Supporting Information

A Facile Exfoliation–Crystal Growth Route to Multicomponent
Ag₂CO₃/Ag–Ti₅NbO₁₄ Nanohybrids with Improved Visible Light
Photocatalytic Activity

Suhye Park, Jang Mee Lee, Yun Kyung Jo, In Young Kim, and Seong-Ju Hwang*

Department of Chemistry and Nano Sciences, College of Natural Sciences, Ewha Womans University, Seoul
120-750, Korea
Table S1. Results of deconvolution analysis for Ag 3d XPS spectra of the Ag$_2$CO$_3$/Ag–Ti$_5$NbO$_{14}$ nanohybrids.

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>AT1 BE (eV)</th>
<th>Area (%)</th>
<th>AT2 BE (eV)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$^0$</td>
<td>368.20</td>
<td>27.6</td>
<td>368.18</td>
<td>33.3</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>367.77</td>
<td>72.4</td>
<td>367.78</td>
<td>66.7</td>
</tr>
</tbody>
</table>

The Ag 3d XPS spectra of the present Ag$_2$CO$_3$/Ag–Ti$_5$NbO$_{14}$ nanohybrids can be commonly resolved into two components corresponding to monovalent Ag$^+$ cation and neutral Ag$^0$ element. Table S1 summarizes the components of silver species. According to the peak convolution analysis, the observed XPS spectra of the present AT nanohybrids are well-reproduced with the summation of the spectra of Ag$_2$CO$_3$ and Ag metal, indicating the presence of these two phases. The ratio of Ag metal/Ag$_2$CO$_3$ is determined to be 0.38 and 0.50 for the AT1 and AT2 nanohybrids, suggesting the increase of Ag metal upon the increase of Ag content.
Fig. S1. Schematic model for the electronic structure of the Ag$_2$CO$_3$/Ag–Ti$_5$NbO$_{14}$ nanohybrids.

As plotted in Fig. S1, taking into account the relative band positions of titanoniobate and silver carbonate, photoinduced holes in the valence band (VB) of Ag$_2$CO$_3$ can be transferred into the upper-lying VB of Ti$_5$NbO$_{14}$, leading to the spatial separation of electrons and holes and the increase of their lifetime. The presence of minor metallic silver phase is believed to promote the electron transfer between Ag$_2$CO$_3$ and Ti$_5$NbO$_{14}$. 
Fig. S2. Three successive photocatalyst test for visible light ($\lambda > 420$ nm)-induced degradation of 4-CP molecule by the AT2 nanohybrid (circle) and the unhybridized Ag$_2$CO$_3$ (square) for (a) the 1st cycle, (b) the 2nd cycle, and (c) the 3rd cycle.

To probe the photostability of the present Ag$_2$CO$_3$/Ag–Ti$_5$NbO$_{14}$ nanohybrids, the photocatalytic performance of the AT2 nanohybrid is repeatedly examined for consecutive three cycles. As illustrated in Fig. S2, the depression of photocatalytic activity for the degradation of 4-CP is much weaker for the AT2 nanohybrid (~85% retention after the 3rd cycle) than for Ag$_2$CO$_3$ (~45% retention after the 3rd cycle), confirming the positive effect of hybridization on the photostability of silver carbonate.
**Fig. S3.** $N_2$ adsorption–desorption isotherms of the AT2 nanohybrid subjected to the photocatalyst test under the illumination of visible light ($\lambda > 420$ nm). The close and open symbols represent the adsorption and desorption data, respectively.

: As illustrated in **Fig. S3**, the surface area of the AT2 nanohybrid subjected to the photocatalyst test is determined to be ~70 m$^2$g$^{-1}$, which is quite similar to that of the as-prepared AT2 nanohybrid. This result clearly demonstrates the maintenance of the porous structure of the $\text{Ag}_2\text{CO}_3$/Ag–$\text{Ti}_5\text{NbO}_{14}$ nanohybrid.
Fig. S4. Ag 3d XPS spectra of the AT2 nanohybrid (a) before and (b) after the photocatalyst test under the illumination of visible light ($\lambda > 420$ nm).

As plotted in Fig. S4, the photocatalyst test induces only a weak variation in Ag 3d XPS spectra of the AT2 nanohybrid. This result clearly demonstrates the maintenance of the chemical nature of silver species ($\text{Ag}_2\text{CO}_3$ and Ag metal) in the $\text{Ag}_2\text{CO}_3$/Ag–$\text{Ti}_5\text{NbO}_{14}$ nanohybrid. The deconvolution analysis for the present XPS spectra demonstrates that the ratio of $\text{Ag}^0$/Ag$^+$ shows only a slight increase from 0.50 to 0.52 upon the photocatalyst test, underscoring the weak influence of photoreaction on the chemical bonding nature of silver species.