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Multisite luminescence of rare earth doped TiO_2 anatase nanoparticles

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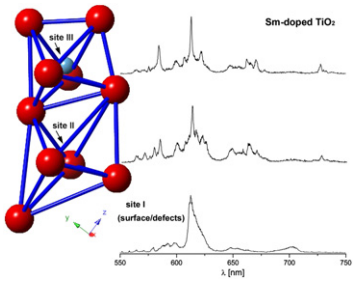
HIGHLIGHTS

- Sm^{3+}, Eu^{3+} and Tb^{3+} are incorporated into anatase nanocrystals via sol–gel route.
- Sm^{3+} and Eu^{3+} luminescence originate from 3 different sites in TiO_2 nanocrystals.
- Details on multisite structure for Sm^{3+} doped TiO_2 are presented for the first time.

GRAPHICAL ABSTRACT



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ABSTRACT

Eu^{3+}, Sm^{3+} and Tb^{3+} ions have been incorporated into anatase TiO_2 nanocrystals via hydrolytic sol–gel method. Pure anatase phase was confirmed with XRD and TEM measurements. Band gap energies change slightly with rare earth incorporation, from 3.32 eV for undoped TiO_2 to 3.15 eV, 3.25 eV and 3.29 eV for Tb^{3+}, Sm^{3+} and Eu^{3+} doped TiO_2. Photoluminescence of Eu^{3+} and Sm^{3+} originated from three different sites in TiO_2 nanocrystals have been identified with the laser-excited site-selective spectroscopy measurements at 10 K. One site exhibits broad emission peaks, which are ascribed to the distorted lattice site near the surface. Other two sites, associated with the inner lattice, show significantly sharper fluorescence lines as a consequence of an ordered crystalline environment. The emission decays of Eu^{3+} and Sm^{3+} have similar values for inner-lattice sites and longer lifetimes for near-surface sites. The luminescence of Tb^{3+} doped TiO_2 nanocrystals was immeasurably weak.

1. Introduction

Titanium (IV)-oxide occurs in nature in three mineral forms: anatase, brookite and rutile. All three phases are characterized with high refractive index ($n_{anatase}$ = 2.488, n_{rutile} = 2.609, $n_{brookite}$ = 2.583), low absorption and low dispersion in visible and near-infrared spectral regions, high chemical and thermal stabilities. This important metal-oxide semiconductor with relatively wide band gap (3.25 eV for anatase, 3.0 eV for rutile, 1.9 eV for brookite) [1] and low phonon energy (<700 cm^{-1}) is an excellent host for various rare earth (RE) impurities providing their efficient emission in visible range [2–6]. These systems are of possible interest in white light emission diode (LED) industry [7–10] and as photocatalysts [11,12]. At the same time, being non-toxic and biocompatible, rare-earth doped anatase has strong potential to replace standard types of fluorophores (quantum dots, organic dyes, etc.), traditionally used as fluorescent markers in medicine and biological applications [13].

In particular anatase phase is considered very promising and has been widely investigated for various applications in lithium-ion batteries, filters, waveguides, anti-reflective and highly reflective coatings [14–19], but it still remains a challenge to keep this phase

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