

Facile Synthesis of Porous TiO₂ Nanoppearl and Nanorice toward Visible–Light Photocatalysts

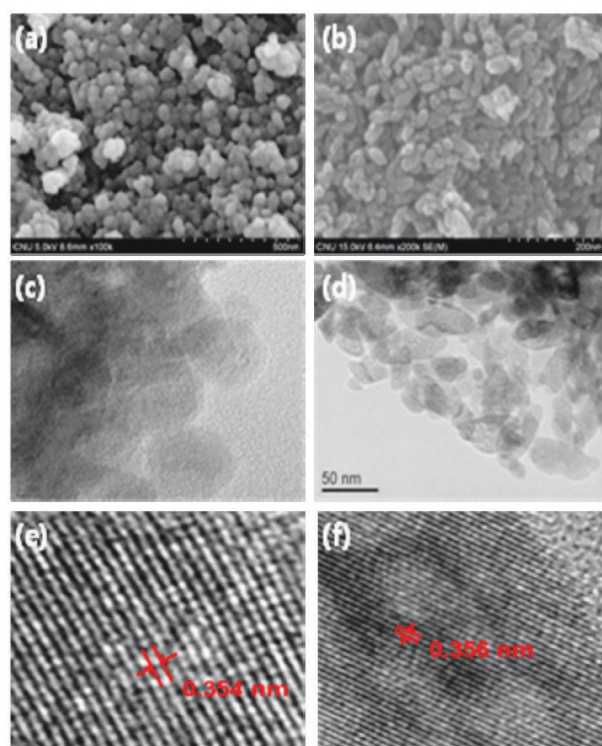
Jooran Lee, Eunju Bae and Minjoong Yoon*

Molecular/Nano Photochemistry & Photonics Lab, Department of Chemistry, Chungnam National University, 79 Daehak-ro, Yuseong-gu, Daejeon, 305–764, Republic of Korea

ABSTRACT: New porous TiO₂ nanostructures with shapes of pearl and rice were synthesized by hydrothermal treatment of TiO₂–liposome nanocomposites in acid and base solutions, respectively, as identified by scanning electron microscopy (SEM), transmission electron microscopy (TEM) images and large Brunauer–Emmett–Teller (BET) surface areas. The x–ray diffraction (XRD) patterns and selected area electron diffraction proved them to be well–defined anatase crystals. Their UV–visible reflectance absorption spectra were observed to have low band gap energy (3.03 and 3.07 eV, respectively), exhibiting surface absorption band in the visible range from 400 to 600 nm. The degradation of methylene blue (MB) over the TiO₂ nanostructures was observed upon visible–light irradiation, which was found to be very efficient as compared with any other conventional visible–light responsive TiO₂ nanostructures.

TiO₂ nanoparticles are non–toxic, highly photostable and cheap, providing quantum surface states to trap the photoinduced electron and holes so that electron or hole is separated to be used for the redox reaction. Thus, they are useful as photocatalysts, being widely used as photocatalysts for solar application to environmental purification, production of solar fuels from water^{1–7} and solar cells^{8,9} and solar fuels alternative to the traditional silicon solar cells.^{8,10} However, due to their wide band gap corresponding to UV energy, their practical uses of solar energy remain limited in achieving higher solar energy conversion efficiencies, because visible light is dominant in the solar radiation. Thus, a great deal of attention has been paid to surface modification of TiO₂ nanoparticles to enhance visible light harvesting as well as the charge separation. One of the interesting surface modifications to develop the visible light–absorbing TiO₂ nanomaterials has been done by doping some metals (as in MTiO₂ (M= Fe, V, Mn)^{11,12}) and N, C, and S into the lattice of TiO₂ (as in TiO₂–xNx,¹³ TiO₂–xCx,^{14,15} and Sm₂Ti₂O₅S₂)¹⁶) nanoparticles so that the O 2p states of TiO₂ are modified by narrowing the band gap through chemical vapor deposition¹⁷ and physical vapor deposition.^{15,16} However, the behaviors of fast exciton recombination and poor electron transport still remain problematic, leading to low photocatalytic efficiency

by visible light. This may be because doping disturbs the surface states to increase exciton recombination. Thus, it has been highly required to modify TiO₂ surface states intrinsically without doping. The promising way is to fabricate low dimensional Nanostructures. Actually they are known to have high density of surface states so that electron–hole is well separated to retard exciton recombination, and the interfacial electron transfer is facilitated. Also the band gap energy is decreased to absorb visible light. Nevertheless, there are only few reports on the morphology dependence on photocatalysis and solar energy conversion of different TiO₂ nanostructures. This leads us to fabricate new TiO₂ nanostructures having shapes of nanoppearl (TNP) and nanorice (TNR) by simple hydrothermal treatment of the TiO₂–liposome composites in different pH conditions (0.54 and 11.0, respectively) by modifying previously reported method.¹⁸ FESEM images (Figure 1a and 1b) and TEM images (Figure 1c and 1d) confirm the pearl (~35 nm diameter) and rice shapes (~70 nm diameter) of the as–synthesized nanostructures, respectively. The high resolution



*To whom correspondence should be addressed.
E–mail: mjyoon@cnu.ac.kr
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TEM images exhibit well-defined lattice structures of 0.354 and 0.356 nm spaces (Figure 1e and 1f), indicating that both TNP and TNR has typical anatase crystalline phase. This was supported by observation of XRD patterns (Figure S-1) characteristic of anatase crystal in addition to the fast Fourier transform (FFT) patterns and selected area electron diffraction patterns (SAED) of (101) plane (Figure S-2). The FESEM images also exhibited porous surfaces.

