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Short Communication

Hydrogels dispersed by doped rare earth fluoride nanocrystals: Ionic liquid dispersion and down/up-conversion luminescence

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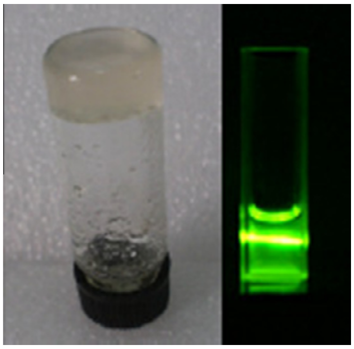
HIGHLIGHTS

- New luminescent hydrogels are prepared.
- Rare earth fluoride nanocrystals are dispersed into ionic liquid compound.
- Up-conversion luminescence of the fluoride dispersed hydrogel are obtained.

GRAPHICAL ABSTRACT

Two typical kinds of hydrogels are prepared with codoped rare earth fluoride nanocrystals dispersed in ion liquid compound ([C_6mim][Cl]) assisted by agarose, which present the up-conversion luminescence of the immobilized rare earth fluoride nanocrystals.



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ABSTRACT

Two typical kinds of rare earth fluoride nanocrystals codoped with rare earth ions (Eu^{3+} and $Tm^{3+}/Er^{3+},Yb^{3+}$) are synthesized and dispersed in ionic liquid compound (1-chlorohexane-3-methylimidazolium chloride, abbreviated as [C_6mim][Cl]). Assisted by agarose, the luminescent hydrogels are prepared homogeneously. The down/up-conversion luminescence of these hydrogels can be realized for the dispersed rare earth fluoride nanocrystals. The results provide a strategy to prepare luminescent (especially up-conversion luminescent) hydrogels with ionic liquid to disperse rare earth fluoride nanocrystals.

Introduction

Rare earth fluorides possess low phonon vibration energy and so they are suitable to behave as host for near infrared luminescent RE^{3+} ions which is easily quenched [1,2]. Subsequently, rare earth fluorides have been developed in so many practical applications fields as up/down-conversion luminescent materials or laser devices [2–4]. Especially it is worthy pointing out that the present research are focused on rare earth fluorides up-conversion nanocrystals for their further biological imaging, whose reports are becoming more and more [5–8]. Among β-$NaYF_4$ is generally regarded as the most efficient up-conversion host for Yb–Er and Yb–Tm ion pairs and serving as the workhouse for photon up-conversion, whose near infrared excitation at 980 nm and visible

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emission at 550, 650 nm make them low background noise [9–12]. Li and Lin have reviewed the synthesis, surface modification and applications of rare earth fluorides nano-/microcrystals [13].

Ionic liquids (ILs) are stabilized by ionic interaction through hydrogen bonds and van der Waals forces [14]. ILs salts consist of anion organic and cations. Imidazolium, pyridinium, pyrrolidinium, quaternary ammonium, or phosphonium type of ILs have been widely studied. The most famous species in this field is 1-alkyl-3-methylimidazolium. ILs bond with different group show different properties, ILs with fluorinated groups are prone to hydrolysis [15]. However, ILs with Cl^- and Br^- provide hydrophilic properties which is miscible with water [14]. Many research uses the feature of ILs (can link the rest of the group) to synthesize functionalized ionic liquids [15,16]. Recently, much work has been done focused on luminescent lanthanide β-diketonate complexes doped ionic liquids, which show favorable luminescent performance like high quantum yield and stationary photo-stability [17–20]. But the ionic liquids were used as solvents to disperse luminescent doped lanthanide inorganic compound such as fluorides are rarely reported except for that $LaF_3:Ln^{3+}$ nanocrystals (Ln = Eu, Nd) were dispersed in ionic liquids with different stabilizing ligand [21].

In this paper, we try to disperse some down/up-conversion luminescent rare earth fluoride nanocrystals in ionic liquid and further prepare the ionic gel with the assistance of agarose. The down/up-conversion luminescence are checked for Eu^{3+} and Yb^{3+},Er^{3+}/Tm^{3+} systems, respectively, which is benefit for further development and application of luminescent (especially up-conversion luminescent) rare earth fluoride nanocrystals in practical fields. Recently, we have realized the dispersion of complex fluoride up-conversion nanocrystals into ionic liquid with alkoxy (triethoxysilyl) groups to form the hybrid iongels [22].

