

Support Information

Double-Diffusion-Based Synthesis of BiVO₄ Mesoporous Single Crystals with Enhanced Photocatalytic Activity for Oxygen Evolution

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■ Synthetic Procedures

(1) Preparation of silica template

Silica spheres with diameter of 50 nm were synthesized by the Stöber method. The detailed procedure is as follows: 167.2 mL of absolute ethanol, 28.8 mL of water, and 4.0 mL of ammonia water (28 wt.%) were mixed in a breaker to obtain Solution A. Similarly, Solution B was obtained by mixing 18.0 mL of tetraethoxysilane (TEOS) and 182.0 mL of absolute ethanol. Under magnetic stirring, Solution B was added to Solution A and reacted at room temperature for 24 h to obtain silica colloids. Finally, the close-packed silica template was synthesized by centrifugation at 12000 rpm for 1 h and sintering at 500 °C for 30 min.

(2) Synthesis of acidified BiVO₄ precursor solution immersed SiO₂ template.

Firstly, 0.97 g of Bi(NO₃)₃•5H₂O (2 mmol) and 0.234 g of NH₄VO₃ (2 mmol) were dissolved in 7.5 mL of nitric acid solution (2 M) to obtain a bright yellow solution. Then, the as-prepared silica template was immersed into the above solution and the system was vacuumed by a pump to extract the gas in silica template and make precursor solution enter into the intervals of silica template. After immersing for 2 h, the silica template containing BiVO₄ precursor solution was taken out for next synthetic process.

(3) Synthesis of BiVO₄ MSCs.

In a typical synthetic procedure, 17.46g (36 mmol) of Bi(NO₃)₃•5H₂O and 4.212 g (36 mmol) of NH₄VO₃ were dissolved in 300 mL of nitric acid solution (2 M). The pH value of the above solution was

adjusted to 2.0 with ammonia water (28 wt.%). In this process, the clarified yellow solution was turned to orange suspension. After aged for 2 h, the obtained precipitate was collected and transferred into an 80 mL autoclave containing 2.0 g BiVO₄ precursor solution immersed silica template, followed by hydrothermal treatment at 240 °C for 24 h. The obtained product was washed by ultrapure water and further selectively etched with NaOH solution (0.5 M) at 80 °C for 3 h to remove SiO₂ template. Finally, the BiVO₄ MSCs were obtained by centrifugation and washed several times with ultrapure water and dried at 70 °C for 24 h.

(4) Synthesis of BiVO₄ bulk single crystals (BSCs).

BiVO₄ bulk single crystals (BSCs) was fabricated by a modified hydrothermal method, according to the previous literature.¹

(1) Li, R. G.; Han, H. X.; Zhang, F. X.; Wang D. E.; Li, C. *Energy Environ. Sci.* **2014**, 7, 1369.

(5) Synthesis of BiVO₄ nanoparticles (NPs)

Firstly, 17.46 g (36 mmol) of Bi(NO₃)₃•5H₂O and 4.212 g (36 mmol) of NH₄VO₃ were dissolved in 300 mL of nitric acid solution (2 M). The pH value of the above solution was adjusted to 2.0 with ammonia water (28 wt.%). In this process, the clarified yellow solution was turned to orange suspension. After aged for 2 h, the precipitate was collected by centrifugation. Then, the production was washed with ultrapure water for 3 times and dried at 70 °C for 24 h.

■ Characterization

The morphologies of the synthesized BiVO₄ samples were characterized by field emission scanning electron microscope (EFSEM, NOVA Nano SEM450) and transmission electron microscope (TEM, JEM2100). X-ray diffraction measurements were carried on a X-ray diffractometer (Rigaku D/max 2550 VB/PC, Cu Ka radiation, $\lambda = 1.5406 \text{ \AA}$). The surface electric status was studied on a Perkin-Elmer PHI 5000 X-ray photoelectron spectroscope. The N₂ adsorption-desorption isotherm was measured at 77 K using a Micromeritics ASAP2020 instrument. The chemical states were identified by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000). UV-vis diffuse reflectance spectra (DRS) were measured with a SHIMADZU UV-2450 spectroscopy equipped with an integrating sphere assembly, using BaSO₄ as the reference material. Raman spectra were taken by a Via Reflex Raman spectrometer. Photoluminescence emission spectra were measured with a SHIMADZU RF5301PC by using 380 nm line of Xe lamp as excitation source at room temperature.

