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Blue-emitting yttria-stabilized tetragonal zirconia nanoparticles capped by PVA

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ABSTRACT

Polycrystalline yttria-stabilized tetragonal zirconia nanoparticles having a grain size around 50-80 nm were fabricated in aqueous poly (vinyl alcohol) (PVA) solution by mechanical attrition in a planetary mill, with the PVA used as a capping agent. The surface-modified nanoparticles displayed a significant near-band-edge photoluminescence with emission band centered at 428 nm due to the good surface passivation of the nanoparticles by the PVA molecules. An enhancement of the blue emission was observed when the nanoparticles were embedded in solid PVA matrix. Elevating the temperature of the zirconia nanoparticle solution from 337.5 to 357.5 K lead to temperature quenching of the luminescence due to the decrease of emissive centers caused by desorption of PVA from the nanoparticle surface.

1. Introduction

Zirconia, ZrO_2, is of great interest because of its wide band-gap (5.0–5.5 eV) as well as excellent mechanical, thermal, optical, and electrical properties. It can be used in a wide range of applications such as catalysts [1], semiconductor substrates [2], thermal barrier coatings [3], solid electrolyte in fuel cells [4–6], and gas sensors [7,8]. Pure ZrO_2 has three main polymorphs-monoclinic, tetragonal and cubic. Only the monoclinic form is stable enough at room temperature. However, by incorporation of some aliovalent species, the metastable cubic and tetragonal phase can be well stabilized. For example, Muccillo recently prepared cubic zirconia containing 10 mol% Sc_2O_3 by precursor techniques [9]; Stefanic et al. reported that addition of Cu^{2+} ions stabilizes the tetragonal polymorph of ZrO_2 [10].

Of the doped alloys of ZrO_2, yttria-stabilized zirconia (YSZ) plays an important role owing to its wide applications and exceptional properties such as high mechanical strength, good chemical stability, high level of oxygen-ion conductivity, corrosion resistance, low thermal conductivity, and interesting luminescent functions [11,12]. The luminescence of YSZ has been studied by a number of researches with consideration of effects of oxygen vacancies and dopant impurities [13–18]. Nevertheless, the luminescence of YSZ is still not fully understood, especially for the emission of the tetragonal phase probably because that the luminescence intensity of tetragonal ZrO_2 is always very weak [19,20].

In recent years, modifications of nano-sized inorganic semiconductors by organics were reported to influence the luminescence of the semiconductors remarkably. An enhancement of band edge luminescence had been observed from ZnO, CdS and CdSe nanocrystallines capped by various polymers or surfactants [21–24]. The energy transfer between organic and inorganic semiconductor has also been studied in several hybrid systems comprising an organic oligomer or polymer host and a semiconductor guest [25–28]. Very recently, Anni and co-workers typically investigated the excitation process of CdSe/ZnS nanocrystals, and their excitation density dependence in the host of luminescent poly (9,9-dioctylfuorene) [29]. They demonstrated that the presence of amplified spontaneous emission from the host conjugated polymers leads to a strong excitation density dependence of the nanocrystal excitation processes. These results suggest an effective route to explore the luminescence of inorganic semiconductors for future applications, in addition to extend the understanding of the excitation transfer from organics to semiconductors. However, up to date, little is known about the effect of organics on the luminescence of YSZ.

Here we report that upon excitation with UV light in the 260–275 nm range, remarkable blue luminescence can be emitted from yttria tetragonal zirconia polycrystal (Y-TZP) nanoparticles containing 3 mol% Y_2O_3 at room temperature provided that the Y-TZP nanoparticle surface can be properly passivated by PVA molecules. Besides its scientific interests for the mechanism of the electronic excitation in YSZ, the resulted luminescent PVA/zirconia nanocomposite is also an interesting photo-active material for blue light emitters, light-emitting diodes and photovoltaic devices.

