-type WO$_3$ overlayers and W metal layer as an Ohmic junction. This NCPC showed unprecedented high activity for the photocatalytic oxidation of water, photocurrent generation, and acetaldehyde decomposition under visible light irradiation ($\lambda > 420$ nm). © 2006 American Institute of Physics. [DOI: 10.1063/1.2266237]

Photon induced chemical conversion using solar radiation has been under evolution for an efficient pollution abatement and energy conversion. The new concepts and methods are explored to fabricate more efficient photocatalysts by utilization of modern material processing techniques.

In this report, we describe the fabrication of ingenious nanocomposite photocatalyst powders with the configuration of $p$-semiconductor/metal/$n$-semiconductor. The materials are made by combining solid-state reaction (SSR) with chemical vapor deposition (CVD). Thus, the WO$_3$/W/PbBi$_2$Nb$_{1.9}$Ti$_{0.1}$O$_9$ photocatalyst (PC) was fabricated by depositing the tungsten clusters over the $p$-type perovskite base material, and later partly oxidizing the surfaces of these clusters to obtain $n$-type WO$_3$ overlayers on the top of metallic W layers. Figure 1(a) briefly illustrates the schematic for fabrication process of the nanocomposite photocatalyst (NCPC).1

The VLNPCP obtained using this process showed very high photocatalytic activities particularly for the oxidation of water, the degradation of acetaldehyde to CO$_2$, and photocurrent generation, all under visible light (VL) hereafter VL refers to $\lambda > 420$ nm. It has been demonstrated earlier in photovoltaic cells and photoelectrochemical (PEC) cells that the diode structures made of $n$- and $p$-type semiconductors show greatly enhanced activities compared to the devices consisting of a single semiconductor.$^{2,3}$ In addition, a monolithic PEC cell with a conducting Ohmic junction sandwiched by the $p$-$n$ semiconductor junctions showed further improvement.$^{3}$ Recently we reported$^6$ that photocatalytic nanodiodes formed by $p$-type CaFe$_2$O$_4$/n-type PbBi$_2$Nb$_{0.9}$W$_{0.1}$O$_9$ indeed yielded greatly enhanced and stable photocatalytic activity under VL than single component PCs. In a step forward, we have adopted in the present work the concept of a $p$-$n$ diode structure with the Ohmic junction. We met the challenge of introducing an Ohmic layer in the miniaturized particulate device by using the CVD technique followed by careful surface oxidation. By proper choice of an oxide semiconductor combination, we have discovered that this modified composite material gives extremely high and stable photocatalytic activities for various reactions under VL.

Figure 1(b) shows high resolution transmission electron microscopy (HRTEM) of typical NCPC particles that clearly exhibit the existence of 30–40 nm WO$_3$ clusters stacking over the surface of a large PbBi$_2$Nb$_{1.9}$Ti$_{0.1}$O$_9$ (PBNTO) particle of 150–200 nm. The phase identification was also confirmed by elemental analysis with in situ energy dispersive x-ray analysis carried out during the microscopic study. The WO$_3$ is a well-known $n$-type semiconductor,$^7$ but PBNTO is derived from PbBi$_2$Nb$_2$O$_9$ (PBNO) doped with Ti$^{4+}$ in order to obtain $p$-type semiconductivity. The original material is an Aurivillius-phase layered perovskite and has been recently reported by us to be an efficient PC for H$_2$O oxidation into O$_2$ and C$_2$H$_5$OH degradation to CO$_2$, all under VL.$^8$

Based on the experimental observations, we propose a schematic model for NCPC as illustrated in Fig. 1(c). The WO$_3$-encapsulated W layer above the base material of PBNTO appears to play a critical role of Ohmic junction in the photocatalytic process. Its presence was confirmed by observing both W$^0$ and W$^{6+}$ in x-rayphotoelectron spectroscopy (XPS) analysis$^1$ where the deconvolution of peaks indicated a WO$_3$/W kind$^9$ of configuration in the Ar$^+$ etched samples which otherwise dominantly showed peaks only due to WO$_3$. The working principle of NCPC is schematically shown in Fig. 2, in the form of an energy band model for the system described in Fig. 1(c). The band positions for PBNTO were determined from flatband potential measurements.$^9$ The band positions for tungsten oxide were obtained from literature.$^7$

At thermal equilibrium, the Fermi levels of two semiconductors align. When the device is immersed in an electrolyte, the band edges of the conduction and valence bands bend and the interface adopts energies relative to standard reference energy as shown for $p$-PBNTO. However, it is difficult to expect the band bending for WO$_3$ nanoparticles of 30–40 nm. Thus the band positions for WO$_3$ are shown flat in Fig. 2. The operation of NCPC is initiated by the absorption of the band gap (BG) photons in both the $n$- and $p$-type semiconducting regions. Upon photon absorption the holes

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$^{a}$Author to whom correspondence should be addressed; electronic mail: jlee@postech.ac.kr
and electrons are separated in space-charge regions of respective semiconductors and become available for redox reactions. Accordingly, the generated minority carriers, viz., holes in \( n \)-type and electrons in \( p \)-type semiconductors, move to the front of the surface and are injected to the electrolyte solution to initiate oxidation and reduction reactions, respectively. In addition, the photogenerated majority carriers in each semiconductor region are then bound to migrate towards the Ohmic W layer interfaced between two semiconductors, where the carriers undergo nonradiative recombination. Thus, the optimal population of electrons and holes formed in the former process can promote the redox reactions at the semiconductor-fluid interface, thereby facilitating the reduction reaction on \( p \)-type PBNTO and the oxidation reaction on \( n \)-type WO$_3$. The gross effect of NCPC is the attainment of higher net photon energies needed for the redox reactions by partial addition of two PGs, while individual PGs still absorb VL. These effects lead to the higher photocatalytic activity.

