Enhanced photocatalytic activity for hydrogen evolution of SrZrO$_3$ modified with earth abundant metal oxides (MO, M = Cu, Ni, Fe, Co)

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**Highlights**
- SrZrO$_3$ photocatalysts catalyzed hydrogen evolution under UV light.
- SrZrO$_3$ photocatalytic activity was improved by co-catalysts addition.
- Best catalytic activity was exhibited by SrZrO$_3$ modified with CuO.
- Charge separation mechanism in SrZrO$_3$–CuO interface is discussed.

**Graphical Abstract**

**Abstract**

In this work, we report the photocatalytic activity of a SrZrO$_3$ semiconductor modified with earth abundant metal oxides as co-catalysts (MO, M = Cu, Ni, Fe, Co) dispersed by the impregnation method for hydrogen evolution from pure water. SrZrO$_3$ powders are prepared by traditional solid-state synthesis at 1100°C by 24 h and then modified by the dispersion of different amounts (0.5%, 1%, 2% and 5%) of metal oxide nanoparticles at 400°C. The structural, morphological, optical and textural properties of the modified powders were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS) and the Brunauer–Emmet–Teller (BET) method. The evaluation of the powders as photocatalysts for hydrogen evolution from pure water under UV light is presented, and the effect of loading metal oxide nanoparticles on the photocatalytic activity is discussed. The results confirm that the activity of the SrZrO$_3$ photocatalyst is increased by metal oxide particle loading, which promotes charge separation and higher photocatalytic efficiency. The best activity (1165 μmol g$^{-1}$ h$^{-1}$) was obtained by 1% CuO loading, corresponding to an increase of 28 times the activity of pure SrZrO$_3$.

**1. Introduction**

The use of solar energy for the photocatalytic conversion of water into hydrogen and oxygen is a desirable option for the development of new and clean fuel sources. Semiconductor
Oxides have shown promising performance in photocatalytic processes with the possibility of optimizing their properties through the design of their crystal and electronic band structures to achieve the required potential for the overall water splitting reaction. However, they usually have large band gaps that make them active only under UV light [1]. Photocatalysts with the ability to utilize visible light and suitable band structures are needed for the water splitting reaction. The overall photocatalytic process involves the absorption of light with an energy equivalent to or greater than the band gap of the semiconductor to generate...
electron–hole pairs in the bulk semiconductor. The photogenerated charges are transported to the surface, where oxidation–reduction reactions are carried out. To achieve overall water splitting, the minimum photon energy that is thermodynamically required to produce H2 and O2 is 1.23 eV [2]. To improve the charge separation and reaction efficiency on the surface, several noble metals (Pt [3–7], Au [8], Pd [9], Ag [10], Ru [11] and Rh [12]) have been employed as co-catalysts to obtain higher photocatalytic activities [13]. Some materials that rely on low cost and earth-abundant elements (e.g., Fe, Co, Ni, Mo, Cu) have been utilized as metal co-catalysts for hydrogen production [16]. Recently, oxides of transition metals have been studied as co-catalysts, with NiO demonstrating the best performance [17,18]. The method of co-catalyst deposition directly influences the photocatalytic activity of the semiconductor. The most frequently used routes for the deposition of co-catalysts are the impregnation, electrochemical and electroless plating methods. Recently, our research group reported the synthesis of SrZrO3 powders, which have favorable properties for hydrogen evolution from water splitting [19]. A few works have reported on the photocatalytic properties of SrZrO3. Zhou et al. [20] studied the MoS2/SrZrO3 heterostructure and its application for water splitting, while Ashiq et al. [21] tested SrZrO3 nanoparticles for carbon dioxide photoreduction with promising results. In this work, the modification of SrZrO3 by the deposition of metal oxide particles to enhance its photocatalytic activity in the water splitting reaction is presented. To the best of our knowledge, this is the first report on modifying SrZrO3 with metal oxide particles and using them as photocatalysts for water splitting under UV irradiation.

