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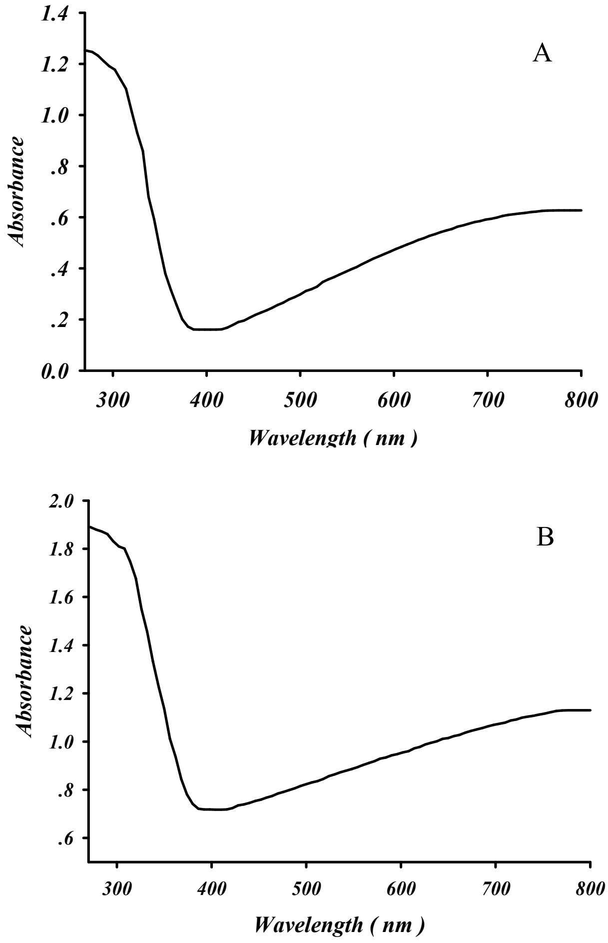

Figure S1 UV-Vis absorption spectra of nanoleaf arrays (A), nanowire/nanoleaf arrays (B) .

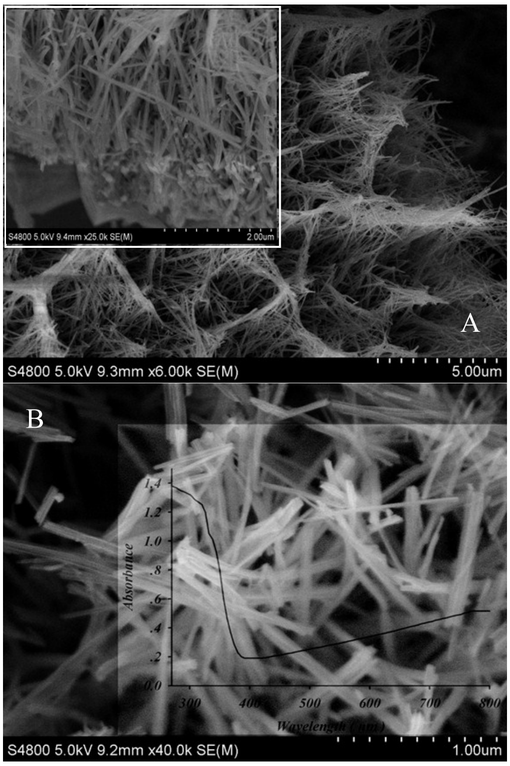

Figure S2 Titanate nanostructures prepared by hydrothermal process under 250 ℃ with 3 h in 4 M NaOH solution. B is the tips shape of A.

