Supporting Information

for the

Effective Near-Infrared-Absorbent: Ammonium Tungsten Bronze Nanocubes

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Figure S1 Batch reaction system (Akico Co. Ltd., Japan) and reactors.

Fig.S1 shows the batch reaction system used in this study together with the reactors. The reactor possesses an inner diameter of 12 mm, and can resist the pressure of 45 MPa. The maximum operation-temperature is 450 °C, and the block heater is usually preheated to the set temperature prior to the setting of reactors to start the reaction.



Figure S2 Full range XPS spectra of (NH₄)_xWO₃ nanocube.



Fig. S3 (a) TG curve recorded at a heating rate of 10 oC/min and (b) MS results for the gas produced during the heating.



Figure S4 TEM images of samples synthesized with addition of (a) 1 ml or (b) 5 ml oleylamine, while keeping other parameters the same to the standard conditions; (c) proposed crystal growth process for the formation of tungsten bronzes in the presence or absence of the capping agent.





(b)



Fig.S5 (a) XRD pattern and (b) TEM image of sample synthesized in pure oleic acid solution



Fig.S6 TEM image of sample synthesized after (a) 0.5 and (b) 2 h reaction



Fig.S7 SEM image of commercial $Cs_{0.33}WO_3$ obtained from Sumitomo Metal Mining Co., Ltd, Japan.



Fig.S8 Absorbance spectra of $(NH_4)_xWO_3$ nanocubes; Inset shows the photograph of blue powder



Fig. S9 The transmittance spectra of $(NH_4)_xWO_3$ film irradiated by varied powder density (3.5 - 35.3 x $10^5 \text{ W} \cdot \text{m}^{-2}$) of 1064 nm light. The $(NH_4)_xWO_3$ film was set on the light path for 10s and then taken out, alternately.



Fig.S9 Zeta potential versus pH for $(NH_4)_xWO_3$ nanocube. Inset shows the suspension of $(NH_4)_xWO_3$ nanocube.

During the process of experiment, it has been found that the $(NH_4)_xWO_3$ nanocubes are easily dispersed into the aqueous solution to form a stable suspension which is able to save for a long time, as shown inset of Fig.S5. To uncover the inherent reason for such a phenomenon, the zeta potential of $(NH_4)_xWO_3$ nanocube was studied. The surface charge of particle switched from -15.7 mV to -1.08 mV with increasing of pH value. This increase in zeta potential with a decrease in pH could be explained by the promoted protonation of sample in a lower pH environment, that is, when pH decreases, the absorption of hydroxonium ion is enhanced, thus a less negative surface charge is acquired. However, in general, the $(NH_4)_xWO_3$ nanocubes are obviously negative charged in nearly neutral solution, leading to strong electrostatic repulsion between particles to prevent sedimentation under aqueous condition.