Table 1
Quantitative analysis by EDS of representative samples of SrZrO3 modified with metal oxide particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical weight deposited (%)</th>
<th>Weight determined by EDS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrZrO3 1% CuO</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>SrZrO3 2% NiO</td>
<td>2</td>
<td>1.7</td>
</tr>
<tr>
<td>SrZrO3 1% FeO</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>SrZrO3 5% CoO</td>
<td>5</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Fig. 3. SEM images of (a) pure SrZrO3 and SrZrO3 modified with (b) 1% CuO, (c) 2% NiO, (d) 1% FeO and (e) 5% CoO.
calcined at 400 °C for 1 h. The mixture was stirred for 1 h, and then, the sol–precursor solution (metal acetates, Sigma Aldrich 99%) in ethanol was evaporated by heating at 80 °C under stirring. The specific surface area ($S_{BET}$) of the materials was calculated by the physical adsorption of nitrogen at 77 K with a Belsorp II mini (Bel Japan), degassing the samples at 300 °C for 1 h prior to the analysis. The optical properties of the samples were analyzed between 200 and 800 nm using a UV–vis NIR spectrophotometer (Cary 5000) coupled with an integration sphere for diffuse reflectance measurements, calculating the band gap energy ($E_g$) through the Kubelka–Munk function. The conduction band and valence band potentials of the semiconductors studied in this work at the point of zero charge were calculated using the empirical equation: $E_{VB} = EN - E' + 0.5 \times E_g$, where $E_{VB}$ is the top of valence band; $EN$ is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms; $E'$ is the energy of free electrons on the hydrogen scale (~4.5 eV); $E_g$ is the band-gap energy of the semiconductor; and $E_{CB}$, the bottom of the conduction band, can be determined by $E_{CB} = E_{VB} - E_g$ [22]. The solar to hydrogen efficiency (%STH) was calculated considering the input power (4400 µW/cm$^2$) and the area (24.28 cm$^2$) of the pen-ray lamp used in the photocatalytic test with the equation: \[
\%STH = \frac{100 \times [(\text{mmol H}_2 \text{s}^{-1}) \times (237 \text{kJ/mol}) \times (P_{in} \text{mW cm}^{-2})] \times (\text{area \ cm}^2)}{(\text{input power} \times \text{area \ cm}^2)}
\]
where $P_{in}$ is the power of the incident light [23]. The enhancement factor was obtained by dividing the activity of the SrZrO$_3$-modified samples by the activity of pure SrZrO$_3$ [16].

The photoluminescence spectra of the samples were measured at room temperature on a fluorescence spectrophotometer (Agilent Cary Eclipse) with an excitation wavelength of 229 nm (SrZrO$_3$ absorption band) and a scanning speed of 1000 nm/min. The width of excitation and emission slit were both 5 nm. The photocurrent response was measured on a potentiostat–galvanostat (Metrohm Autolab) using a conventional three electrode photoelectrochemical quartz cell with a 0.5 M Na$_2$SO$_4$ aqueous solution. The working electrode was prepared using the sample of interest (0.2 g), terpineol (0.05 g) and 2 mL of ethanol to make a slurry. The slurry was applied by screen printing onto an ITO substrate (1 cm × 1 cm). Then, the electrodes were dried and calcined at 400 °C for 30 min. The active area of the working electrodes was 1 cm$^2$. A platinum wire and Ag/AgCl were used as the counter and reference electrodes, respectively; and the cell was illuminated with a pen–ray lamp (UVP, 254 nm and 4400 µW/cm$^2$).

### 2. Photocatalytic test

The photocatalytic activity for hydrogen evolution of the materials was performed at room temperature in a 250-ml Pyrex reactor. In all cases, the photocatalyst (0.2 g) was dispersed in 200 mL of deionized water by vigorous stirring, deaerating the sample by bubbling nitrogen for 30 min prior to the reaction. Then, the solution was irradiated with a pen–ray lamp (UVP, 254 nm and 4400 µW/cm$^2$) and hydrogen evolution was monitored by gas chromatography using an online Thermo Scientific gas chromatograph equipped with a thermal conductivity detector (TCD) and a fused silica capillary column (30 m × 0.53 mm) with nitrogen gas as the carrier. Samples were taken at 30 min time intervals over 3 h. To obtain the true hydrogen production efficiency of the water-splitting reaction on the samples under irradiation, the solar to hydrogen efficiency (%STH) was calculated.
3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of the powders modified with copper, nickel, iron and cobalt oxide nanoparticles are presented in Fig. 2(a)–(d), respectively. It can be seen that all of the observed peaks correspond to the orthorhombic phase of the perovskite SrZrO$_3$ (JCPDS: 44-0161). All of the peaks are well-defined and correspond in relative height to the peaks reported in the pattern, discarding preferential orientation. An increase of the crystallinity of the samples was observed after the impregnation process, probably due to the thermal treatment required to obtain the metal oxide nanoparticles. The position and width of the peaks were not affected by the addition of metal oxide particles, so we assume that the SrZrO$_3$ crystal lattice was not modified and metal oxides particles are located at the surface of the material. No signals corresponding to metal oxide particles were observed, likely because their size is smaller than the detection limit of XRD (~3 nm) [24] and due to the small amount of material deposited.