Experiment section

Materials

Lanthanide oxides were all dissolved into hydrochloride to convert their chlorides $RECl_3 \cdot xH_2O$ (RE = Eu, Y, Er, Tm, Yb, Lu). 1-Chlorobutane (98%), 1-methylimidazole (98%) and $Ba(NO_3)_2$ (98%) were from Aldrich. Agarose, $NaNO_2$ (98%), oleic acid (OA, 90%) and linoleic acid (LA, 90%), ethylenediamine (EDA, 98%, Alfa Aesar) and ethylenediamine dihydrofluoride (EDADF, 98%) were all from Alfa Aesar. Oleylamine (OM, C18, 80–90%) was from Aladdin. All these reagents were used without further purification.

Hydrothermal synthesis of barium rare earth fluoride nanocrystals ($BaYF_5$ and $BLuF_5$)

At first, 5 mL ethanol, 2.4 mL (7.5 mmol) OM, 6 mL (19 mmol) OA/LA and 2 mL H_2O were mixed well under vigorous stirring at 20 °C. 0.5 mmol $RE(NO_3)_3 \cdot xH_2O$ and 0.5 mmol $Ba(NO_3)_2$ were added into the above mixture under 10 min vigorous stirring until that transparent solution appears. Then, 2.3 mL (1.15 mmol) NH_4F (0.25 M) was dropped into the above solution under vigorous stirring for 10 min. Then, the mixture was transferred to a 50 mL PTFE autoclave which were gradually heated to 220 °C for 10 h, and cooled slowly to room temperature naturally. The products were collected by filtration and washed with ethanol and cyclohexane after several times. The mother liquor was decanted from the products and the washed products were placed in an oven to dry at about 85 °C for 10 h. The final products were white powder. Throughout the synthesis process, barium rare earth fluorides ($BaYF_5$ and $BLuF_5$) were prepared respectively, using OA as solvent and stabilizing agent, NH_4F as fluoride source.

Hydrothermal synthesis of β-$NaYF_4$ nanocrystals

Yb, Er/Tm, Eu/Tb nanocrystals synthesized by hydrothermal method. In the usual synthesis, 2.5 mmol of ethylenediamine (EDA), 2 mL deionized water, 7.5 mL of anhydrous ethanol and 2.25 mL linoleic acid (LA, 7.23 mmol) were mixed by magnetic stirring at room temperature for 10 min. Dropping 1.5 mL deionized water with 1.25 mol and 0.625 mol $NaNO_2$ aqueous solution (Y/Yb, Er,$TmCl_3$) (20, 2 mol%) were mixed. Then 4 mL deionized water and 4 mmol ethylenediamine dihydrofluoride (EDADF) was added dropwise in it. After 2 min, the prepared aqueous solution was moved into a 100 mL PTFE autoclave, sealing 120 °C hydrothermal reaction for 2 h. We used the moles ratio of the starting material: $EDA:LA:Na^+:RE^{3+}:F^- = 2.5:7.23:1.25:0.625:8$. Until the reaction completed, the autoclave was cooled to room temperature naturally. Sample is dissolved in cyclohexane and using ethanol precipitation samples, we got target product by centrifugal and dried, stored in a desiccator.

Chemical synthesis of 1-chlorohexane-3-methylimidazolium chloride ([C_6mim][Cl])

Equal molar amounts 1-chlorohexane and 1-methylimidazole (0.1 mol) was put together in a round-bottom flask, under magnetic stirrer, an argon atmosphere and reflux condensation. Then the mixture was refluxed for 36 h at 85 °C. Ethyl acetate was used to clean unwanted substances in ionic liquid. Then the ionic liquid obtained by evaporation of the solvent under vacuum (60 °C). After final cleansing, colorless, transparent and viscous liquid was to be obtained. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.557 (s, 1H, H-Ring), 7.127 (s, 1H, H-Ring), 7.519 (s, 1H, H-Ring), 4.327 (t, 2H, CH_2–N), 4.136 (s, 3H, N–CH_3), 1.917 (m, 2H, CH_2–N.), 1.316 (m, 6H, –$(CH_2)_3$–), 0.871 (t, 3H, CH_3–).