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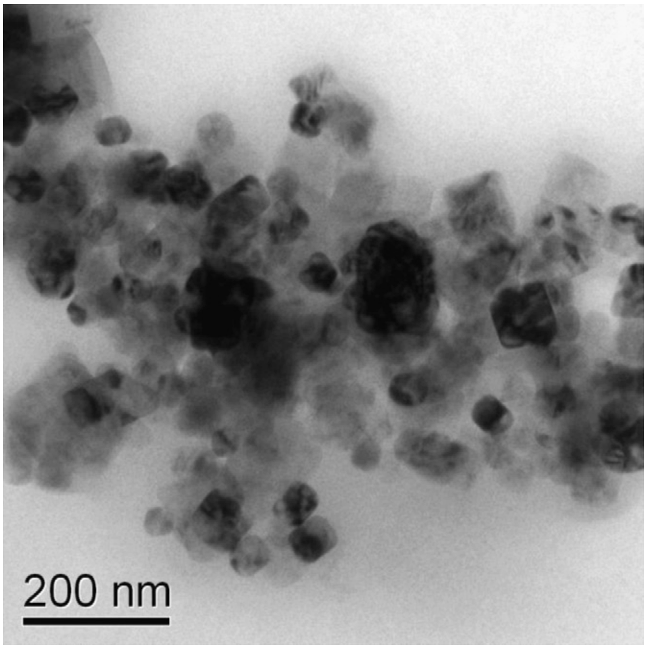

Fig. 1. TEM image of Y-TZP nanoparticles in the presence of PVA.

2. Experimental

2.1. Materials

Tetragonal zirconia balls stabilized with 3 mol% Y_2O_3 were applied as the source material for the preparation of zirconia nanoparticles. PVA with MW ≈1750 g/mol obtained from Sinopharm Chemical Reagent Co. Ltd. (China) was used as received.

2.2. Preparation of Y-TZP nanoparticles in aqueous PVA solution

Zirconia balls immersed in aqueous PVA solution were introduced into a poly(tetrafluoroethylene) vial and placed on rotating tray of a planetary mill (QM-3SP2, China) at a rotation speed 580 rpm to run for 30 h. Under the violent impulsive stress applied by the ball impact, zirconia nanoparticles were therefore generated from the bulk balls and then were readily immobilized by the dissolved PVA which serve as a capping reagent. After removing the balls, the as-obtained colloidal system was centrifugated at 6000 rpm for 20 min to remove any large pieces, creating a stable colloidal solution of Y-TZP nanoparticles finally.

2.3. Characterization

Morphology of the resulted Y-TZP nanoparticles in solution was observed using a JEM-2010 JEOL transmission electron microscope (TEM). Optical absorbance was measured by a UV–visible spectrophotometer (UV-1600, China) at room temperature. Luminescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer with 5 nm of emission monochromator slit.

3. Results and discussion

3.1. TEM analysis

Fig. 1 shows the typical TEM image of the resulted Y-TZP nanoparticles embedded in PVA matrix. The nanoparticles have a diameter of around 50–80 nm. In addition, their edges appear indistinct from the matrix, indicating an effective combining of PVA on the nanoparticle surface.

3.2. Optical absorption

Optical absorption spectrum of the colloidal system of Y-TZP nanoparticles in aqueous PVA solution is presented in Fig. 2. The absorption band was at 260 nm which is longer than the intrinsic absorption of tetragonal zirconia at 226 nm [30]. The lower energy suggests the 260 nm band is an extrinsic light absorption associated with impurities and surface states of the nanocrystal [31].

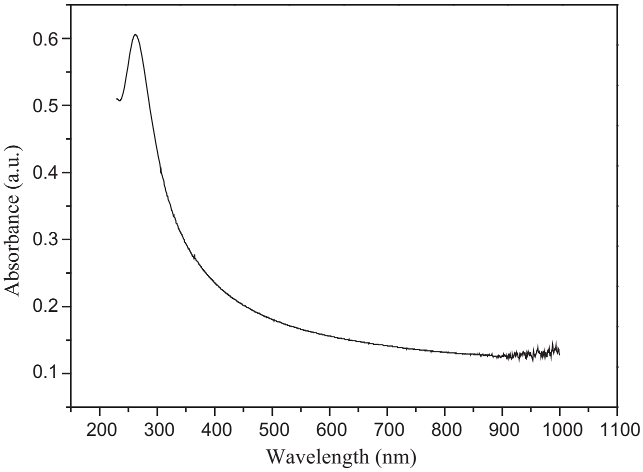

Fig. 2. UV–Vis absorption spectrum of Y-TZP nanoparticle solution in water with 30 mg ml^{-1} of PVA.

