Experimental

Materials

All the reagents (analytical-grade purity) were purchased from Shanghai Chemical Reagents Co. and used without any further purification.

Synthesis procedures

In a typical procedure, 5 ml of the aqueous solution that contained dissolved AgNO₃ (0.10 mmol) and In(NO₃)ₓ₄·4.5H₂O (0.10 mmol) was mixed with 5 mL of the aqueous solution that contained dissolved Na₂WO₄·2H₂O (0.20 mmol). The suspension containing white precipitates was stirred for another 40 min. Then, 6 mL of the suspension was transferred into the 10 mL microwave glass vessel. The suspension was heated to 180 °C by microwave irradiation under magnetic stirring and was maintained for 20 min. Then the resulting precipitates were filtered off and washed with deionized water and finally air-dried to room temperature.

Characterization

X-ray powder diffraction (XRD) analyses were carried out on a Philips X’Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54056 Å) and the operation voltage and current were maintained at 40 kV and 40 mA, respectively. Transmission electron microscope (TEM) imaging was performed on a Hitachi (Tokyo, Japan) H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 kV, and high-resolution transmission electron microscope (HRTEM) imaging was operated on a JEOL JEM-2010 at an acceleration voltage of 200 kV. The energy dispersive X-ray (EDX) spectroscopy analysis was performed also on a JEOL JEM-2010 HRTEM with an Oxford windowless Si(Li) detector equipped with a 4-pulse processor. Field emission scanning electron microscopy (FESEM) was applied to investigate the size and morphology, which were carried out with a field emission scanning electron microanalyzer (JEOL-6700F). The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a VGESCALAB MKⅡ X-ray photoelectron spectrometer using a nonmonochromatized Ma-Kα X-ray as the excitation source. The microwave system was a CEM Discover Microwave Synthesizer (CEM Corporation, USA).

The photocatalytic activities of the AgIn(WO₄)₂ nanostructures were evaluated by the degradation of organic dyes aqueous solution (10⁻⁵ M) in a cylindrical Pyrex flask. The degradation was carried out under UV-vis light from a 300 W Xe lamp (modeling sunlight). About
80 mg of the AgIn(WO₄)₂ nanomaterials were put into 100 mL of the dye solution as the photocatalyst. After being stirred in the dark for 15 min, the whole reaction system was exposed to the UV-vis light from a 300 W Xe lamp under stirring. UV-vis absorption spectra were recorded at different intervals to monitor the reaction.

**Table S1.** XRF data of the samples prepared by microwave-assisted reaction of a solution comprising AgNO₃ (0.06 mmol), In(NO₃)₃·4.5H₂O (0.06 mmol), Na₂WO₄·2H₂O (0.12 mmol), and deionized water(6 mL) at 180°C for different time: 5 min, 10 min, 15 min, and 20 min.

<table>
<thead>
<tr>
<th>Reaction Time (min)</th>
<th>Ag (atom %)</th>
<th>In (atom %)</th>
<th>W (atom %)</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>31.43</td>
<td>29.50</td>
<td>39.07</td>
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<tr>
<td>10</td>
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<tr>
<td>15</td>
<td>32.25</td>
<td>27.03</td>
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<tr>
<td>20</td>
<td>30.84</td>
<td>27.49</td>
<td>41.67</td>
</tr>
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</table>

**Fig. S1** (a) TEM image taken from the attached part on the outgrowth. (b) The magnified TEM image of the attached part on the outgrowth (area marked by the square in (a)), in which the amorphous parts A had been signed with white curve. (c) and (d) HRTEM image taken from the attached part on the outgrowth (the area marked by the circle in (b)).
Fig. S2 EDX spectrum of the clean outgrowth without attached part on the AgIn(WO₄)₂ mesocrystals.

Fig. S3 EDX spectrum of the attached part on the outgrowth of the AgIn(WO₄)₂ mesocrystals.

Fig. S4 XPS spectrum of the AgIn(WO₄)₂ mesocrystals.
**Fig. S5** XRD pattern of the calcined AgIn(WO₄)₂ mesocrystals at 800 °C for 2h.

**Fig. S6** XRD patterns of the samples which are synthesized in the microwave-assisted reaction of a solution at 180 °C for different reaction time: (a) 0.5 min, (b) 2 min, (c) 5 min, (d) 10 min, and (e) 20 min, respectively.

**Fig. S7** XRD patterns of the samples synthesized by microwave-assisted approach for 20 min at 180 °C at different pH values: (a) pH 1.03, pH 2.01, pH 3.01, and pH 4.03, respectively. (b) pH 8.05, pH 10.10, and pH 11.95 respectively. +: denoted WO₃ (JCPDS Card No. 20-1324); *: In₀.₃₃WO₃ (JCPDS Card No. 51-0958); △: AgIn(WO₄)₂ (JCPDS Card No. 77-2098); O: Ag₂WO₄ (JCPDS Card No. 34-0061); ☆: AgInO₂ (JCPDS Card No. 84-1461); ■: In₂O₃ (JCPDS Card No. 73-1809).
Fig. S8 TEM images of the samples synthesized by microwave assisted approach for 20 min at 180 °C at different pH values, (a) and (b) pH 1.01, (c) pH 3.01, (d) and (e) pH 4.03, (f) pH 8.05, (g) pH 10.10, and (h) pH 11.95, respectively.