Characterization of photocatalytic performance of silver deposited TiO$_2$ nanorods

Hyeong Jin Yun$^a$, Hyunjoo Lee$^b$, Nam Dong Kim$^a$, Jongheop Yi$^{a,*}$

$^a$School of Chemical and Bioengineering, Seoul National University, Seoul 443-749, South Korea
$^b$Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, South Korea

ARTICLE INFO

Article history:
Received 15 November 2008
Received in revised form 26 November 2008
Accepted 28 November 2008
Available online 9 December 2008

Keywords:
Photocatalyst
Silver deposited TiO$_2$
Surface modification
Shape effect
Photocatalytic decomposition

ABSTRACT

Ag–TiO$_2$ nanorods were synthesized via gel–sol methods. Cyclic voltammetry results showed that surface modification of TiO$_2$ nanorods using Ag led better electrochemical activity involving fast electron transfer to electrode. Electrochemical impedance spectroscopy results revealed that the increase in aspect ratio of TiO$_2$ nanorods and surface modification resulted in synergistic effect of reduction of e$^-$/h$^+$ recombination and charge transfer resistance. Consequently the use of Ag–TiO$_2$ nanorods as photocatalysts exhibited significant increase in photocatalytic decomposition rate of acid red 44.

1. Introduction

Titanium dioxide (TiO$_2$) is one of the semiconductor materials with wide band-gap energy of 3.0–3.2 eV. It has applications such as water purification [1,2], hydrogen production [3,4], and dye-sensitized solar cells [5,6], and so on.

One dimensional (1D) TiO$_2$ nanomaterial has been an attractive research field due to their excellent photocatalytic performance [6–9]. When a semiconductor electrode is immersed in the electrolyte, a space charge region is formed at inner surface of the electrode. For 1D nanomaterials, the space charge region is well constructed along the longitudinal direction of crystal, therefore photogenerated electrons can flow in the direction of the crystal length. It can lead to decrease in probability of e$^-$/h$^+$ recombination. Thus there exists a large amount of e$^-$/h$^+$ on the crystal surface, resulting in higher photocatalytic activity.

Surface modification via the addition of metals can enhance the photocatalytic activities. Transition metals deposited on semiconductor materials increase the charge transfer rate between reactants and photocatalyst as the intermediary in electron pathway [10–13]. Therefore, it is envisaged that metal deposited TiO$_2$ nanorods should show superior photocatalytic activities because of low probability of e$^-$/h$^+$ recombination and high charge transfer rate. In this work we synthesized Ag–TiO$_2$ nanorods and compared their photocatalytic activities with TiO$_2$ nanospheres and nanorods. We demonstrated the synergistic effect of crystals shape and surface modification on photocatalytic properties.

2. Experimental

TiO$_2$ nanospheres and nanorods were synthesized by the gel–sol method [14]. A total of 0.1 mol of titanium tetraisopropoxide (TTIP, Advanced Materials Institute, 98%) was added to 0.2 mol of triethanolamine (Fluka, 99%); deionized water was then added to achieve 200 ml Ti$^{4+}$ aqueous solution. Thirty milliliters of this solution was mixed with 30 ml of 0.02 M of oleic acid (Samchun, 99.9%), and 0.1 M of ethylenediamine (Aldrich, 99%) aqueous solution to synthesize TiO$_2$ nanospheres and nanorods, respectively. The mixtures were placed into Teflon-lined autoclaves and heated at 100 °C for 24 h. Then they are heated at 250 °C for 72 h for crystallization. Finally, TiO$_2$ powder was obtained by drying at 70 °C for 12 h. Ag–TiO$_2$ nanorods were synthesized via similar procedure except introducing 0.002 mol of AgNO$_3$ in the procedure to make Ti$^{3+}$ solution. The shapes of synthesized samples were characterized using a high-resolution transmission electron microscope (HR-TEM, JEM 3010-JEOL, 300 kV).

Electrochemical analyses were performed using a standard three-electrode cell with a platinum-coated titanium mesh and a saturated Ag/AgCl electrode used as a counter and a reference electrode, respectively. For electrochemical analyses working electrode was made via the following process; a total of 4 mg of synthesized samples was dropped on the ITO glass and the resulting films were heated in air at 500 °C for 1 h to improve adhesion. Test electrolyte was prepared by dissolving acid red 44 (Aldrich, 80%) with a concentration of 20 ppm.