The electrochemical analysis was carried on a Zahner electrochemical work station by a standard three-electrode system consisting of a working electrode (FTO glass with 0.2 mg as-prepared samples with an active area of 1.5 cm²), a Pt wire as the counter electrode, and a saturated calomel electrode as the reference electrode. Transient photocurrent responses of different samples were carried out in 0.5 M Na₂SO₄ aqueous solution under 300 W Xe lamp with 420 nm cut-off filter. The electrochemical impedance spectroscopy was measured in 2.0 mM K₃[Fe(CN)₆], 2.0 mM K₄[Fe(CN)₆] and 0.5 M KCl mixed aqueous

solution.

■ Photocatalytic O₂ Evolution Measurement

The photocatalytic O₂ evolution reactions were carried out in a closed gas circulation system. Typically, 0.1 g photocatalyst was dispersed in 80 mL NaIO₃ aqueous solution (0.02 M) in a Pyrex reactor. The reactor was thoroughly degassed to drive off the air inside and irradiated by a 300 W Xe Lamp (Au-Light) with optical cutoff filter (420 nm). The amount of evolved O₂ was determined by an online gas chromatograph (INESA GC122, TCD, Ar carrier).

■ Figures

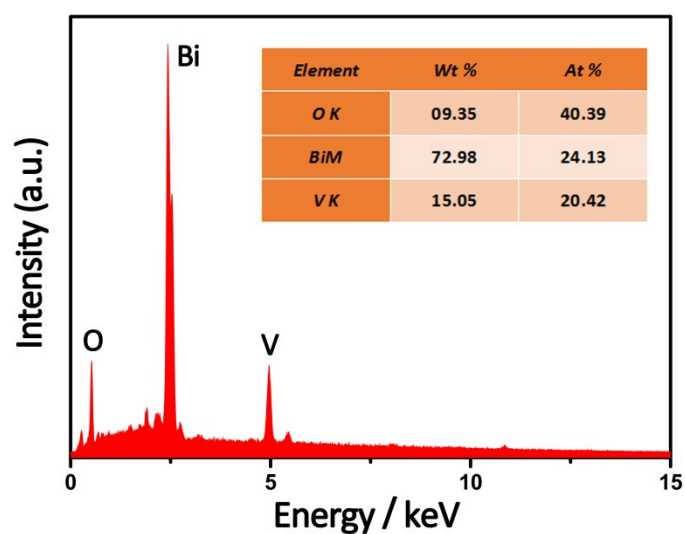


Fig. S1. Energy dispersive spectra (EDS) of BiVO₄ MSCs.

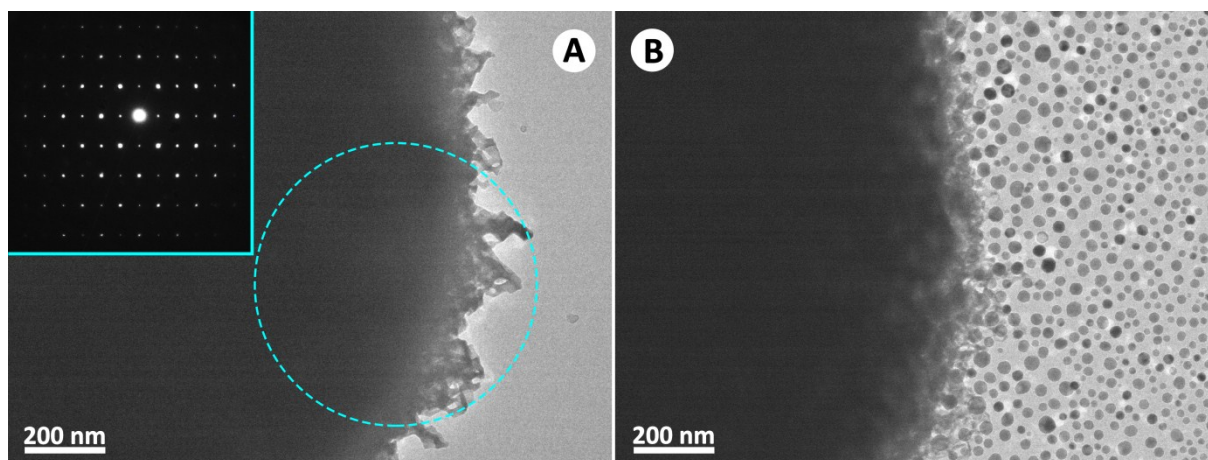


Fig. S2. TEM images of as-prepared BiVO_4 MSCs (A) at lower current density; (B) at higher current density. The insert of Fig. S2A is the SAED pattern with an enlarged selected area (the diameter of the circle is 500 nm).

