Supporting Information

Photoactive WS_2 nanosheets bearing plasmonic nanoparticles for visible light-driven reduction of nitrophenol

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The content of supporting information:

1. Materials

All reagents and solvents were obtained commercially and used without further purification. Tungsten (IV) sulfide (WS_2), silver nitrate ($AgNO_3$), polyvinylpyrrolidone (PVP), octylamine (OA), 4-nitrophenol (4-NP), and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethylene glycol (EG), ethanol (EtOH) and *N*-methyl-2-pyrrolidone (NMP) were purchased from Dae-Jung Chemicals (Busan, Korea).

2. Instruments

The UV-vis absorption spectra of WS_2, AgNPs and AgNP@WS_2 hybrids were measured using a UV-vis spectrometer (Mega-2100, Scinco, Korea). The photoluminescence spectrum was obtained by a spectrofluorometer (Nano Log®, Horiba Scientific, Japan). The images of WS_2, AgNPs and AgNP@WS_2 were acquired by field emission transmission electron microscope (FE-TEM 200kV with EDS, JEM-2100F, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) spectra were obtained using X-ray photoelectron spectrometer (AXIS Nova, Kratos Analytical, UK) with a monochromatic Al-Kα X-ray source.

3. Experimental method

A. Preparation of WS_2 nanosheets

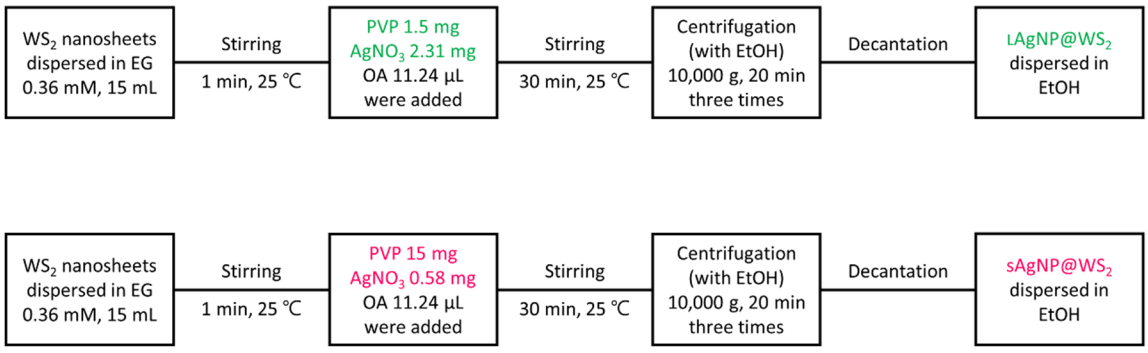
A modified liquid exfoliation method was used for the preparation of WS_2 nanosheets. A 120 mg portion of bulk WS_2 powder was added to 120 mL of NMP. Then, the mixture was sonicated in an ice bath for 90 min using an ultrasonic probe sonicator (100 W power). The

resulting dispersion was finally centrifuged at 300 g for 1 h to collect exfoliated WS_2 nanosheets. The NMP solvent was then exchanged to EG for the synthesis of AgNP@WS_2 nanohybrids by a centrifugation (20,000 g, 30 min) and redispersion method.

B. Synthesis of AgNP@WS_2 nanohybrids

In order to introduce a large size of AgNPs on the surface of WS_2 nanosheets (LAgNP@WS_2), 15 mL of WS_2/EG solution (0.36 mM) was added to a 50 mL round-bottom flask with stirring. After 1 min, 1.5 mg of PVP and 2.31 mg of $AgNO_3$ were added to the as-prepared WS_2/EG solution (0.36 mM, 15 mL) with stirring, followed by the addition of 11.24 μL of OA (d: 0.782 g/mL). The reaction mixture was then sufficiently stirred for 30 min at 25 °C. The final product was washed with EtOH by centrifugation (10,000 g, 20 min, three times), and it was stored in EtOH for further use.

For the preparation of sAgNP@WS_2 nanohybrids, 15 mg of PVP and 0.58 mg of $AgNO_3$ were added to the WS_2/EG solution (0.36 mM, 15 mL), and the rest of the procedures was same with that for LAgNP@WS_2. The flowchart depicting the procedures for the preparation of both AgNP@WS_2 nanohybrids is shown below.



