Pure phase orthorhombic MgTi$_2$O$_5$ photocatalyst for H$_2$ production

Ning Zhang, Kaifu Zhang, Wei Zhou, Baojiang Jiang, Kai Pan, Yang Qu* and Guofeng Wang*

1. Quantum efficiency calculations

The determination of the apparent quantum efficiency for hydrogen generation was performed using the same closed circulating system under illumination of a 300 W Xe lamp with bandpass filter (313 nm) system. The light intensity was measured using a Si photodiode (oreal 91105V). The total light intensities were 36.69 mW·s$^{-1}$ for 313 nm, 6.63 mW·s$^{-1}$ for 365 nm. The irradiation area was around 7 cm$^2$. Apparent quantum efficiency (AQE) at different wavelengths was calculated by the following equation.

$$AQE = \frac{2 \times \text{the number of evolved } H_2 \text{molecules}}{\text{the number of incident photons}} \times 100\%$$

2. Solar to hydrogen (STH) conversion efficiency calculations from solar simulator measurements.

The solar energy conversion was evaluated by using AM 1.5 solar simulator as the light source with MgTi$_2$O$_5$ nanocrystals as the catalyst (20 mg catalyst in 80 mL water and 20 ml methanol). After 1h of illumination, the total indident power over the 7 cm$^2$ irradiation area was 1.21 W, so that the total input energy in 1 hours was

$$E_{\text{Solar}} = 4.36 \times 10^3 \text{ J.}$$

During the photocatalytic reaction, 94.72 $\mu$mol H$_2$ was detected by gas chromatography, which indicated that the energy generated by water splitting is $E_f = 22.57 \text{ J.}$

$$E_f = 94.72 \times 10^{-6} \times 6.02 \times 10^{23} \times 2.46 \times 1.609 \times 10^{-19}; 2.46 \text{ eV is the free energy of water splitting.}$$

The “solar-to-hydrogen” conversion efficiency of MgTi$_2$O$_5$ nanocrystals was determined to be:

$$\text{STH} = \frac{E_f}{E_{\text{Solar}}} = 0.517\%$$
Table S1. Control experiments to prepare pure phase $\text{MgTi}_2\text{O}_5$

<table>
<thead>
<tr>
<th>Name</th>
<th>$C_{\text{Mg}}$ (mol/L)</th>
<th>Molar Ratios</th>
<th>T(°C)</th>
<th>Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMT</td>
<td>0.0104</td>
<td>1 1</td>
<td>17</td>
<td>$\text{MgTi}_2\text{O}_5$</td>
</tr>
<tr>
<td>MMT-1</td>
<td>0.0104</td>
<td>1 2</td>
<td>17</td>
<td>Mixed phase</td>
</tr>
<tr>
<td>MMT-2</td>
<td>0.0104</td>
<td>2 1</td>
<td>17</td>
<td>Mixed phase</td>
</tr>
<tr>
<td>MMT-3</td>
<td>0.0278</td>
<td>1 1</td>
<td>17</td>
<td>Mixed phase</td>
</tr>
<tr>
<td>MMT-4</td>
<td>0.0278</td>
<td>1 2</td>
<td>25</td>
<td>Mixed phase</td>
</tr>
</tbody>
</table>

$C_{\text{Mg}}$ is the concentration of Mg$^{2+}$ ions in solution. Mixed phase contains $\text{MgTi}_3\text{O}_4$ and $\text{MgTi}_2\text{O}_5$.

Figure S1. XRD patterns of mixed phase magnesium titanates (the red star is phase of $\text{MgTi}_2\text{O}_5$ and the blue triangle is phase of $\text{MgTi}_3\text{O}_4$).

Figure S2. Raman spectra of $\text{MgTi}_2\text{O}_5$ nanocrystals and commercial $\text{MgTi}_2\text{O}_5$. 
Figure S3. UV-vis absorption spectrum (a) of PMT and CMT, and XRD pattern of CMT (b).

Figure S4. N$_2$ adsorption-desorption isotherm curves and pore size distribution (inset) of pure MgTi$_2$O$_5$ nanocrystals, mixed phase MgTiO$_3$/MgTi$_2$O$_5$ and commercial MgTi$_2$O$_5$.

Figure S5. XRD patterns of PMT before and after five times recycles of H$_2$ production.