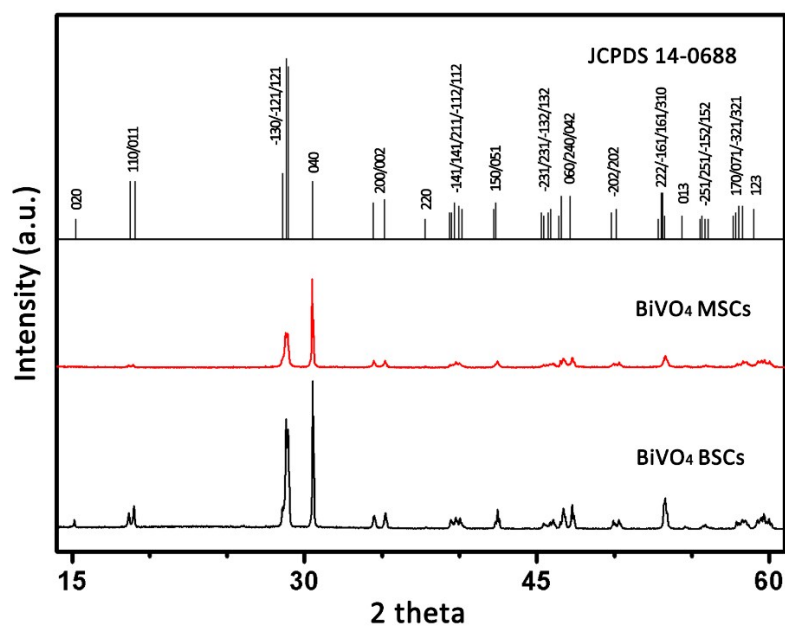


Fig. S3. XRD patterns of BiVO_4 MSCs (red line) and BiVO_4 BSCs (black line).