3.3. Photoluminescence properties

The PL spectra measured at room temperature on the Y-TZP nanoparticle solution are shown in Fig. 3a (curves 1–4). Upon excitation in the optical absorption region from 260 to 275 nm which are similar to the previously reported data of yttria-doped zirconia [32], an efficient blue luminescence centered at 428 nm was observed, while aqueous PVA solutions without ZrO_2 cannot give any emission in the same wavelength region (Fig. 3a, curve 5). PL results similar to that of PVA solutions were also observed for pure PVA films, where no luminescence was observed too. This indicates that the luminescence is factually due to nanoparticles of ZrO_2 enhanced by PVA, but not due to PVA itself. The PL intensity relative to standard sodium salicylate dissolved in water (0.5 μg/ml) was about 0.97 at the 265 nm excitation wavelength. The energies of the excitation lights (4.77–4.51 eV) are lower than the band gap energy of YSZ (5–5.5 eV), suggesting that the PL is extrinsic [33]. The PL peak location coincides well with that of the absorption band edge in the UV–Vis absorption spectra (Fig. 2), revealing that the luminescence is actually a near band-edge emission, which is typical of surface-passivated nanocrystalline semiconductor [34].

It is understandable that the violent ball impacting will certainly cause a large number of defects at the resulted nanoparticle surface. A gradual phase transformation of the zirconia nanoparticles from tetragonal to cubic may also occur due to the increasing lattice expansion during the ball milling process [35,36]. Unless the resulted defects are passivated, the PL will be quenched efficiently from the zirconia due to the occurrence of non-radiative surface recombination. YSZ nanoparticles have been reported to show a strong absorption to PVA in aqueous solution [37]. In our research, by introducing the PVA served as capping molecules into the milling medium to modify the fresh nanoparticles instantaneously as they are formed, surface-passivated Y-TZP nanoparticles were generated effectively. The near-band-edge emission probably originated from the charge transfer of photo-excited holes trapped at the surface defects into the PVA molecules [21].

After exposing the nanoparticle solution to heating, a double decrease in the PL intensity taken place in the temperature range from 337.5 to 357.5 K, indicative of thermo-bleaching (Fig. 3b). It is understood that as the solution temperature is increased