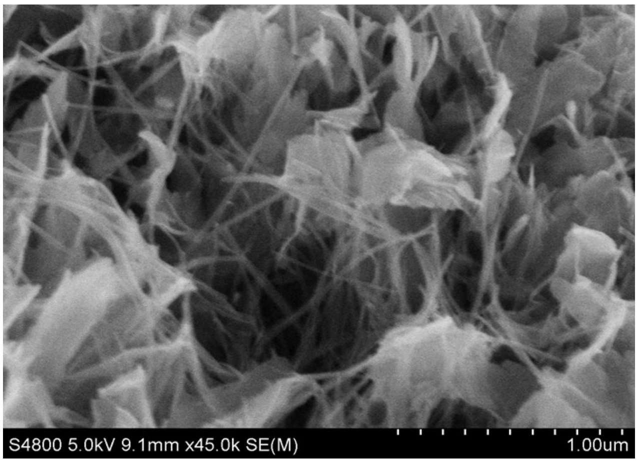

Figure S3 High magnification image of Figure 1F

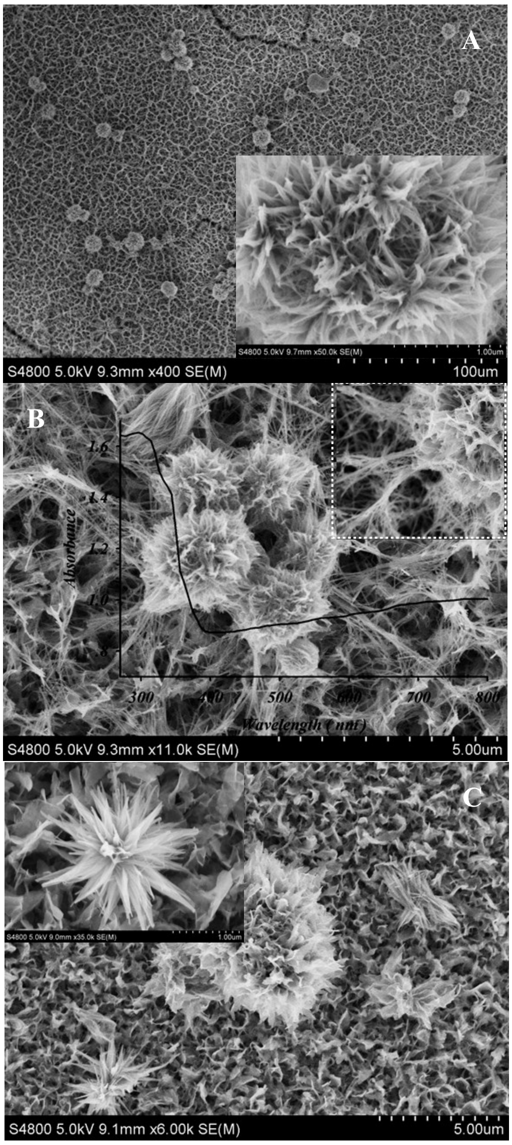

Figure S4 TiO_2 nanostructures were prepared by hydrothermal process under A (250 ℃, 4 M NaOH, 8 h), B (200 ℃, 4 M NaOH, 8 h) and C (150 ℃, 4 M NaOH, 8 h). Insets are corresponding high magnification images and UV-Vis absorption spectra .

Formation mechanism of TiO_2 nanostructures

It is proposed that the nanowire, nanoleaf or hybrid arrays undergo Ostwald ripening induced hierarchical architectures formation. There are many chemical equilibria between the solid-liquid interfaces under each experimental setting for the synthesis of colloidal nanomaterials owing to differences in the nonuniformity of nanomaterials and concentrations of growth nutrients across the bulk solution. The homogenization of these concentration gradients ultimately results in complete dissolution of small nanomaterials as a result of the growth of the large nanoflowers.

In order to investigate our-proposed formation mechanism of the hierarchical TiO_2 architectures, detailed time-dependent experiments were carried out at 250℃. After 1 h hydrothermal growth, there appeared sparse nanowires on the Ti foil, as shown in Figure S5A, the length of nanowires ranged from hundreds of nanometers to several micrometers, which could be ascribed to the fact that not all nanowires are nucleated at the same time due to the inhomogeneity of the initial surface structure and surface roughness of the titanium foil. Especially, the surface roughness could result in different nucleation and growth rates at various locations on the foil and ultimately in the distribution of nanowires length. But, the nanowire diameters are very small (less than 50 nm). Note that the remained reaction solution was still clear after this duration. If the reaction time was prolonged to 3h, both length and diameter increased obviously (Figure S2), but the solution began to turn light cloudy. Meanwhile, one hardly find fragments on the top of nanowire array film. However, lots of fragments appeared both on the top of nanowires array film (Figure S5B, note that the tips of nanowires turn into a network completely) and in the solution (Figure S5C).

Based on above facts, one can speculate that these tiny fragments originated from the continuously cracking and dissolving of the nanowire arrays. And as time prolonged, these broken nanowires supporting by Ti foil will directly act as nucleation centers to initiate nanostructures growth. Because the reaction temperature is far beyond the boiling point of the solvent, which results in continuous agitation of the mixture in all directions, and breaks the dissolution-recrystallization equilibrium and accelerate the undersaturation of dissolution regions on the nanowire arrays surface. Interestingly, the fragments scattered in the solution could hardly initiate the nanoflowers formation (there is little nanoflowers in solution, SEM image is not shown here). In our opinion, this phenomenon just indicates that the tips of the broken nanowires supporting by Ti foil provide the nucleation centers for nanoflowers growth (Inset of Figure S4B).