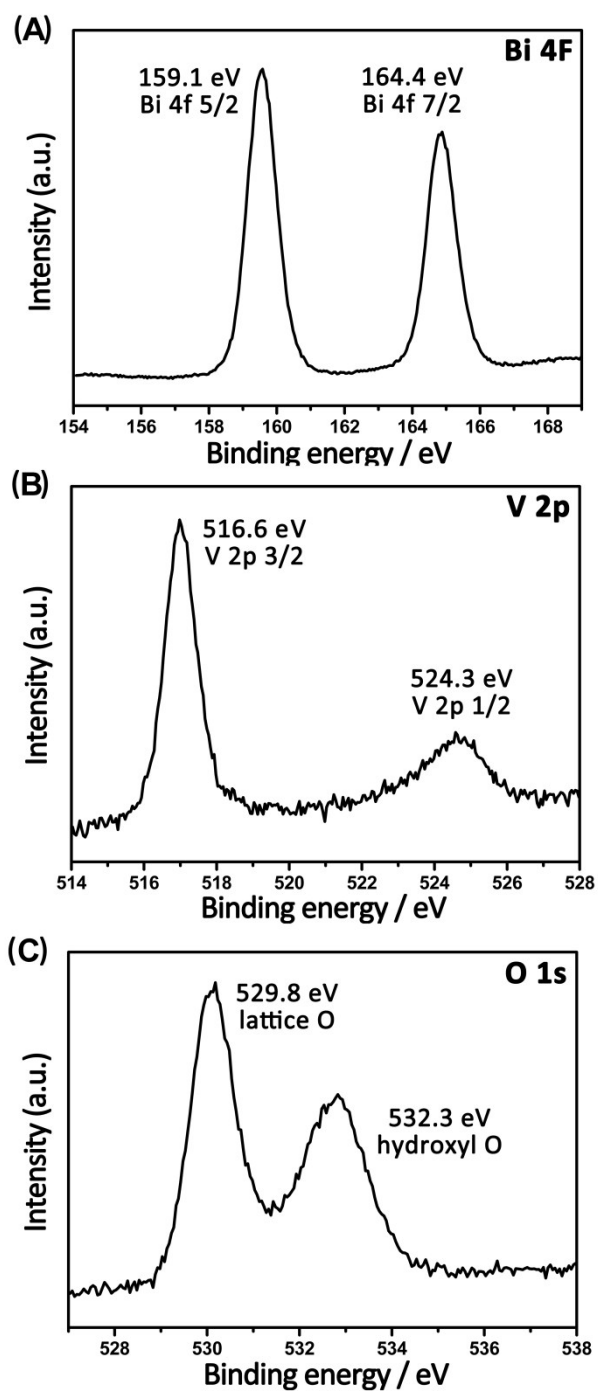


Fig. S4. XPS spectra of BiVO₄ MSCs: (A) Bi 4f; (B) V 2p; (C) O 1s.

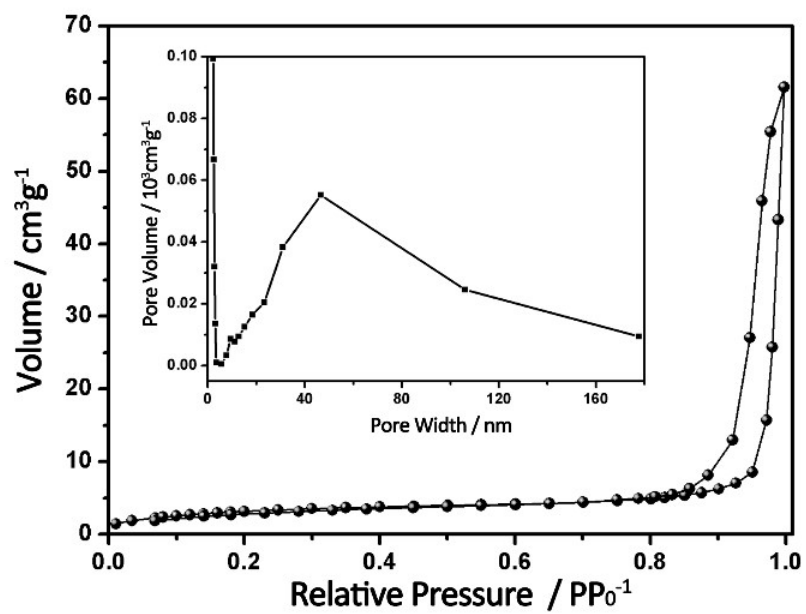


Fig. S5. Nitrogen adsorption–desorption isotherm and the corresponding pore size distributions (inset) of BiVO₄ MSCs.

