

Synthesis and Phase Transfer of Well-Defined BiVO₄ Nanocrystals for Photocatalytic Water Splitting

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Supporting information

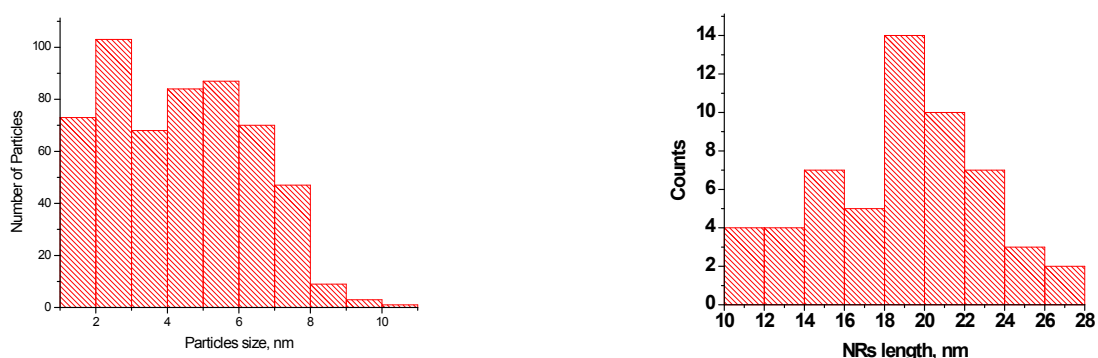


Figure S1. (a) Size distribution of the BiVO₄ NPs, with an average diameter of 4.4nm (b) Size distribution of the BiVO₄ NRs, with an average diameter of 18.64nm. It should be noted that to determine the NR distribution, any NPs that existed were first excluded from the analysis.

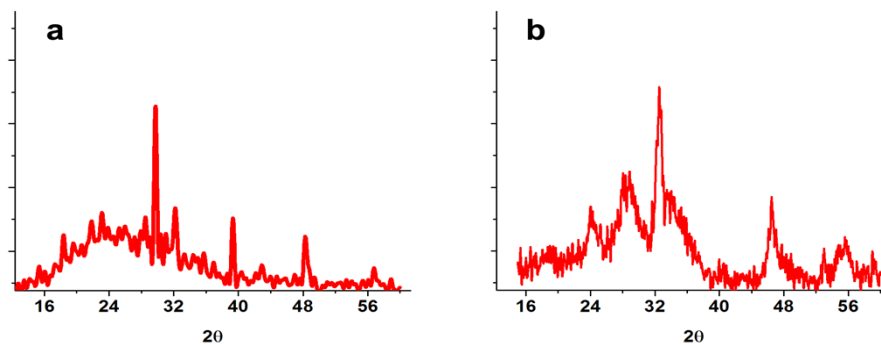


Figure S2. XRD analysis of the as-synthesized BiVO₄ nanoparticles (NPs) (left) and nanorods (NRs) (right). The data was collected using a Scintag XDS 2000 X-ray diffractometer. The measurements were performed using Cu K α radiation at 45 kV and 40mA, 1° per min. NPs (left), NRs (right).

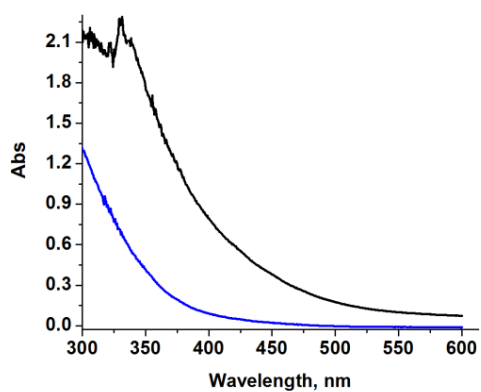


Figure S3. UV/Vis absorbance of the as prepared nano-sized BiVO₄: NRs (black), NPs (blue).

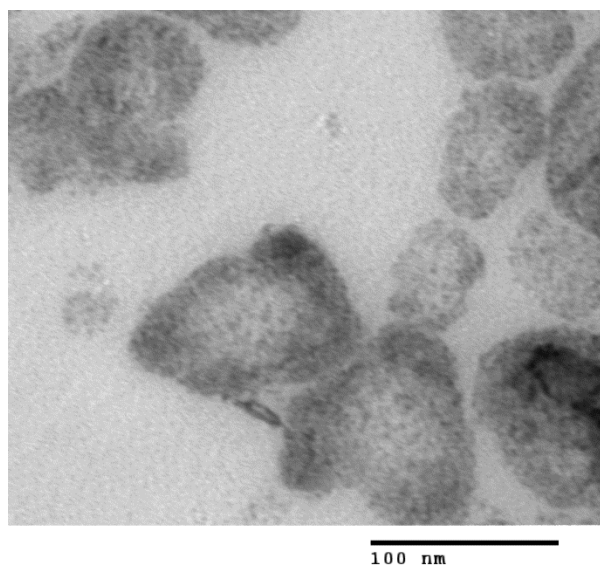


Figure S4. TEM of the aggregated DMSA conjugated BiVO₄ NPs after several days in water.

