Photocatalytic water splitting on different oxide-based systems

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Introduction

The photocatalytic splitting of water into hydrogen and oxygen using solar energy is a challenging research topic which has received much attention in recent years for its potential to provide clean and renewable H\textsubscript{2} as an energy resource. We present the preliminary photocatalytic activity results obtained in a closed recirculation laboratory scale photoreactor, designed to investigate the activity in water photosplitting of suspended particles in the absence of any sacrificial agent or applied bias. A set of semiconductor oxides of general formula A\textsubscript{x}B\textsubscript{y}O\textsubscript{z}, with A = Sr and B = Ti, V, Nb, Ta, prepared by flame hydrolysis (FH) or sol-gel synthesis, has been tested as photocatalysts in H\textsubscript{2} production and their activity has been compared to that of the widely employed titanium dioxide, also modified by Au nanoparticles deposition.

Experimental

Some of the mixed oxide photocatalysts were prepared by FH of aqueous solutions of their precursor salts, which guarantees a relatively high surface area and a very high thermal stability of the material [1]. SrTiO\textsubscript{3} and Sr\textsubscript{2}Ta\textsubscript{2}O\textsubscript{7} were prepared by the well-known sol-gel-citrate (SGC) procedure [2]. They were characterised by BET, SEM, XRD and UV-vis reflectance analyses. Gold nanoparticles were deposited on TiO\textsubscript{2} (P25 from Degussa) either by deposition-precipitation (DP, 1% Au) [3] or by immobilisation of polyvinyl alcohol-stabilised preformed metallic sols (PVA, 5% Au) [4]. Gold deposition did not affect the XRD patterns.

The experimental set up of the apparatus is sketched in Fig. 1. The reactor consisted of a 45 mL, magnetically stirred quartz vessel containing the photoactive suspension, connected to a closed stainless steel circulation system, in which an inert gas (either helium or nitrogen) continuously flowed. The analysis of the species evolved from the aqueous suspension under irradiation was performed by gas chromatography (GC, with TCD detector) or quadrupolar mass spectrometry (QMS). The signals at m/z = 2, 18, 28, 32 and 44 were monitored during the runs. The signals recorded by both detectors were calibrated by injections of known volumes of H\textsubscript{2} (or O\textsubscript{2}) in the system, through a six ways valve.

The light source was an iron halogenide mercury arc lamp, emitting in the 315-400 nm wavelength range with an irradiation intensity in the reactor of 3 x 10\textsuperscript{-7} Einstein s\textsuperscript{-1} cm\textsuperscript{-2}. All photocatalysts (10 mg) were suspended in water, sonicated for 20 min and thoroughly flushed with inert gas in the photoreactor, prior to the beginning of irradiation.

A = reactor
B = refrigerator
C = pump
D = detector (QMS or GC)
E = six ways valve

Figure 1
Results and discussion

As shown in Fig. 2, mixed oxides present an adsorption edge typical of semiconducting materials, which is slightly shifted toward the visible region in the case of SrTiO$_3$. All of the investigated oxide systems showed active as photocatalysts for water photolysis under the selected experimental conditions, with hydrogen always evolving from the suspensions at an almost constant rate. Rate values, normalized with respect to unmodified TiO$_2$, are reported in Table 1.

Higher surface area, leading to higher photocatalytic activity, was obtained with photocatalysts obtained by FH, while the sol-gel synthesis led to lower active surfaces and lower activities. The highest rate of hydrogen production from water photolysis was attained with gold-modified titanium dioxide: metal nanoparticles on the semiconductor surface are able to capture photo-promoted conduction band electrons, thus favoring interface electron transfer and increasing the efficiency of charge separation of the electron-hole pairs light-generated in the semiconductor [5].

Table 1. Results of BET analysis and relative rates of H$_2$ photoproduction of the investigated mixed oxides.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>S$_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Mean pore diameter (Å)</th>
<th>Relative rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$Ta$_2$O$_7$ (SGC)</td>
<td>3.1</td>
<td>335</td>
<td>0.30</td>
</tr>
<tr>
<td>SrTiO$_3$ (SGC)</td>
<td>1.1</td>
<td>173</td>
<td>0.32</td>
</tr>
<tr>
<td>Sr$_2$Nb$_2$O$_7$ (FH)</td>
<td>7.9</td>
<td>248</td>
<td>0.66</td>
</tr>
<tr>
<td>Sr$_3$(VO$_4$)$_2$ (FH)</td>
<td>7.7</td>
<td>244</td>
<td>0.70</td>
</tr>
<tr>
<td>TiO$_2$ (P25)</td>
<td>35</td>
<td>260</td>
<td>1.00</td>
</tr>
<tr>
<td>Au/TiO$_2$ (1% Au)</td>
<td>-</td>
<td>-</td>
<td>1.12</td>
</tr>
<tr>
<td>Au/TiO$_2$ (5% Au)</td>
<td>-</td>
<td>-</td>
<td>1.16</td>
</tr>
</tbody>
</table>

References