In order to estimate the photocatalytic activities of the synthesized nanoparticles, the photocatalytic decomposition of acid red 44 was carried out under UV irradiation using a Xe arc lamp
A total of 0.1 g of each photocatalyst was suspended in aqueous solution of 20 ppm acid red 44 (200 ml) under vigorous stirring. The concentrations of acid red 44 were measured by ultraviolet–visible light spectroscopy (UV–vis, V670-Jasco).

3. Results and discussion

We prepared three types of TiO$_2$ nanostructured materials to compare the photocatalytic activities; TiO$_2$ nanospheres, nanorods, and Ag–TiO$_2$ nanorods, as shown in Fig. 1a–c, respectively. They show an approximately monodispersed distribution in their sizes and shapes. TiO$_2$ nanospheres have an average diameter of 30.8 ± 4.3 nm, and nanorods have an average dimension of 134.8 ± 37.3 nm in length and 26.2 ± 3.6 nm in width. Ag–TiO$_2$ nanorods have a similar dimension to bare-TiO$_2$ nanorods. Fig. 1d shows the silver nanoparticles with average diameter of 4.8 ± 0.4 nm deposited on TiO$_2$ nanorods. Ag nanoparticles are well distributed on the TiO$_2$ nanorods surface with uniform particle sizes.

Fig. 2 shows cyclic voltammograms of aqueous electrolyte containing 20 ppm acid red 44 at the nanoparticulated TiO$_2$ electrodes. In this case the potential was scanned from 0 V to more negative direction up to −1.0 V, then turned to more positive direction up to 1.5 V, and ended at 0 V. The scan rate was 30 mV s$^{-1}$. TiO$_2$ nanorods showed higher current density than nanospheres in oxidative decomposition of acid red 44. At TiO$_2$ nanorods, space charge region is well developed along the longitudinal direction, thus photogenerated electron flow to the bulk TiO$_2$ electrode through space charge region easily. It leads to decrease in the probability of $e^{-}/h^{+}$ recombination as exhibiting higher electron transfer rate from acid red 44 molecules. By the way bare-TiO$_2$ electrodes do not show any significant peaks. The current density, however, reaches the limiting current density at 1 V on the backward scan when the Ag–TiO$_2$ nanorods electrode was used. The photocatalytic decomposition of acid red 44 occurs through an oxidative reaction. The appearance of a significant anodic limiting current means the better electrochemical activities involving electron transfer to electrode. Acid red 44 molecules adsorb on the silver nanoparticles deposited on TiO$_2$ surface, and the electrons are transferred to TiO$_2$ through silver nanoparticles easily. On the contrary bare-TiO$_2$ has less electrochemical activity for photocatalytic decomposition of acid red 44. Thus Ag–TiO$_2$ nanorods have better photocatalytic performance than bare-TiO$_2$.

EIS technique was used to characterize electrochemical interfacial reactions. Fig. 3 is Nyquist plot for (a) TiO$_2$ nanospheres, (b) nanorods and (c) Ag–TiO$_2$ nanorods in aqueous electrolyte of acid red 44 under UV irradiation. EIS experiments were performed in the frequency range between 1 kHz and 10 MHz with an ac voltage amplitude of 10 mV at dc bias of 0.7 V. Each marker in Fig. 3 represents experimental data and the solid lines are theoretical impedance spectra derived from the equivalent circuit proposed in inset of Fig. 3. Experimental data have a good agreement with the theoretical impedance spectra, thus proposed equivalent circuit is validated in this reaction. Proposed circuit was designed with serial combination of bulk electrolyte resistance ($R_X$), interfacial reaction impedance, and inner surface charge transfer impedance.