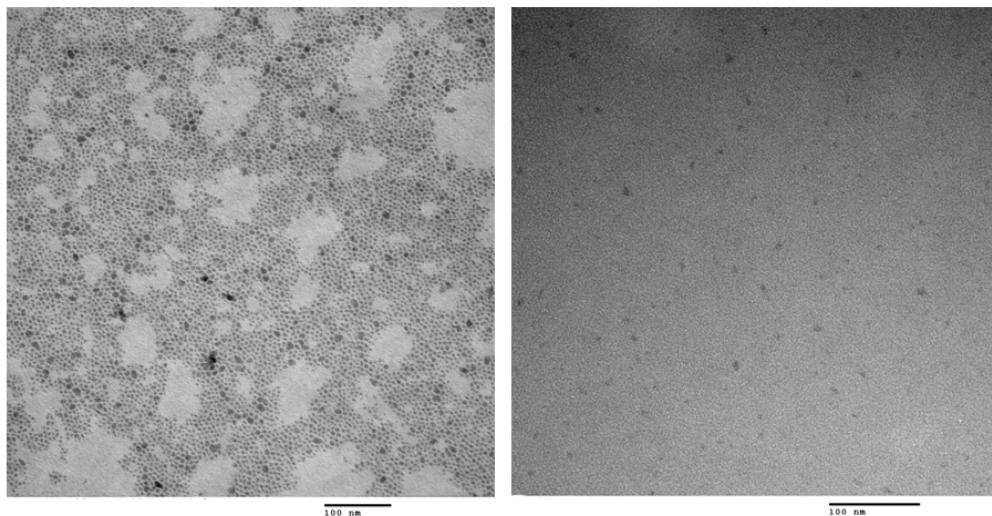


Figure S5. TEM images of the oleic acid conjugated BiVO_4 NPs before (left) and after (right) ligand exchange with DMSA-EMCA.

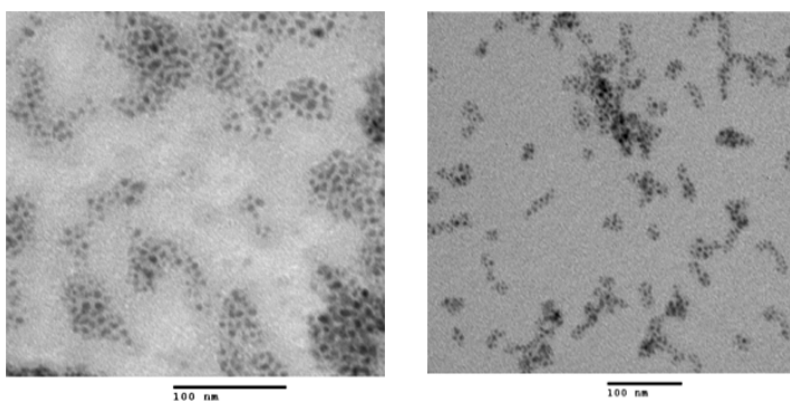


Figure S6. TEM images of DMSA-EMCA conjugated BiVO_4 NPs (left) and TA-bound BiVO_4 NPs (right). The samples were kept dry for several weeks and re-dissolved in water before the TEM imaging.

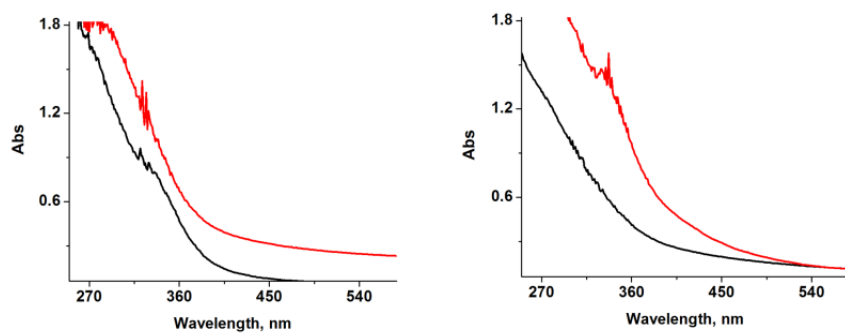


Figure S7. UV/Vis absorption spectra of the DMSA-EMSA (red) or tartaric acid (black) modified nano-BiVO₄ (a) NPs (b) NRs.

