

Supporting Information for

α -MnO₂ nanowires as building blocks for the construction of 3-D macro-assemblies

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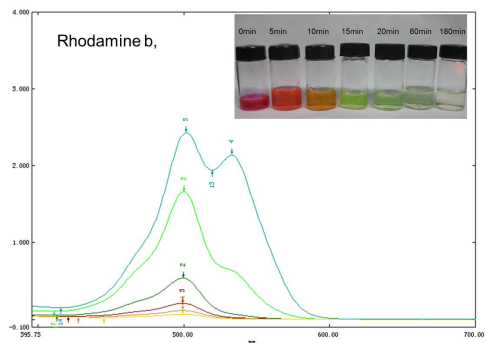
Experimental Section

Chemicals Manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). Deionized water was used throughout the experiment. All the chemicals used were from Beijing Chemical Reagent Company. All were analyticals grade and all were used directly as received without further purification.

Synthesis and assembly of the 3D macrostructure

In a typical hydrothermal synthetic procedure, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.008 mol) and an equal amount of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) were dissolved into distilled water at room temperature. After the solution becomes clear, 0.023mol ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) was added into the solution. After the final solution became transparent again, it was transferred into a 40 mL Teflon-lined autoclave, sealed and reacted at 180°C for 12h. After the reaction was completed, the resulting black sample was carefully transferred to a beaker, filling with deionized water to sop the as-obtained sample for 3h so as to wash away the inorganic salts. After that, a freeze-drying process was applied to keep the 3D structure.

The UV-spectrum of Rhodamine b aqueous solution which was treated by the as-obtained sample (S1).



The adsorption results of heavy metal ions

Table1†

C Metalion	Initial (mg/L)	Final (mg/L)	Ionic radius (nm)
Cr^{3+}	62.61	36.73	0.0615
Fe^{3+}	62.2	17.91	0.0645
Cu^{2+}	65.29	64.09	0.0732
Zn^{2+}	53.69	52.2	0.074
Cd^{3+}	203.5	167.7	0.095
Pb^{2+}	233.2	4.669	0.119
Ba^{2+}	29.37	24.24	0.135
Ag^{+}	139.9	127.2	0.126

The crystallographic structure of the α -MnO₂ (Fig. S2)

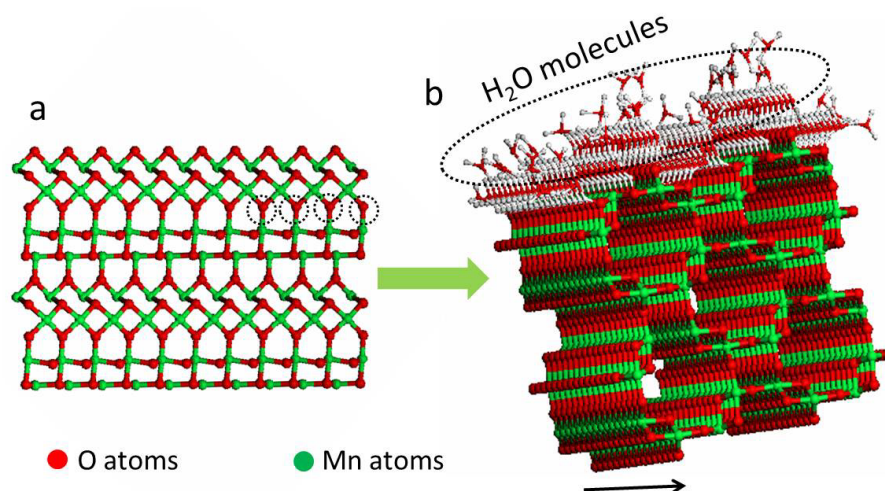


Fig. S2 the crystallographic structure of α -MnO₂. (a) A part of the crystal's intrinsic surface of the α -MnO₂. (b) The surface of the as-obtained α -MnO₂ nanowires covered with H₂O molecules based on H-bond.

As for the formation of hydrogen bond in our sample, we believe there are two determinants which should be greatly taken into consideration. One is the designed synthetic reaction system; the other is due to the surface structure of the MnO₂ nanowires.

As for the former, water, which, as is known to all, can absolutely serve as excellent hydrogen bond donors and accepters, was used as the reaction solvent in our reaction system. It provided a necessary precondition and a good environment for hydrogen bonds.

As for the latter, we deem that the surface structure of the as-prepared MnO₂ nanowires played a great role. From the crystallographic structure of α -MnO₂ (Fig. S2a), we can see that there are innumerable oxygen atoms exposed on the surfaces of the MnO₂ NWs. Naturally, these oxygen atoms serve exactly as the hydrogen bond acceptors (with water molecules in the solvent as the donors), supplying the binding sites for connecting water molecules due to the attractive interaction between the hydrogen bond acceptors and donors. Consequently, the surfaces of the MnO₂ NWs were eventually covered with a dense water layer (Fig. S2b).

It is mainly the collaborative effect of these two factors that made the formation of hydrogen bonds.