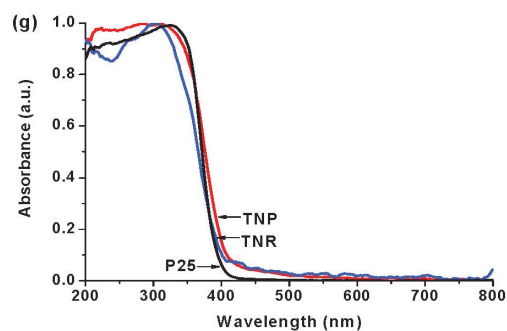


Figure 1. FESEM images of TNP (a) and TNR (b). The TEM images of TNP (c) and TNR (d), and high resolution TEM images of TNP (e) and TNR (f). (g) Diffuse reflectance absorption spectra of TNP, TNR and Degussa P25.

Being consistent with this, the pore sizes were determined to be 2~ 50 nm diameter by the Barret–Joyner–Halenda (BJH) method (Figure S-3), and specific surface areas of TNP and TNR were determined to be 105 and 85 m²/g, respectively, by measurement of Brunauer–Emmett–Teller (BET) isotherm (Figure S-4), which were significantly larger than that of Degussa P25. The reflectance UV–visible absorption spectra of TNP and TNR (Figure 1g) exhibited the surface state absorption of the visible light beyond 400 nm with band gap energies, 3.03 and 3.07 eV, respectively, which is significantly red–shifted from that of the Degussa 25, indicating the two nanostructures would be useful for the visible light–sensitive photocatalysts. Figure 2(A) shows the relative photodegradation of methylene blue (MB) in the presence and absence of different TiO₂ materials upon irradiation with visible light. MB was observed to be degraded by more than 80 % upon irradiation in the presence of TNP and TNR whereas photodegradation in the presence of P25 is negligible. This supports that TNP and TNR are efficient visible light–sensitive photocatalysts. Particularly they are more active in the visible light photocatalysis by bubbling with oxygen (Figure 2(B)). In conclusion the TNP and TNR would be very useful for solar applications.

Table 1. BET surface area of Degussa P25, TNP and TNR

TiO ₂ nanomaterials	S _{BET} (m ² /g)
Degussa p25	50
TNP	105
TNR	85

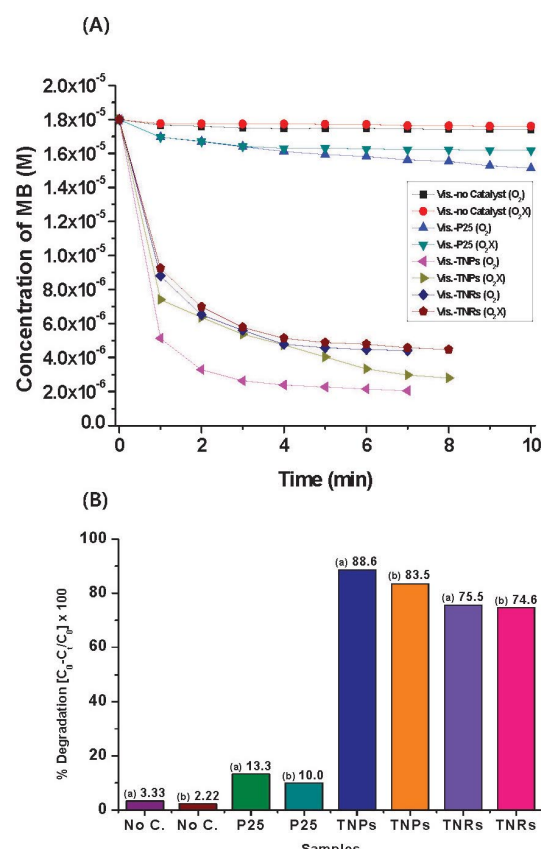


Figure 2. (A) photodegradation of MB as a function of visible light ($\lambda > 400$ nm) irradiation time with (o) or without (x)O₂ bubbling for 7 min. (B) comparison between the photocatalytic efficiencies of P25, TNP and TNR in the degradation of MB under visible light irradiation. The irradiation light was spectrally cut off with 400nm long pass filter.

KEYWORDS: TiO₂ nanostructures, Nanopearl, Nanorice, Visiblelightphotocatalysis, Liposome template synthesis, Solarapplication

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SUPPORTING INFORMATION

Experimental procedures; characterization, XRD, FFT, SAED BET isotherm and FT-IR data. This material is available free of charge via the Internet at <http://www.rcp.or.kr>

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