C. Synthesis of AgNP colloid

In order to synthesize a AgNP colloid, 1.5 mg of PVP and 2.31 mg of $AgNO_3$ were added to the 15 mL of EG, followed by the addition of 11.24 μL of OA (d: 0.782 g/mL). The reaction mixture was then sufficiently stirred for 30 min at 25 ^oC. The final product was washed with EtOH three times by centrifugation (15,000 g, 20 min).

D. Photocatalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP)

A 1.82 μg of LAgNP@WS_2 (5 mol% silver) and 34.8 μg of 4-NP were added to 2.5 mL of deionized water (H_2O). In case of sAgNP@WS_2, a 2.78 μg of catalyst (5 mol% silver) and 34.8 μg of 4-NP were added to 2.5 mL of deionized H_2O. A 0.5 mL portion of $NaBH_4$ aqueous solution (16.7 mM) was added to the reaction solution, and the reaction mixture was irradiated by a 300 W Xe lamp with 400 or 600 nm long-pass filter. Then, the reaction progress was monitored at every 10 min using a UV-vis spectrometer. In order to investigate the effect of light power density and wavelength on the catalytic activity in the reduction reaction of 4-NP, a 2.5 mol% of LAgNP@WS_2 catalyst was used under the same conditions.

In order to evaluate the catalytic activity of an AgNP colloid, a 1.34 μg of as-synthesized AgNPs (5 mol% silver) were employed as a catalyst under the same reaction conditions as mentioned above. A 3.1 μg of WS_2 nanosheets (5 mol% tungsten disulfide) were also used to evaluate their catalytic activity under the same reaction conditions.

4. Supplementary figures

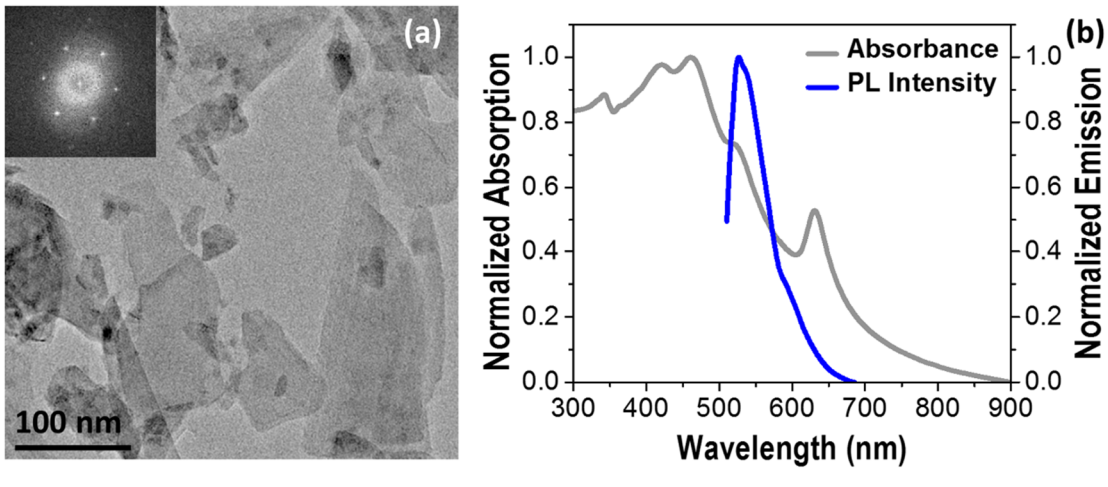


Figure S1. TEM images of (a) exfoliated WS_2 nanosheets (insest: FFT pattern of WS_2 nanosheets), and (b) their absorption and photoluminescence (PL) spectra.