3.2. Scanning electron microscopy

Fig. 3(a)–(e) shows the morphologies obtained for pure SrZrO$_3$, and SrZrO$_3$ modified with metal oxide nanoparticles, and the quantitative results obtained from the chemical analysis by EDS are

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated conduction and valence band edge potentials of SrZrO$_3$ and the transition metal oxides studied in this work. Potentials are referenced versus a normal hydrogen electrode (NHE).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>$E_{BC}$ (eV)</th>
<th>$E_{BV}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrZrO$_3$</td>
<td>$-1.56$</td>
<td>$+2.54$</td>
</tr>
<tr>
<td>CuO</td>
<td>$-0.63$</td>
<td>$+1.98$</td>
</tr>
<tr>
<td>NiO</td>
<td>$-0.62$</td>
<td>$+2.98$</td>
</tr>
<tr>
<td>FeO</td>
<td>$-0.17$</td>
<td>$+2.60$</td>
</tr>
<tr>
<td>CoO</td>
<td>$-0.11$</td>
<td>$+2.49$</td>
</tr>
</tbody>
</table>

Fig. 6. Band diagram of SrZrO$_3$ and the transition metal oxides studied in this work.
shown in Table 1. These analyses confirmed the presence of metal oxide nanoparticles at smaller quantities than those that were calculated, and this difference was attributed to the mass lost during the process. SEM micrographs show irregular particles smaller than 300 nm, with some small individual particles, which are thought to correspond to the deposited metal oxide nanoparticles.

To investigate the distribution of the metal oxide nanoparticles on SrZrO3 substrates, elemental mappings were carried out. The elemental distribution by mapping showed that the metal oxide nanoparticles were fully dispersed on SrZrO3. In general terms, the morphology and size of the SrZrO3 powders were not altered by the deposition of the metal oxide nanoparticles.

### 3.3. X-ray photoelectron spectroscopy

To obtain chemical information of the metal oxide nanoparticles, XPS analyses were carried out. The spectra were fitted using the AAnalyzer software [25]. Fig. 4 shows the Cu 2p and Ni 2p spectra for the SrZrO3 modified samples that showed the highest performance in the hydrogen evolution reaction: (a) SrZrO3 1% CuO and (b) SrZrO3 2% NiO. Fig. 4(a) shows the Cu 2p spectra, with resolvable doublet features 2p_{3/2} and 2p_{1/2} at 932.8 eV and 952.9 eV, respectively. This doublet is associated with Cu^{2+} (CuO) [26–29]. Two additional doublets appear at 940.8 eV and 943.1 eV, respectively, and these are associated with shake-up satellites from the Cu^{2+} signal. Fig. 4(b) shows the Ni 2p spectrum. Two main doublets are associated with Ni^{2+} and Ni^{3+} at 853.3 eV and 855.1 eV, respectively; while two additional doublets at 860.2 and 862.8 eV are associated with satellite features. A spin–orbit splitting of 18.3 eV was used to fit the Ni 2p spectrum [30–33]. This result indicates the existence of nickel oxidized species in the sample, in the form of Ni^{2+}/Ni^{3+}, promoted by the presence of oxide species in the sample. The XPS spectra are shown in Fig. 4.

### 3.4. UV–Vis diffuse reflectance spectroscopy

The diffuse reflectance spectra of the powders modified with metal oxide particles are shown in Fig. 5(a)–(d). The pure SrZrO3 spectrum shows the absorption range of the compound, beginning at wavelengths below to 300 nm, corresponding to the characteristic UV absorption reported in the literature [34]. With the addition of metal oxide particles, the absorption of SrZrO3 in the visible range increased due to the characteristic absorption of transition metal oxides and d–d transitions of the metals (Cu, Ni, Fe and Co) [24]. Higher visible light absorption was observed on SrZrO3 powders modified with copper oxide particles. In this figure, we can also observe the calculated band gaps. These values are smaller than those obtained from pure SrZrO3, and the reduction of the band gap corresponded to an increase of the amount of metal oxide particles that were loaded. This small band gap energy could be

