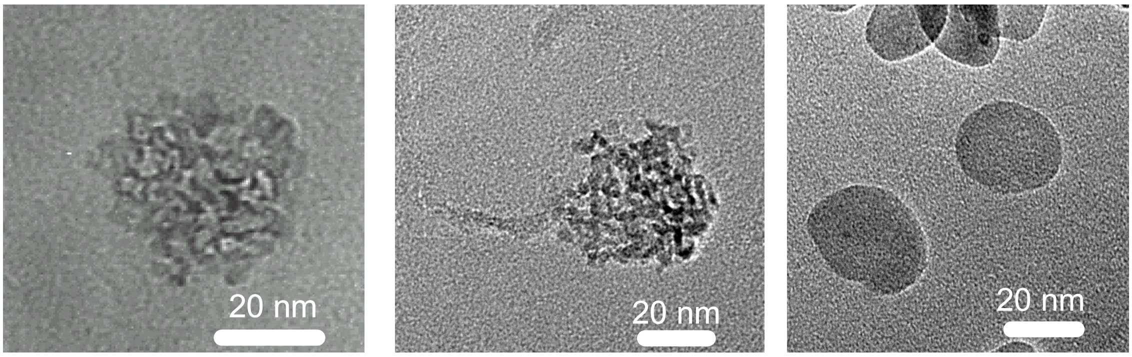
Supplementary Data

1. Pristine particles

The pristine TiO_2 nanoparticles (NPs) used in this work are commercially available from Millennium (reference S5-300) as an aqueous acidic suspension (pH 1, HNO_3). The morphology of the particles is shown in Figure 1Sa. They consist in porous aggregates of about 40 nm (pore volume fraction of 28%) of primary crystallized particles of 8 nm.

TiO_2 NPs are dispersed in the silica mesoporous matrix and TiO_2/SiO_2 nanocomposite powders are annealed in air up to 1000°C. After heating, X-ray diffraction patterns clearly show the conservation of the anatase type structure in nanocomposites (Figure 2S). As the annealing temperature increases up to 1000°C, the coherence length rises from 8 to 20 nm (as deduced from the full width at half-maximum of the diffraction peaks using the Scherrer law) and the surface area of the powders progressively decreases from 350 to 20 $m^2.g^{-1}$ (as deduced from the BET analysis of N_2 adsorption isotherms). This is due to the progressive self-sintering of the aggregates observed in pristine TiO_2 NPs, as confirmed by electron microscopy observations performed on the NPs after the silica dissolution, with dense NPs of about 20-30 nm observed after annealing at 1000 °C (Figure 1Sc). Annealed NPs are dispersed in acidic water leading to colloids as for the pristine NPs (Figure 3S).



Pristine TiO_2 Annealing at 600 °C Annealing at 1000 °C

Figure 1S. TEM images of pristine and annealed TiO_2 NPs after annealing in air of the TiO_2/SiO_2 nanocomposite powders and the subsequent dissolution of silica.

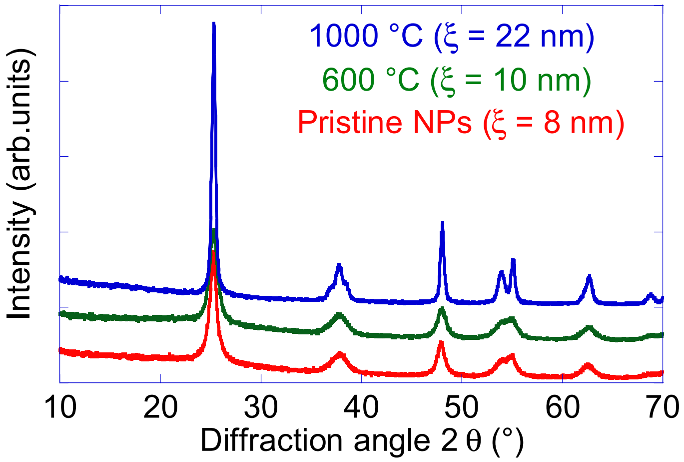


Figure 2S. X-ray diffraction profiles (CuKα) and evolution of the coherence length ξ, as a function of the annealing temperature in air of the TiO_2 NPs powders. All peaks are indexed in the anatase type structure.