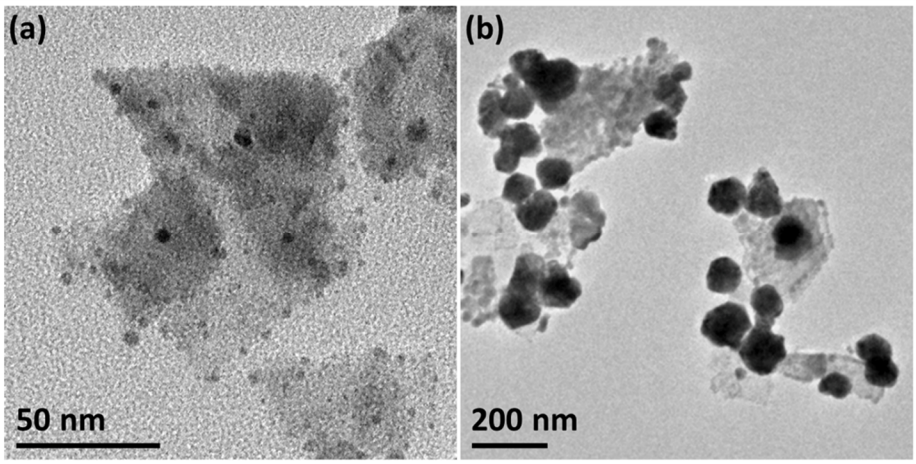


Figure S2. TEM images of (a) sAgNP@WS_2 and (b) LAgNP@WS_2 nanohybrids.

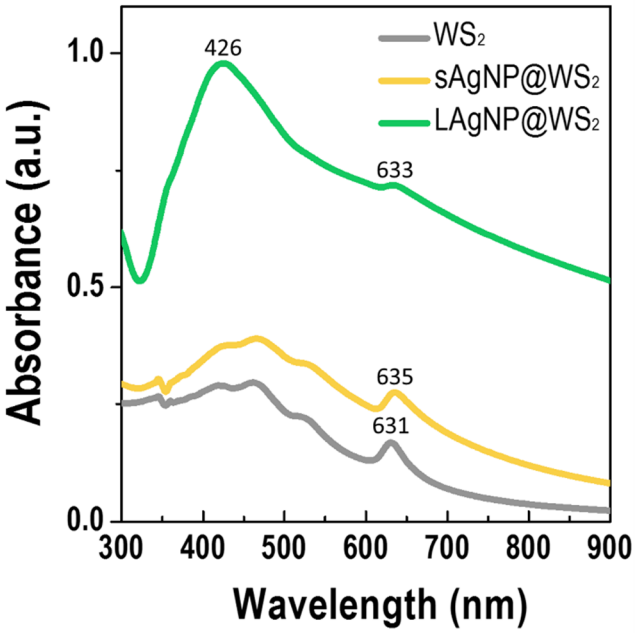


Figure S3. The UV-vis absorption spectra of WS_2 nanosheets, sAgNP@WS_2, and LAgNP@WS_2 nanohybrids.

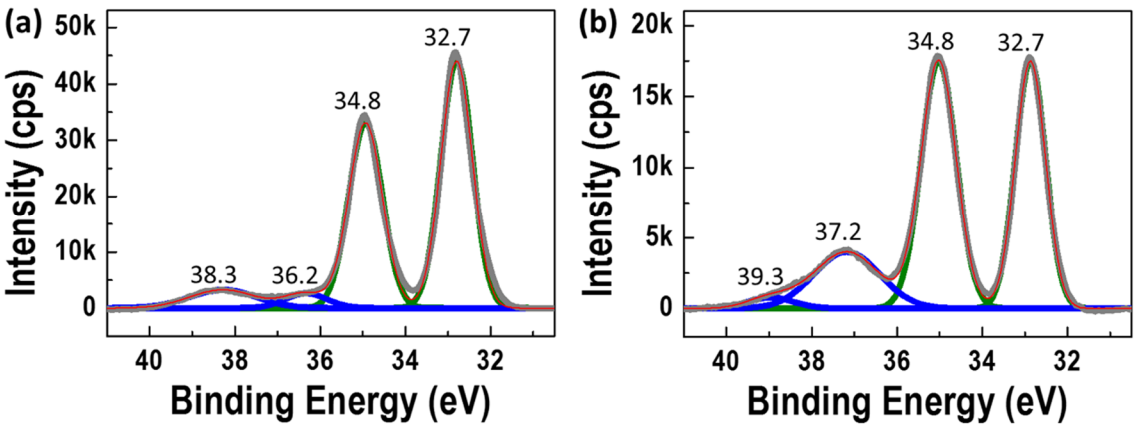


Figure S4. X-ray photoelectron spectroscopy (XPS) spectra of W 4f for (a) sAgNP@WS_2 and (b) LAgNP@WS_2 nanohybrids. The peaks appearing at 32.7 and 34.8 eV are responsible for W $4f_{7/2}$ and $4f_{5/2}$ of 2H-WS_2, respectively.

