Why is the photocatalytic activity higher in the nanosize crystals?

Let us first look at the general sequence of steps in photocatalysis by crystalline materials:

Generation of electrons & holes:

Crystal + Radiation (Photons) → Crystal (with a positive hole)
+ Electron …….I

Oxidative catalysis:

Adsorbate + Holes (+) → Adsorbate (+)
+ Electron……. ……..II

Reductive catalysis:
Adsorbate + Electron (-) → Adsorbate (-) ……. ……..III

A photon impinging upon a photocatalyst generates a pair of holes and electrons (called as excitons). These excitons are labile in semiconducting metal oxides (like TiO_2). The holes have power to cause oxidation of the adsorbate by extracting electrons and thereby triggering a chemical reaction. Similarly the electrons can initiate reductive reactions in the substrate. These reactions will involve intermediate active species like OH radical or superoxygen anion which are the reaction products of excitons with water and oxygen.

When the particle size of the crystalline phase decreases down to the nanoscale, their photocatalytic activity is significantly enhanced. There are three reasons for the enhanced photocatalytic activity of the nanosize crystals:

- Elimination of crystal defects:
  The photochemical reactions are possible only if the excitons survive long enough to interact with the surrounding material. If they recombine soon after their birth, the redox catalytic triggering does not happen. The investigators in the field have found that the defects in the crystals aid the recombination of holes and electrons

soon after they are generated. This recombination leaves fewer excitons for initiating the catalytic reactions in the surrounding material. Hence the photocatalytic activity is retarded in the bulk crystals due to crystal defects.

In the nanoscale crystals, there are far fewer defects than the bulk crystals and hence the recombination of holes and electrons is minimal. This provides larger number of holes and electrons for further catalytic redox reactions of the adsorbate. Therefore nanoscale crystals have far higher photocatalytic activity than the bulk crystalline materials.

- Higher surface area:

Substantially higher surface area of the nanosize crystals allows higher amount of reactants to be adsorbed on the surface. This leads to the higher chemical efficiency of the incident photons by bringing about larger area of contact between the adsorbate and the excitons.

- Quantum Confinement:

In the nanoscale particles, there is restriction on the movement of the excitons among the atoms and this leads to their localization. As a result, the oxidation potential increases with decreasing size, thereby enhancing catalytic activity.