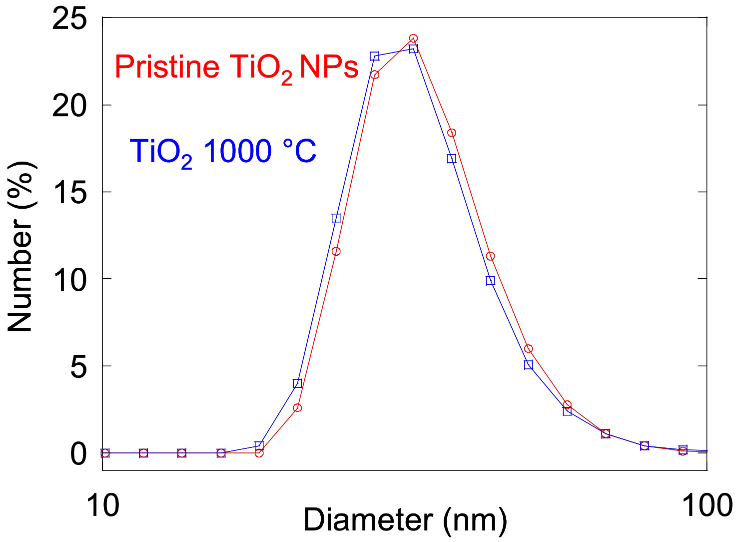


Figure 3S. Characterization of the colloidal suspension of TiO_2 NPs in water by Dynamic Light Scattering, after the annealing at 1000 °C in air of the TiO_2/SiO_2 nanocomposite powders, the dissolution of silica and the NPs dispersion in water. The size distribution is compared to the one obtained for the starting suspension containing pristine TiO_2 NPs.

2. Characterization of nitrogen species in N-doped TiO_2 NPs powders.

For EPR and XPS experiments, TiO_2/SiO_2 nanocomposite powders were treated at room temperature by a diluted aqueous solution of hydrofluoric acid (HF 2 wt %) to dissolve the silica matrix.

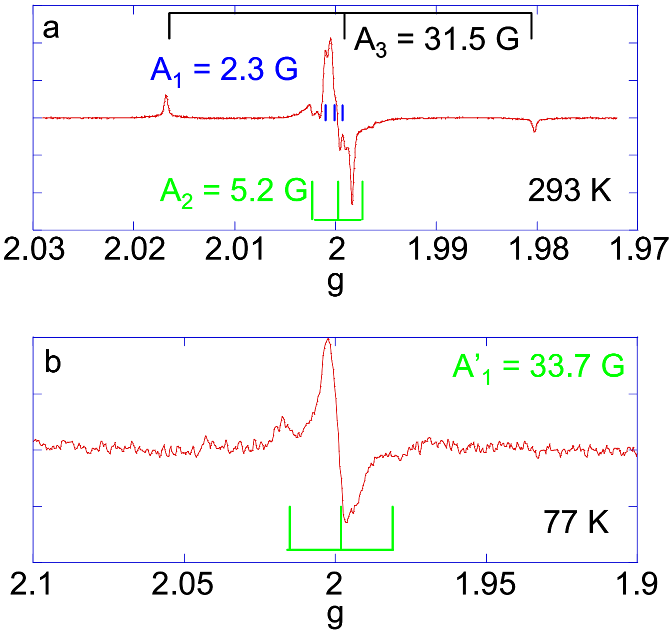


Figure 4S. EPR spectra of N-doped TiO_2 NPs after nitridation at 600 °C and silica dissolution. The two types of N-based paramagnetic species have been previously observed by Livraghi et al..[38-39] (a) EPR spectrum measured at room temperature assigned to species containing a single nitrogen atom trapped in the anatase structure of TiO_2 (ν = 9.836 GHz). (b) EPR spectrum measured at 77 K which is characteristic of the adsorption of nitric oxide molecules (NO) at the surface of different oxides (ν = 9.648 GHz).

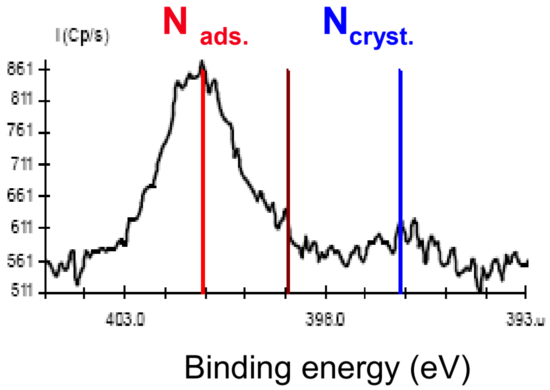


Figure 5S. XPS spectrum of the N 1s core level obtained from N-doped TiO_2 NPs after nitridation at 800 °C and silica dissolution. Two peaks are clearly observed at 396 and 400 eV assigned to substitutional nitrogen dopant and adsorbed nitrogen species, respectively.[16-17]