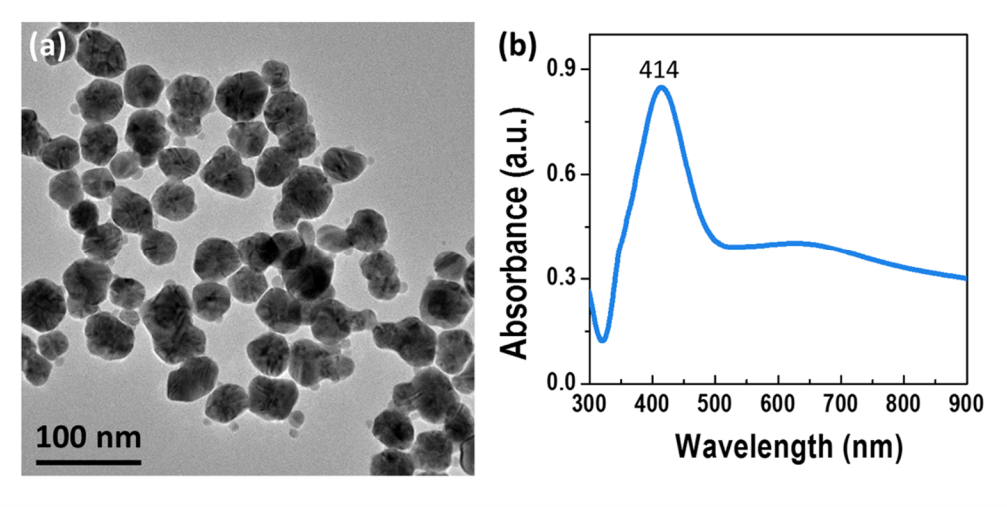


Figure S5. (a) TEM images of synthesized silver nanoparticles (AgNPs), and (b) their plasmonic absorption spectrum.

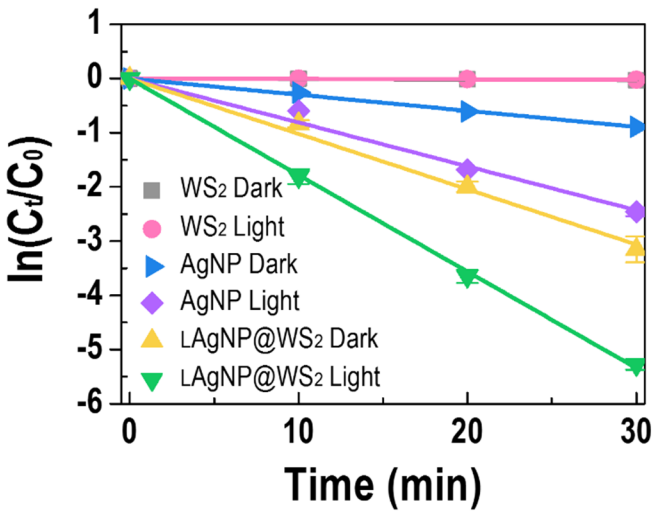


Figure S6. Comparison for the photocatalytic activity of LAgNP@WS_2 nanohybrids against WS_2 nanosheets, and AgNP colloid in the reduction of 4-NP under light irradiation. Conditions: [4-NP] = 8.33×10^{-5} M, [$NaBH_4$] = 1.67×10^{-4} M, 5 mol% catalyst. Visible light was irradiated to the reactor (>400 nm, 30 mW/cm^2).