The optical properties of these compounds were probed by the UV-visible diffuse reflectance spectroscopy\(^9\) as shown in Fig. 3(a). Comparison was made with PBNO\(^8\) and TiO$_2$-$N_x$\(^{10}\). The latter material is thought to be the standard example of a visible light PC, in which the band structure of TiO$_2$ has been modified by nitrogen doping to induce the VL absorption.\(^{10}\) From these spectra, we estimated the BG energies of these materials as summarized in Table I. NCPC showed a steep onset of absorption spectrum at 520 nm, i.e., around the green wavelength sweeping major visible region compared to the other two standards considered here. Thus, NCPC would absorb more VL photons than TiO$_2$-$N_x$, although their absorption edges were almost the same around the green region.

In the following section we discuss the photocatalytic properties of these materials. First, photocurrent generation ability was investigated by VL illumination of aqueous suspensions containing acetate (donor) and Fe$^{3+}$ (acceptor). Figure 3(b) indicates that NCPC generates photocurrent at a higher rate by factors of ca. 3 and ca. 5 in comparison with PBN0 and TiO$_2$-$N_x$, respectively. It is also more active than the simple nanodiode of \( p \)-CaFe$_2$O$_4$/$n$-PbBi$_2$Nb$_0.9$W$_{0.1}$O$_9$.\(^5\) The enhanced activity of NCPC relative to these materials should be considered as the positive effect of construction of a \( p-n \) nanocomposite with Ohmic junction. Unmodified TiO$_2$ with a wide BG did not generate photocurrent as expected.

The materials were then tested for the photocatalytic decomposition of acetaldehyde, a common model compound to gauge the capability of PCs in photodegradation of organic pollutants. The reaction exploits their photooxidation capability under VL. Figure 3(c) shows the time curves of CO$_2$ evolution from photooxidation of acetaldehyde. The concentration of CO$_2$ increased steadily with irradiation time at a decomposition rate of ca. 0.025 \( \mu \)mol/h only under irradiation of light. The CO$_2$ production stopped when light was stopped.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(Color online) (a) Schematic illustrates technique adopted for fabrication of NCPC. The W metal clusters were deposited by MOCVD over the base of \( p \)-PBNTO that was formed by SSRs. The cluster surfaces were subsequently oxidized to attain the configuration shown in part (c). (b) Typical HRTEM of the fabricated NCPC showing the W$_3$ nanodimensional entities stacking over the surfaces of PBNTO base material. (c) Cross sectional schematic of a typical single W$_3$-encapsulated W layer that stacks over base material of \( p \)-type PBNTO.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(Color online) Schematic energy band model diagram of the system shown in Fig. 1(c) displaying the formation of W interlayer between \( p \)-type and \( n \)-type metal oxide semiconductors. The band positions were derived from flatband potential measurements. CB and VB are conduction and valence bands, respectively. NHE=normal hydrogen electrode.}
\end{figure}
turned off and the reaction was resumed at the same rate when light was turned on again. The superiority of NCPC is obvious over PBNO and TiO$_2$–N$_x$.

As the final test reaction, we investigated photosplitting of water in the presence of sacrificial agents. The rates of oxygen evolution from water in the presence of AgNO$_3$ as the electron scavenger are listed in Table I. Again, NCPC demonstrated the best performance. The quantum yield (QY) of O$_2$ evolution (four times the number of generated O$_2$ molecules/the number of absorbed photon) over NCPC was estimated to be ca. 41%. Until now, there have been no reports on such high value of QY for oxidation of water over semiconductor PCs under VL.

Figure 3(d) shows a time course of QY for oxidation of water over semiconductor PCs under VL.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E_g$ (eV)</th>
<th>$\lambda_{ab}$ (nm)</th>
<th>$\mu$mol/g cat. h</th>
<th>QY</th>
<th>QY</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCPC</td>
<td>2.79</td>
<td>443</td>
<td>49.3</td>
<td>6.06</td>
<td>741</td>
</tr>
<tr>
<td>PBNO</td>
<td>2.88</td>
<td>431</td>
<td>7.6</td>
<td>0.95</td>
<td>520</td>
</tr>
<tr>
<td>TiO$_2$–N$_x$</td>
<td>2.73</td>
<td>451</td>
<td>Trace</td>
<td>0</td>
<td>221</td>
</tr>
</tbody>
</table>

TABLE I. Photocatalytic activities for H$_2$ and O$_2$ evolution from aqueous solutions containing sacrificial agents.

Materials showed excellent stability against photoinduced corrosion of the catalyst. As shown in Table I, the QY for hydrogen evolution was also very high, i.e., 6.06% as compared to other two systems.

In conclusion, we have demonstrated an intelligent technique to fabricate a highly efficient PC configuration of NCPC active under VL irradiation. We employed modern nanomaterial synthetic techniques to bring into reality the engineered material. The NCPC has higher net photon energies available for redox reactions by partial addition of two BGs, and it has an efficient electron-hole separation to minimize the energy-wasteful electron-hole recombination. These factors lead to enhancement in photocatalytic activity. The main advancement of our technique is the creation of a W layer to separate two semiconducting, stable metal oxides, yielding an Ohmic contact in between. Attaining such configuration otherwise would be a very challenging task for such stable metal oxides. Without this Ohmic layer, the simple $p$−$n$ junction structure is less effective.

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1See EPAPS Document No. E-APPLAB-89-216632 for detail fabrication procedure of NCPC, details on photocatalytic characterization, flatband potential measurements, and XPS analysis. This document can be reached through a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).