Preparation of luminescent hydrogels composed with rare earth fluoride-ionic liquids-agarose

We tried to disperse different amount of fluoride powder in 1-chlorohexane-3-methylimidazolium chloride ionic liquids. After a large number of attempts, it was impossible to disperse 0.020 g fluoride in 0.800 g [C_6mim][Cl]. In accordance with this proportion, full dispersion was achieved only by ultrasonic. If continue to increase the amount of fluoride, the need after the ultrasound was continuous magnetic stirring in reflux condensation condition, and then slightly further dispersed. When the volume of the dispersion reached saturation, an excess of fluoride particles were deposited at the bottom sediments. By high-speed centrifugation, the excess fluoride below will be removed. Agarose gel was prepared by dissolving 0.010 g agarose in 1.000 g ionic liquid [C_6mim][Cl] heated to 100 °C under the stirring of 12 h and then cooling at room temperature. The final luminescent hydrogels are prepared the dispersion of rare earth fluoride in ionic liquids with the assistance of agarose, resulting in the glue-like products. Fig. S1 shows the selected photograph of the hydrogel dispersed with $NaYF_4$:Yb/Er (20/2 mol%) nanocrystals, which can be see the hydrogel forms apparently.

Physical measurements

XRD patterns were recorded with a Bruker D8 diffractometer using Cu Kα radiation with 40 mA and 40 kV. The morphology of the samples was inspected using field emission scanning electron microscopy (FESEM) (Hitachi S4800). Fourier transform infrared (FTIR) spectra were measured within the 4000–400 cm^{-1} region on a Nexus 912 AO446 spectrophotometer with the KBr pellet technique. Luminescent spectra measurements are carried out on an Edinburgh Instruments FLS920 phosphorimeter using a 450 W xenon lamp as excitation source. ^1H NMR measurements are performed on a Bruker 400 MHz NMR spectrometer.

Results and discussion

The XRD pattern in Fig. 1a of $NaYF_4:Ln^{3+}$ (Ln = Eu (2 mol%), Yb/Er (20/2 mol%), Yb/Tm (20/2 mol%) samples can be indexed as the hexagonal phase of $NaYF_4$ (JCPDS No. 16-0334), which definitely indicates that pure hexagonal β-$NaYF_4$:Yb, Er/Tm upconverting nanocrystals can be synthesized. The XRD patterns of $BaREF_5$ nanocrystals in Fig. 1b (RE = Y, Lu) indicate that all the diffraction peaks can be indexed to the exhibit the peaks of pure crystalline tetragonal $BaYF_5$ and $BaLuF_5$, respectively with space group P-421 m, which are consistent with the standard data (JCPDS No. 24-0098, 46-0039). Combined with the experiment details, it is found that the stabilizing agents OM–OA are important for the nanocrystal formation in the hydrothermal reaction process.

Fig. 2 shows the selected transmission electron microscopy (TEM) images for $NaYF_4:Yb^{3+}/Er^{3+}$ (20/2 mol%) (a) and $BaLuF_5:Yb^{3+}/Er^{3+}$ (20/2 mol%) nanocrystals (b). TEM image of $NaYF_4:Yb^{3+}/Er^{3+}$ nanocrystals (20/2 mol%) in Fig. S2a shows that they are about 30–50 nm dimension for sphere-like particles, while the TEM image of $BaYF_4:Yb^{3+}/Er^{3+}$ (20/2 mol%) nanocrystals further prove the sphere-like particle with smaller size of 20–30 nm (Fig. S2b). This takes agreement with the data from the estimation from XRD pattern.