As we know, the overall rate of formation of titanate nanostructures is controlled by the rates of diffusion and chemical reaction between titania precursor and sodium hydroxide. Under hydrothermal process, the reaction temperature is far beyond the boiling point of the solvent, which results in continuous agitation of the mixture, and breaks the dissolution-recrystallization equilibrium rapidly. Ultimately, reaction rate was greatly increased. As duration prolonged continuously, fragments increased continuously. While, Ti foil still reacted with NaOH to form $Na_2Ti_2O_5$. H_2O nanowires at the same time. This means that supersaturation of the reaction solution (mainly contributed by the dissolved nanowire fragments) increased as time prolonged. Lastly, the constant motion of solution prevents sedimentation and forces the intimate mixing, ensuring the homogeneous hydrothermal reaction to occur in all directions. Thus, it is able to generate the uniform morphology of nanoflowers in large scale on the top of nanowire arrays. Besides, petal shapes and nanoflowers density also depend on reaction temperature, which are closely related to reaction conditions (for example, nucleation and recrystallization rates) and need to be further studied.

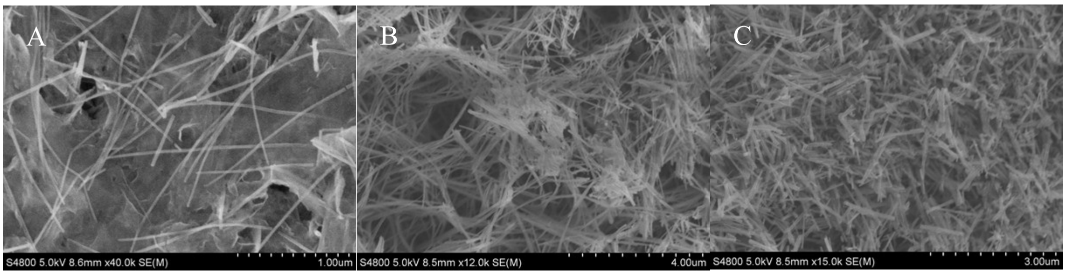

Figure S5 TiO_2 nanostructures were prepared by hydrothermal process under 250 ℃ and 4 M NaOH, A (1 h), B and C (4h). Especially, C was obtained from the reaction solution.

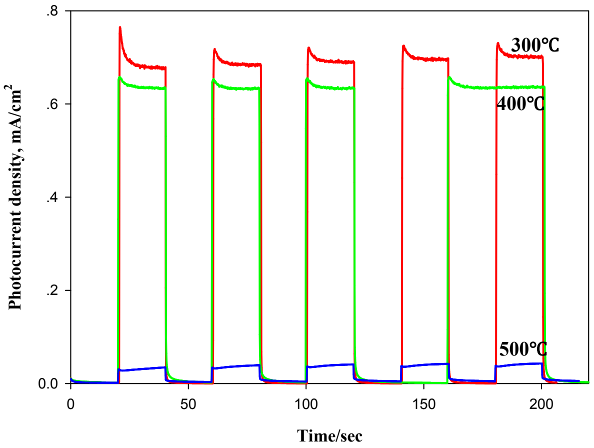

Figure S6 Photocurrent response abilities of nanowire/nanoleaf arrays under at different temperatures with NH_3 for 30min.

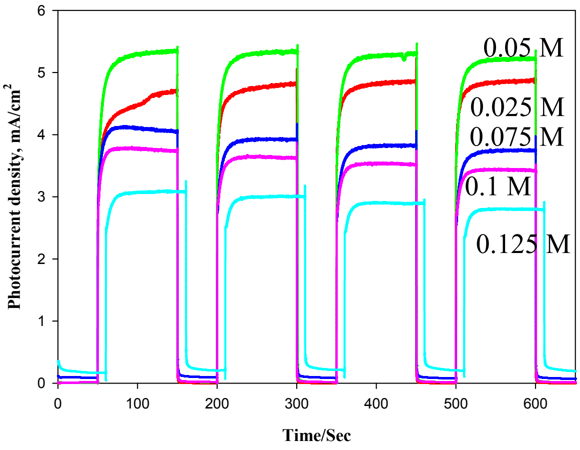

Figure S7 Photocurrent response abilities of CdS-Mn/TiO_2 nanowire/nanoleaf arrays with different Mn^{2+} concentrations.