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**Table 3**

The properties of the SrZrO3 photocatalysts prepared in this work and their activities for the hydrogen evolution reaction.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Co-catalyst</th>
<th>S BET (m² g⁻¹)</th>
<th>E g (eV)</th>
<th>H₂ evolution activity (μmol g⁻¹ h⁻¹)</th>
<th>STH (%)</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrZrO3</td>
<td>–</td>
<td>4.1</td>
<td>42</td>
<td>0.65</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>0.5%</td>
<td>3.0</td>
<td>718</td>
<td>11.06</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>2.9</td>
<td>1165</td>
<td>17.95</td>
<td>27.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>2.5</td>
<td>890</td>
<td>13.71</td>
<td>21.2</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>0.5%</td>
<td>3.5</td>
<td>40</td>
<td>0.75</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>3.5</td>
<td>85</td>
<td>1.31</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>3.0</td>
<td>106</td>
<td>1.63</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>2.8</td>
<td>75</td>
<td>1.16</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>0.5%</td>
<td>3.5</td>
<td>61</td>
<td>0.46</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>3.5</td>
<td>77</td>
<td>0.58</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>3.1</td>
<td>65</td>
<td>0.49</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>CoO</td>
<td>0.5%</td>
<td>3.5</td>
<td>43</td>
<td>0.66</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>2.9</td>
<td>49</td>
<td>0.75</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>2.7</td>
<td>52</td>
<td>0.80</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>2.5</td>
<td>53</td>
<td>0.82</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 7. Comparison of the PL spectra of pure SrZrO3 and modified SrZrO3 samples excited at 229 nm.

Fig. 8. Photocurrent responses of pure SrZrO3 and MO–SrZrO3 under UV light.
produced by a transition from the valence band of the metal oxide to the conduction band of SrZrO₃ due to good contact and interdispersion between the two semiconductor oxides [35].

3.5. Band structure calculation

The calculated values of the conduction (CB) and valence (VB) bands and the proposed band structures of SrZrO₃ and metal oxides studied as co-catalysts are shown in Table 2 and Fig. 6, respectively. The SrZrO₃ conduction band is shown to be sufficiently negative to perform water reduction, and its valence band is more positive than water oxidation potential, indicating that this material is thermodynamically suitable to perform the water splitting reaction. In this material, the CB is mainly composed of Zr 4d, Sr 4d and O 2p empty orbitals, while the valence band is composed of O 2p atomic orbitals [21]. Under light irradiation, the O 2p orbitals in VB transfer electrons to the CB and the photogenerated charges perform the reduction and oxidation of water on the surface of the photocatalyst. In contrast, in the transition metal oxides studied as co-catalysts, the conduction band is mainly composed of metal M 3d (M = Cu, Ni, Fe, Co) orbitals, and the valence band is primarily composed of O 2p orbitals. As explained by Domen and Maeda [36], due to the electronic configuration of these transition metals, their corresponding oxides are suitable for visible light absorption (with the exception of nickel oxide) and for creating reaction active sites as co-catalysts.

3.6. Physisorption analysis

To investigate the effect of metal oxide deposition on the SrZrO₃ surface area, physisorption analyses were performed. The results are shown in Table 3. The BET surface areas were calculated to be approximately 1 m² g⁻¹, which corresponds to the expected area from powders prepared by the solid state reaction. The surface areas of SrZrO₃ powders after loading metal oxide nanoparticles were not altered significantly, so we can assume that the SrZrO₃ pore structure was not modified after deposition.

3.7. Photoluminescence spectroscopy

The analysis of the photoluminescence spectra of the samples was carried out to investigate the efficiency of charge carrier migration, transfer and separation as well as to understand the path of the photogenerated electrons and holes in the samples, since photoluminescence emission is the product of the recombination of free carriers [37,38]. Fig. 7 represents the photoluminescence spectra of the SrZrO₃ samples modified with the optimal load of metal oxides. A decrease in the photoluminescence intensity was observed, indicating the effective separation of photogenerated charges. The photoluminescent intensity of pure and modified SrZrO₃ powders is as follows: SrZrO₃ > 5% CuO > 1% FeO > 2% NiO > 1% CoO. SrZrO₃ modified with 1% CuO shows the lower recombination rate of electron and holes, which is attributed to a better separation of photogenerated charges. A lower recombination rate is directly associated with a higher photocatalytic activity [37,39].

3.8. Photocurrent response

The photocurrent responses of pure and modified SrZrO₃ samples are shown in Fig. 8. A significant increase in the current density is seen with the addition of metal oxides particles on SrZrO₃. The highest photocurrent density was obtained with the sample with 1% CuO due to the better charge separation efficiency of this material.
sample, as confirmed by photoluminescence measurements. Nickel, iron and cobalt oxides also showed a higher photocurrent density compared to pure SrZrO$_3$. These results indicate that metal oxide particles on SrZrO$_3$ effectively promote enhanced charge separation.