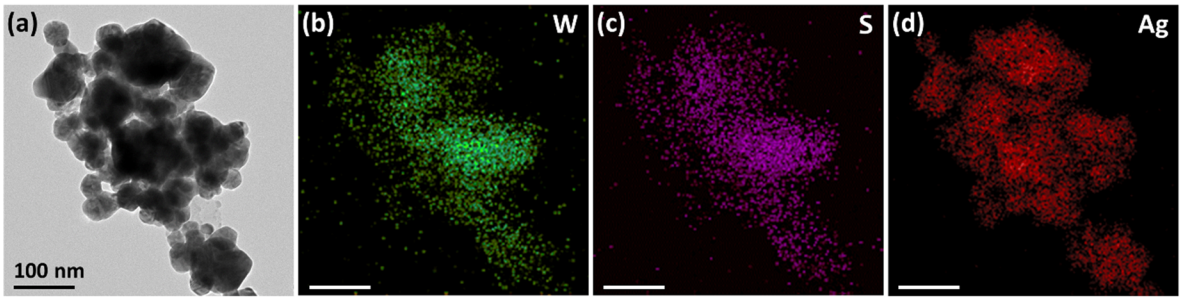


Figure S7. (a) TEM image and (b-d) atomic mapping of XLAgNP@WS_2 nanohybrid.

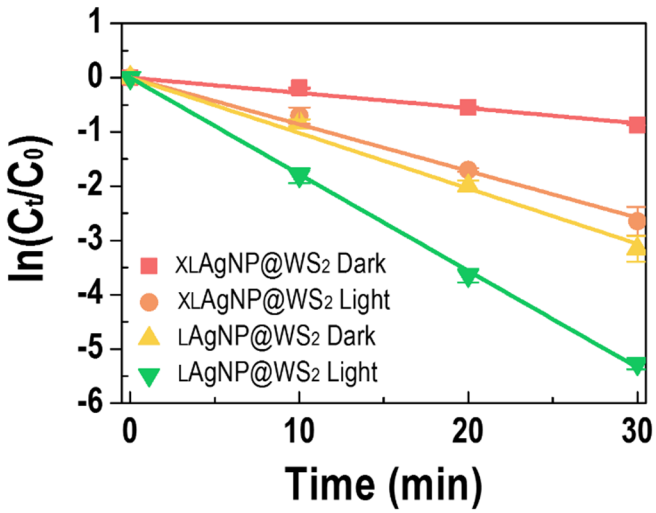


Figure S8. Comparison for the photocatalytic activity of LAgNP@WS_2 nanohybrids against XLAgNP@WS_2 in the reduction of 4-NP under light irradiation. Conditions: [4-NP] = 8.33×10^{-5} M, [$NaBH_4$] = 1.67×10^{-4} M, 5 mol% catalyst. Visible light was irradiated to the reactor (>400 nm, 30 mW/cm^2).

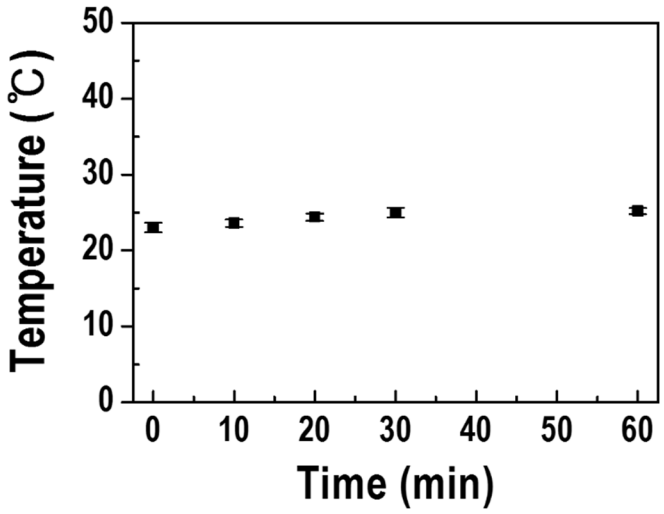


Figure S9. Solution temperature change as a function of reaction time in the reduction of 4-NP using LAg@WS_2 as a catalyst.

Table S1. Comparison of photocatalytic activity among various photocatalysts.

Catalyst	**Amount$_{cat}$ [wt%]**	**$NaBH_4$ [equiv.]**	**k_{app} [min^{-1}]**	**TOF [μmol g^{-1} s^{-1}]**	**Reference**
CdS	1667	-	0.0073	0.053	1
ZnS-Bipy	1667	-	0.031	0.223	2
ZnS-MPA	N/A	N/A (2 mM)	0.096	N/A	3
Au-Cu	149.5	100	0.312	25	4
Ag-TiO_2	4000	1111	1.500	4.5	5
LAgNP@WS_2	5.23	200	0.178	408	**this work**

All reactions were conducted at room temperature. N/A: not applicable. "-": nonuse.

5. References

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