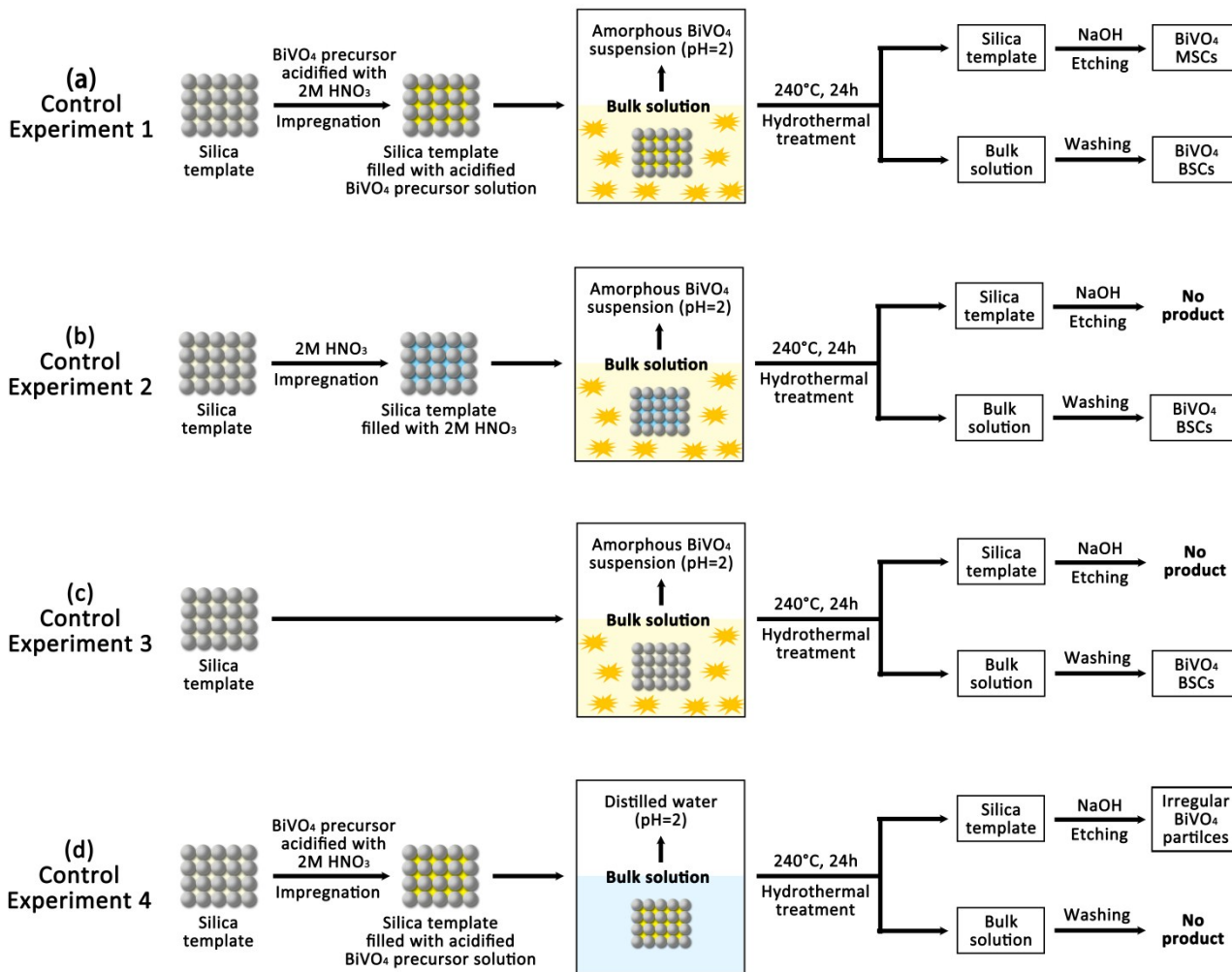


Fig. S6. Control experiments carried out under different conditions to explore the formation mechanism of BiVO_4 MSCs.



Fig. S7. Photos of silica templates obtained in different control experiments (after hydrothermal treatment): (a) Control experiment 1, (b) Control experiment 2, (c) Control experiment 3, and (d) Control experiment 4. FE-SEM images of the products obtained in different control experiments: (a') Control experiment 1 and (d') Control experiment 4.

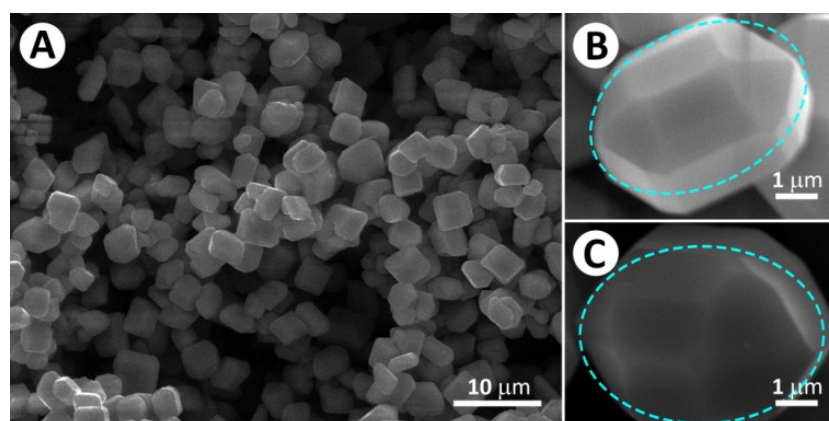


Fig. S8. SEM images of the BiVO_4 single crystals prepared in the absence of silica template

