# Near-infrared active $NaYF_4$: $Yb^{3+}/Tm^{3+}@TiO_2$ photocatalyst with tailored morphology for photocatalytic applications using solar light

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Heterogeneous photocatalysis based on semiconductor materials, especially $TiO_2$ nanoparticles (NPs), is an efficient method for environmental clean-up. However, practical applications of $TiO_2$–based photocatalysts, beside other factors such as recombination of charge carriers ($e^-$–h+ recombination) and tendency of NPs agglomeration, are limited by the requirement of continuous supply of UV light which is only around 6% of the solar spectrum. The development of $TiO_2$–based composite photocatalysts responsive towards visible and near infrared (NIR) radiation is a relevant subject of study. Therefore, we attempted to extend the application of $TiO_2$ to NIR region by coupling $TiO_2$ with up conversion (UC) particles based on rare earth metal-doped $NaYF_4$ ($NaYF_4$: $Yb^{3+}/Tm^{3+}$). The UV light emitted by the UC component upon absorption of NIR radiation can be used to excite $TiO_2$ coated as thin film on the surface UC particles. The doubly doped $NaYF_4$ UC NPs were prepared by a very straightforward microwave-assisted hydrothermal method, as opposed to the convention hydrothermal treatment that usually requires prolong heating. This microwave-assisted method allows a control of morphology as well as crystalline phase of UC particles by simply varying the microwave treatment time and other process parameters. Under 980 nm excitation, the photoluminescence spectrum of the UC particles (Fig. 1a) shows the characteristic $Tm^{3+}$ emission lines both in UV and visible region at around 344 nm ($^1I_6 \rightarrow {}^3F_4$), 361 nm ($^1D_2 \rightarrow {}^3H_6$), 452 nm (UC@$TiO_2$ photocatalyst $^1D_2 \rightarrow {}^3F_4$), 475 nm ($^1G_4 \rightarrow {}^3H_6$), 647 nm ($^1G_4 \rightarrow {}^3F_4$) and 800 nm ($^3H_4 \rightarrow {}^3H_6$). The emission in UV region (344 nm and 361 nm) could be used to photoexcite the $TiO_2$ coated on the surface of UC (UC@$TiO_2$ sample) as confirmed by around 90% photodegradation of crystal violet (CV) dye within 5h of illumination (11 am to 4 pm, clear sunny sky) under natural solar light (Fig. 1b).

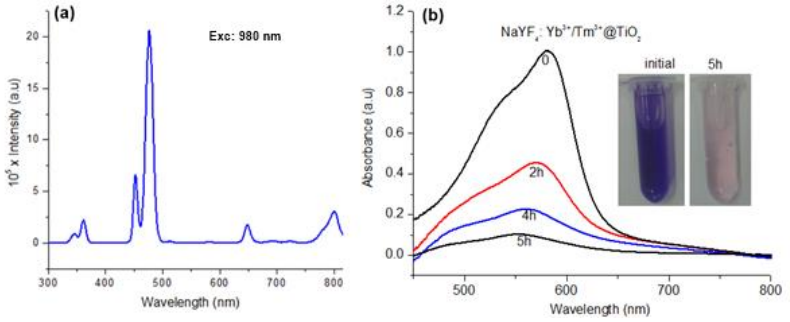


Figure 1: Photoluminescence spectrum of $NaYF_4$:$Yb^{3+}/Tm^{3+}$ UC particles under 980 nm excitation (a) and visible spectra of CV dye after various time of exposure to natural sunlight in the presence of UC@$TiO_2$ photocatalyst. The inset in **b** shows the digital photos of CV before and after exposure to sunlight in the presence of UC@$TiO_2$ photocatalyst.

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