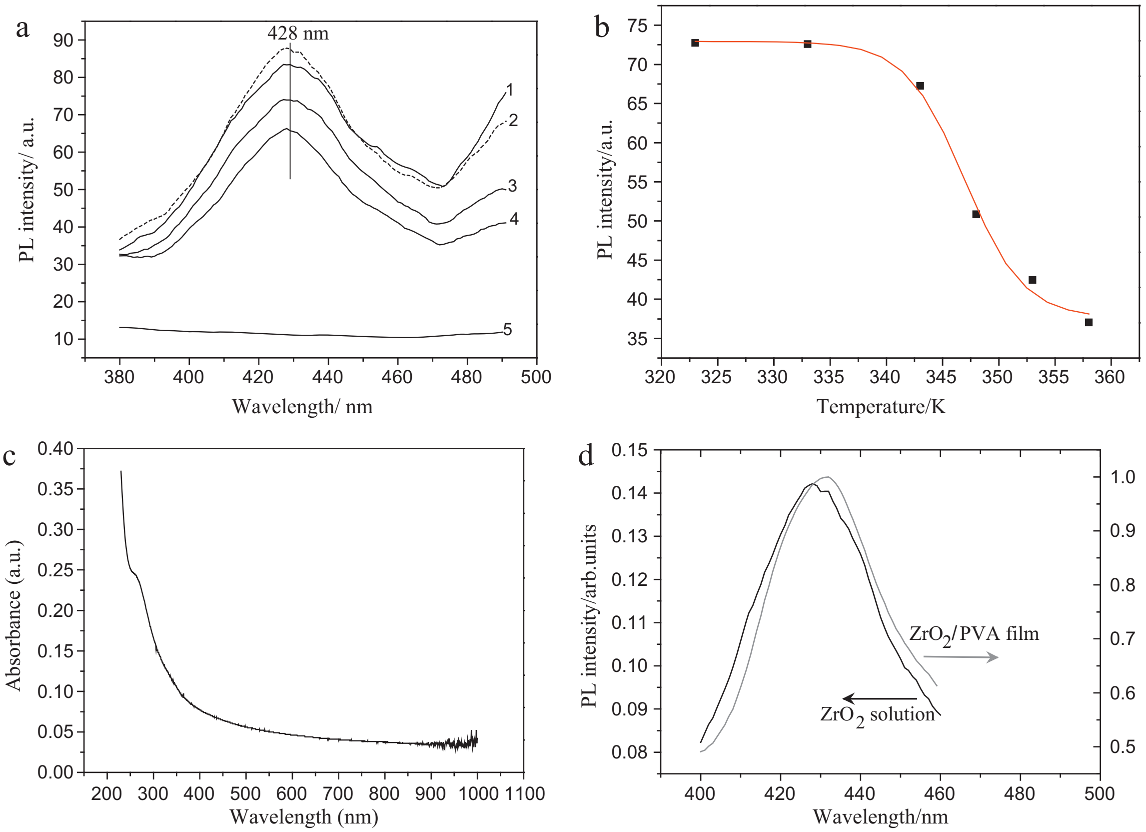

Fig. 3. PL properties of Y-TZP nanoparticles capped by PVA. (a) PL spectrum of the colloidal solution of Y-TZP nanoparticles for (1) 260, (2) 265, (3) 270, (4) 275 nm excitation with 20 mg/ml of PVA content, and (5) the pure PVA solution under 265 nm excitation. (b) Decay curve of the 428 nm luminescence of the nanoparticles in PVA solution heated from 325.5 to 358.5 K; the solid curve is a fit to the experimental data (square symbols). (c) UV–Vis absorption spectrum of nanoparticle solution heated to 363.5 K (PVA concentration 30 mg ml^{-1}). (d) Normalized PL spectra of Y-TZP nanoparticles in aqueous PVA solution and embedded in PVA matrix at room temperature.

some of the emissive centers related to the PVA–surface interactions are destroyed because of desorption of PVA from the nanoparticle surface, hence leading to the heat-caused decrease of the 428 emission. As shown in Fig. 3c, compared with the UV absorption at room temperature (Fig. 2), the optical absorption of the solution system, which is closely associated with the compounding state between PVA and Y-TZP nanoparticle surface, decayed dramatically when the system was heated to 363.5 K. The phenomenon gives evidence of the PVA desorption which lead to changes in the nanoparticle surface states. Moreover, as demonstrated in Fig. 3d, when the colloidal solution was casted into a film, the shape of PL feature maintains rather well, and a remarkable PL enhancement was observed. This again convinces the effective role of PVA in generating surface-passivated Y-TZP nanoparticles and preventing recombination of surface states [22].

4. Conclusions

In summary, PVA-capped Y-TZP nanoparticles were fabricated by attrition of Y-TZP balls in aqueous PVA solution via mechanically milling. Upon excitation with light at the wavelength ranging from 260 to 275 nm, the surface-passivated Y-TZP nanoparticles displayed a significant near band-edge luminescent in the blue light region with the emission band at 428 nm. Due to the improved electronic passivation in their PVA composite film, a remarkable enhancement of the luminescence was observed. The emission from the surface-passivated nanoparticles in solution decays when the system is heated owing to decrease of some emission centers resulted from desorption of PVA at a high temperature.

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