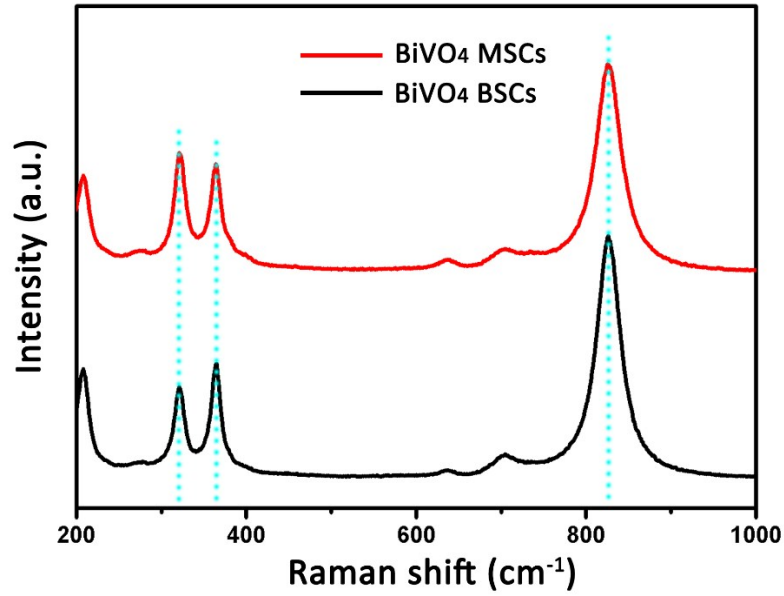


Fig. S9. Raman spectra of BiVO₄ MSCs (red line) and BiVO₄ BSCs (black line).

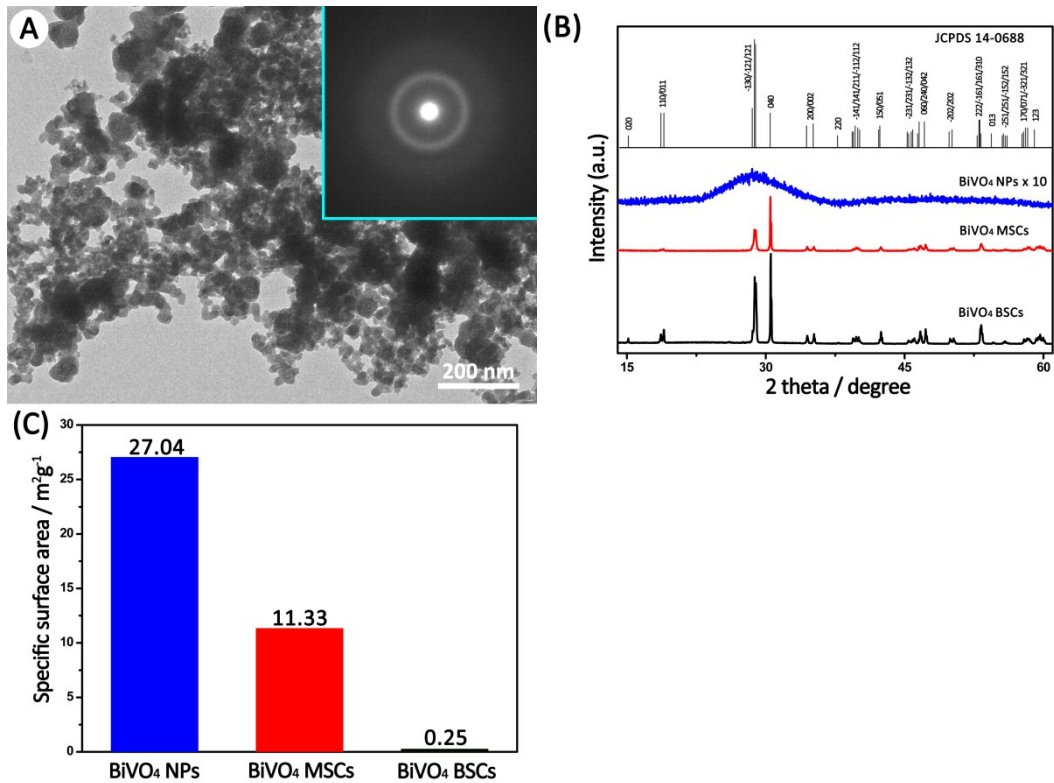


Fig. S10. (A) TEM image of as prepared BiVO₄ nanoparticles (NPs) and insert is the corresponding SAED pattern. (B) XRD patterns of as prepared BiVO₄ MSCs, BSCs and NPs. (C) Specific surface areas (S_{BET}) of BiVO₄ MSCs, BSCs and NPs.