### 3.9. Hydrogen production

The photocatalytic activity of SrZrO$_3$ modified with nickel, copper, cobalt and iron oxide particles under UV light is shown in Fig. 9(a)–(d), respectively. As shown in Fig. 9, the materials presented constant hydrogen production during 3 h. The average H$_2$ evolution rate for SrZrO$_3$ catalysts are summarized in Table 3 along with the calculated solar to hydrogen efficiencies (STH) and enhancement factors. The calculated STH in this work is analogous to the real parameter reported because the UV light employed (254 nm) is not commonly found in the solar light received on the surface of earth (AM1.5G). In Fig. 10(a) the optimized loading amounts of metal oxide nanoparticles on SrZrO$_3$ are shown. The highest activities were obtained with loadings of 1% CuO, 2% NiO, 1% FeO and 5% CoO, as shown in Fig. 10(b). The highest overall activity of the series of SrZrO$_3$ powders modified with metal oxides nanoparticles was obtained by the sample loaded with 1% CuO (1165 μmol g$^{-1}$ h$^{-1}$), a 28-fold increase over the activity of pure SrZrO$_3$, and the sample with the highest calculated solar to hydrogen efficiency (STH). SrZrO$_3$ modified with 2% NiO also showed a hydrogen evolution rate of 106 μmol g$^{-1}$ h$^{-1}$, corresponding to an almost 3-fold increase over unmodified SrZrO$_3$. The highest activity obtained on SrZrO$_3$ modified with CuO particles could be attributed to improved charge separation due to good interdispersion of n-type SrZrO$_3$ and p-type CuO\[40–42\], which promotes a more efficient use of the photogenerated charges. This mechanism is illustrated in Fig. 11. As illustrated in this figure, the photocatalytic process can be described in six steps:

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1. Mott–Schottky plots (1/C$^2$ with respect to potential) were calculated to determine the nature n and p of the SrZrO$_3$ and CuO semiconductors because the slope of 1/C$^2$ with respect to the potential is negative for an n-type semiconductor and positive for a p-type semiconductor \[43\]. These plots are available in the supporting information.
(1) A SrZrO3 semiconductor in the photocatalytic reactor is irradiated with a lamp of 254 nm.

(2) The energy of the irradiated light is greater than the SrZrO3 band gap (4.1 eV–402 nm), promoting the excitation of electrons in the valence band (VB) toward the conduction band (CB), leaving positive holes in the valence band of the material. The irradiation source employed has a principal emission intensity (>95%) at 254 nm. CuO has a band gap of 1.35 eV (918 nm) and thus will not absorb this type of radiation and will not generate electron–hole pairs.

(3) Photogenerated holes are transferred from the SrZrO3 valence band to the CuO valence band because the redox potential of the SrZrO3 VB edge is more positive than the redox potential of the CuO VB edge.

(4) The transfer of holes to CuO VB enhances the charge separation and reduces the recombination process, in agreement with photoluminescence results.

(5) Holes in the CuO VB have an appropriate redox potential for the oxidation of water molecules to produce oxygen and H+ protons.

(6) Electrons on SrZrO3 CB have a redox potential to reduce H+ protons resulting from water oxidation and produce H2. With both processes, water oxidation in CuO VB and proton reduction in SrZrO3 CB, the electroneutrality of the photocatalyst is recovered.

4. Conclusions

SrZrO3 powders were synthesized by the solid state method and successfully modified by the deposition of metal oxide nanoparticle clusters through the impregnation method. The modified SrZrO3 powders showed no change in structural and morphological properties after deposition, resulting in catalysts with highly dispersed and small metal oxide particles on SrZrO3. The absorption in the visible range of SrZrO3 increased after the addition of the metal oxides in accordance with the amount of loading and had a greater effect in the materials modified with CuO. Our study demonstrated that the addition of metal oxide particles on SrZrO3 promoted a better charge carrier separation, resulting in an improvement in photocatalytic activity. The highest catalytic activity was obtained by SrZrO3 modified with 1% of CuO, and it was attributed to the improved charge separation at the interface of n-type SrZrO3 and p-type CuO semiconductor. The results demonstrate that these metal transition oxides are suitable noble metal-free co-catalysts for hydrogen evolution by water splitting.

Acknowledgments


Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2016.05.025.

References


[22] Cui R, Bae ST, Kim DH, Hong KS. Effects of crystal and electronic structures of AIn6O19 (Ca, Sr, Ba) metaniobate compounds on their photocatalytic H2 evolution from pure water. Int J Hydrogen Energy 2010;35:12954.