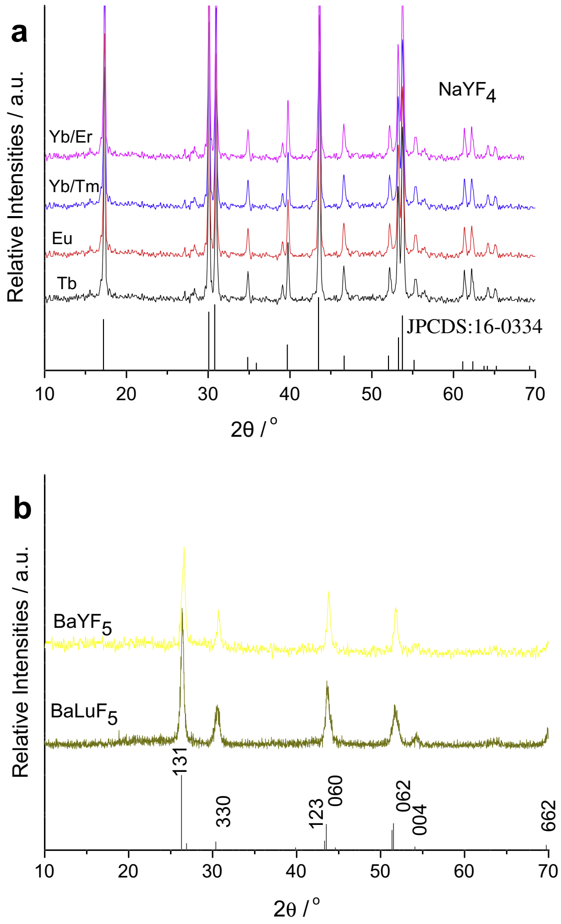

Fig. 1. Selected XRD patterns of $NaYF_4:Ln^{3+}$ (Ln = Eu, Yb/Er, Yb/Tm (20/2 mol%) (a) and $BaREF_5$ (RE = Y, Lu) (b) nanocrystals.

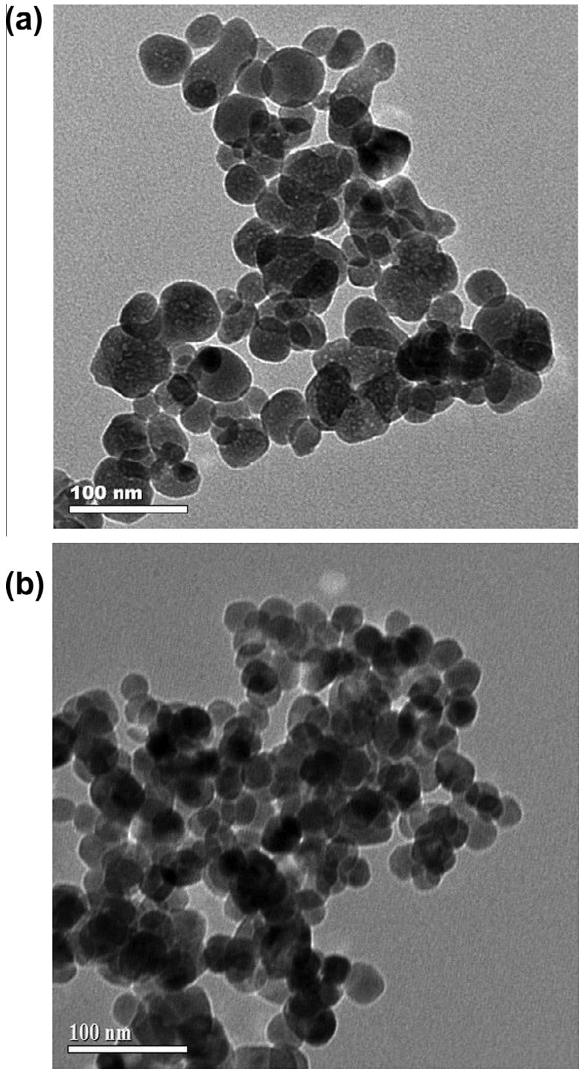

Fig. 2. Selected TEM images of $NaYF_4:Yb^{3+}/Er^{3+}$ (20/2 mol%) (a) and $BaLuF_5:Yb^{3+}/Er^{3+}$ (20/2 mol%) (b) nanocrystals.