![Fig. 1. TEM images of (a) TiO$_2$ nanospheres (b) nanorods, (c) Ag–TiO$_2$ nanorods, and (d) HR-TEM images of Ag–TiO$_2$ nanorods.](image-url)
Interfacial reaction impedance was modeled as a parallel combination of electrochemical double-layer capacitance \((Q_{dl})\), and faradaic process consisting of charge transfer resistance \((R_{ct})\) and Warburg impedance \((Z_w)\). Inner surface charge transfer impedance consists of space charge capacitance \((C_{sc})\), and TiO\(_2\) bulk electrode resistance \((R_T)\). In this circuit, the constant phase element (CPE) \(Q\) can replace the electrochemical double-layer capacitance. CPE is given as \(1/Y_0(j\omega)^n\), where \(Y_0\) is the admittance magnitude of CPE, and \(n\) is the exponent [15]. In this work, the value of \(n\) is fixed at 0.95 to clarify the relation between particle shape and the capacitance of the electrochemical double-layer. The extracted parameters for the equivalent circuit elements are summarized in Table 1. TiO\(_2\) nanospheres showed lower charge transfer resistance than nanospheres in oxidative decomposition of acid red 44. High probability of delocalization of electrons at TiO\(_2\) nanorods leads to decrease in the probability of \(e^-/h^+\) recombination as exhibiting higher electron transfer rate from acid red 44 molecules. When silver nanoparticles were deposited on the TiO\(_2\) nanorods, \(R_{ct}\) decreased significantly because electrons are transferred easily from acid red 44 molecules to electrode through silver nanoparticles. Thus Ag–TiO\(_2\) nanorods showed the lowest charge transfer resistance due to synergetic effect of TiO\(_2\) particles shape and surface modification.

Fig. 4 shows the photocatalytic activities obtained when (a) TiO\(_2\) nanospheres, (b) nanorods and (c) Ag–TiO\(_2\) nanorods were used as photocatalysts, respectively. TiO\(_2\) nanorods showed better photocatalytic activities than nanospheres due to the decrease in probability of \(e^-/h^+\) recombination as demonstrated using electrochemical analyses. And when Ag–TiO\(_2\) nanorods were used as photocatalysts, photocatalytic activity was significantly improved. Surface modification of TiO\(_2\) nanorods with Ag nanoparticles led to fast charge transfer in interfacial region. These findings are in agreement with CV and EIS results. As results, lower probability of \(e^-/h^+\) recombination, and high electron transfer rate at Ag–TiO\(_2\) nanorods gives rise to superior photocatalytic activities.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TiO(_2) nanospheres</th>
<th>TiO(_2) nanorods</th>
<th>Ag–TiO(_2) nanorods</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{ct})</td>
<td>9.051 kΩ</td>
<td>9.072 kΩ</td>
<td>9.054 kΩ</td>
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<tr>
<td>(C_{sc})</td>
<td>3.520 μF</td>
<td>4.042 μF</td>
<td>4.646 μF</td>
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<tr>
<td>(R_T)</td>
<td>2.025 kΩ</td>
<td>2.024 kΩ</td>
<td>2.021 kΩ</td>
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<tr>
<td>(Q_{dl}/\text{Sec}^{0.5})</td>
<td>(1.571 \times 10^{-5})</td>
<td>(1.862 \times 10^{-5})</td>
<td>(1.962 \times 10^{-5})</td>
</tr>
<tr>
<td>(R_{ul})</td>
<td>480.2 kΩ</td>
<td>312.2 kΩ</td>
<td>129.8 kΩ</td>
</tr>
<tr>
<td>(Z_{ul}/\text{Sec}^{n})</td>
<td>(9.882 \times 10^{-5})</td>
<td>(9.713 \times 10^{-5})</td>
<td>(1.012 \times 10^{-4})</td>
</tr>
</tbody>
</table>
4. Conclusions

The synthesis of ellipsoidal Ag–TiO$_2$ nanorods was successfully carried out via gel–sol process. We performed electrochemical studies of photocatalytic decomposition of acid red 44 for Ag–TiO$_2$ nanorods using CV and EIS method, and then compared with TiO$_2$ nanospheres and nanorods. Ag–TiO$_2$ nanorods showed better electrochemical active behavior involving fast electron transfer to electrode caused by surface modification. Moreover decrease in the probability of e$^-$/$h^+$ recombination due to enhanced delocalization of e$^-$ at 1D nanorods induce a synergetic effect with surface modification. Consequently photocatalytic activity increased when Ag–TiO$_2$ nanorods were used for the photocatalytic decomposition of acid red 44.

Acknowledgments

This work was supported by Grant No. R01-2006-000-10239-0 awarded by the Basic Research Program of the Korea Science and Engineering Foundation.

References