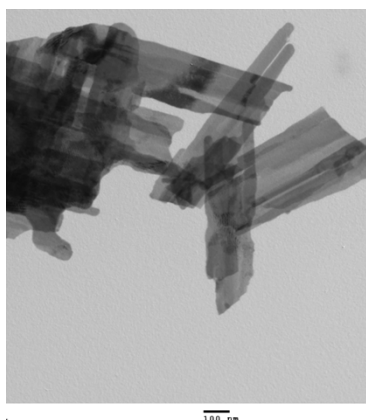


Figure S8. Representative TEM image of the micron-sized BiVO₄ structures obtained using previously reported methods.¹

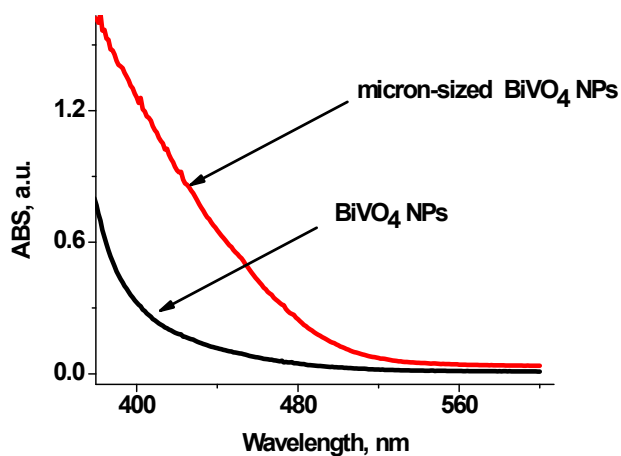


Figure S9. UV/Vis spectrum comparing the absorbances of the micron sized BiVO₄ with that for the NPs.

Experimental:

Chemicals: Bismuth(III) nitrate penta-hydrate, meso-2,3-Dimercaptosuccinic acid (DMSA) and Tartaric acid were purchased from Sigma. Sodium oleate was purchased from TCI, Ammonium

metavanadate was purchased from Stern Chemicals, and N- ϵ -maleimidocaproic acid, (EMCA) from Pierce. The chemicals were used as supplied without further purification.

NPs or NRs synthesis: 1g of $\text{Bi}(\text{NO}_3)_3$ was dissolved in 100ml of DI water and stirred in a 250ml reaction vessel for 10min at room temperature, followed by 5min of ultra-sonication. The temperature was next raised to 60°C at which point 1.825g of sodium oleate was added through stirring. The temperature was then raised to 80°C followed by the dropwise addition of 250mg of NH_4VO_3 dissolved in 50ml of water. The reaction vessel was then sealed and the solution was continuously stirred during which the solution changed slowly from a milky white color to a yellow slurry. At different time points (3-20hrs) the reactions were quenched by removing the flasks from heat and the products were collected by precipitation in water and centrifugation. The solids were then dissolved in toluene to obtain clear yellow-orange solutions. To improve the cleaning step we added into the toluene solution similar amount of water to form two phase solution. This solution was further centrifuged, to form a clear yellow-brownish toluene solution.

Ligand exchange: For the ligand exchange of the nano-sized BiVO_4 we used DMSA, or tartaric acid. The ratio we used was 3.5mg/ml for the tartaric acid ligand exchange, or 4mg of DMSA and 9mg of EMCA. After 20min of stirring equal amount of water added, followed by shaking. Usually after 5 hours most of the BiVO_4 moved into the water phase leaving a clear (upper) solution. The water phase was further cleaned by 30k filters to remove any excess of ligands. Next the nano-sized BiVO_4 was collected, dried, and re-dissolved in water before used.

Photocatalytic activity: the photoelectrocatalytic activity was performed in a sealed quartz cuvette-cell (Strana cells). The cuvette was filled with 100ul of the catalyst (1mg/ml), 500ul of water and 5ul of DCPIP (1mg/ml). Before each run the UV/Vis was blanked with the

water/catalyst solution, then the dye was added, the pH was adjusted to 5 and the cuvette was sealed. Next the cuvette was purged with N₂ for 20min, and between each UV/Vis measurements the cuvette was irradiated by a sun simulator. The oxygen measurements was performed in a similar way with some exceptions: (i) The amount of the catalyst was raised to 1mg (ii) K₂S₂O₈ was added (11mg) as electron acceptor. The cuvette was sealed and purged with Ar, so, remained N₂ could be used as an internal reference to verified that no leaks occurs. The amount of oxygen was monitored by a GC equipped with 5A° column and a TCD detector.

References

- (1) Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C. Nat. Commun. 2013, 4, 1432.