3. Thermal stability of defects in N-doped TiO_2 NPs.

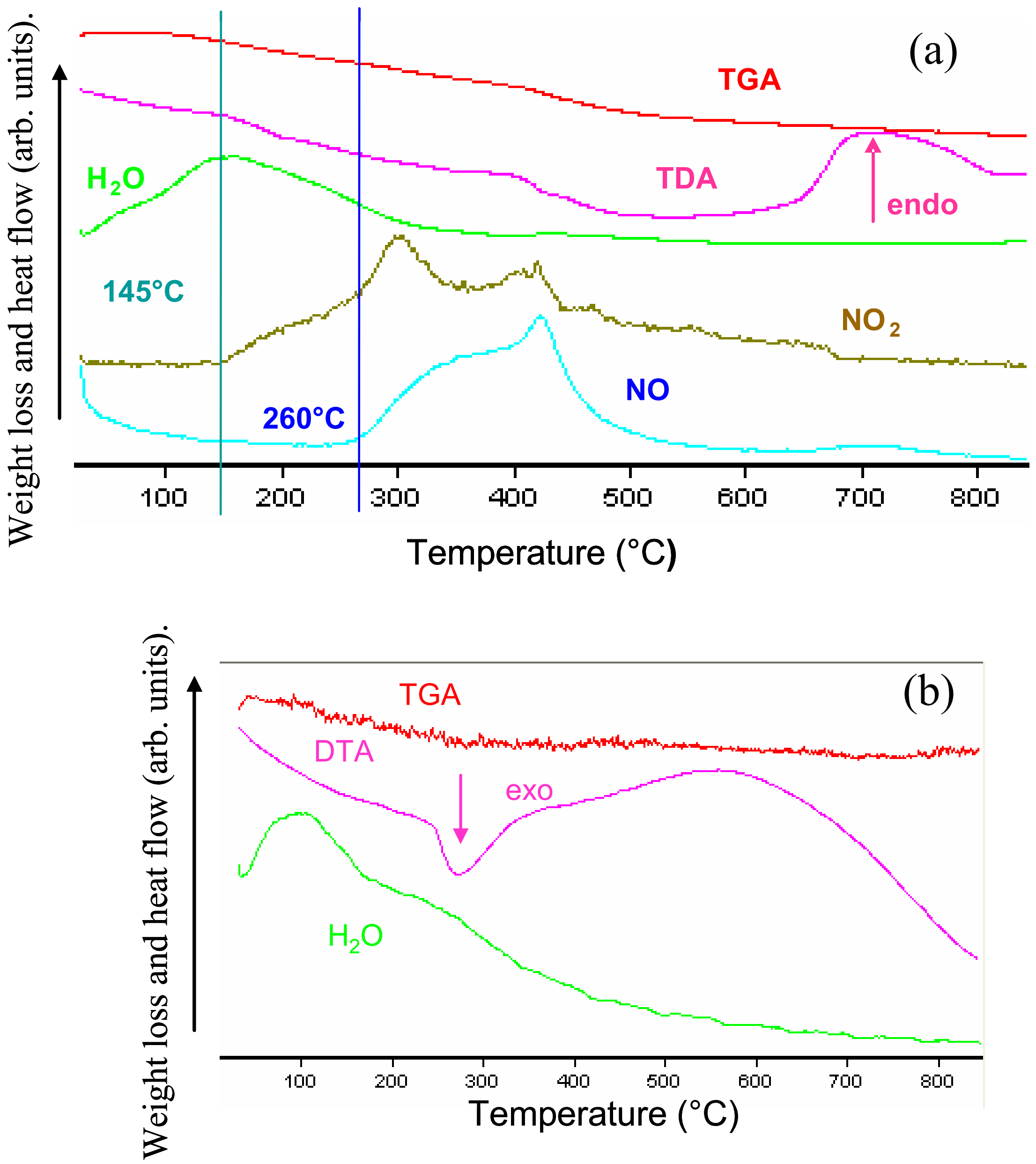


Figure 6S. DTA, TGA and MS curves performed on N-doped TiO_2 powder (10 °C.min^{-1} heating rate) after nitridation at 600 °C. (a) under argon flow, (b) in air. The latter experiments were performed after a sample annealing at 850 °C under Ar flow.