The excitation spectra of hydrogel dispersed by $NaYF_4:Eu^{3+}$ (2 mol%) nanocrystals monitoring at the 614 nm of Eu^{3+} exhibit no apparent strong excitation bands in the short wavelength ultraviolet region 200–350 nm (see Fig. 3). Some weak peaks maybe due to the crystal defect in the fluoride host for the doping lanthanide ions. Besides, in the long wavelength excitation range of 350–500 nm, there exist some sharp excitation bands corresponding to the characteristic 4f–4f transitions of Eu^{3+} in the host lattice, which corresponds to the transitions from the $^7F_0$ ground state to the Eu^{3+} excited states of $^5D_4$ (362 nm), $^5G_2$ (382 nm), $^5L_6$ (397 nm), $^5D_3$ (415 nm), and $^5D_2$ (467 nm), respectively. As a result, four main emission peaks are observed in emission spectrum for $NaYF_4:Eu^{3+}$ (2 mol%) nanocrystals, locating at 590, 614, 650 and 685 (697) nm, which is originated from the $^5D_0 \rightarrow {}^7F_J$ transition (J = 0, 1, 2, 3, 4) of Eu^{3+} [23,24]. It can be observed the orange emission for $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} is stronger and close to the red emission for $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}, which may be due to the local environment around Eu^{3+} in $NaYF_4$ host. Besides, the emission for $^5D_0 \rightarrow {}^7F_0$ transition of Eu^{3+} is too weak to be checked.

Fig. 4a shows the hydrogel dispersed by Yb^{3+}/Er^{3+} codoped $NaYF_4$, which exhibits bright green up-conversion luminescence in visible region under the 980 nm excitation. The spectral peaks can be ascribed to transitions of $Er^{3+}:{}^2H_{11/2} \rightarrow {}^4I_{15/2}$ (∼521,

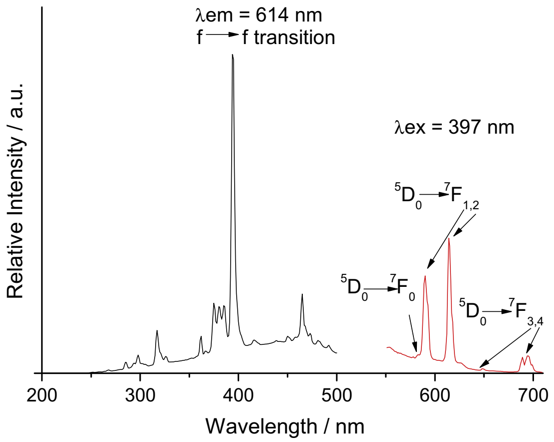

Fig. 3. Luminescent (excitation and emission) spectrum of $NaYF_4$:Eu^{3+} (2 mol%) nanocrystals.

529 nm), $^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ (~549, 550 nm), and $^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ (~654, 661 nm) [25]. Inset of Fig. 4a shows the naked green emission visible to the naked eye. Similarly, the hydrogel dispersed by Yb^{3+}/Tm^{3+} codoped $NaYF_5$ nanocrystals yield blue emission visible to the naked eye under excitation with 980 nm, as shown in the inset of Fig. 4b. The corresponding up-conversion luminescent spectrum shows a weak emission in the indigo centered at about 450 nm and ascribed to the $^{1}D_{2} \rightarrow {}^{3}F_{4}$ transition of Tm^{3+}, whereas very intense blue emissions are observed centered at 477 nm and are assigned to the $^{1}G_{4} \rightarrow {}^{3}H_{6}$ transition. Up-conversion emission can be also detected in the red and NIR regions of the spectra and assigned to the $^{1}G_{4} \rightarrow {}^{3}F_{4}$ (centered at 646 nm), $^{3}F_{3} \rightarrow {}^{3}H_{6}$ (693, 723 nm) and $^{3}H_{4} \rightarrow {}^{3}H_{6}$ (centered at 803 nm) transitions of Tm^{3+} [26]. The NIR emission is much more intense than the blue and red up-conversion emissions.

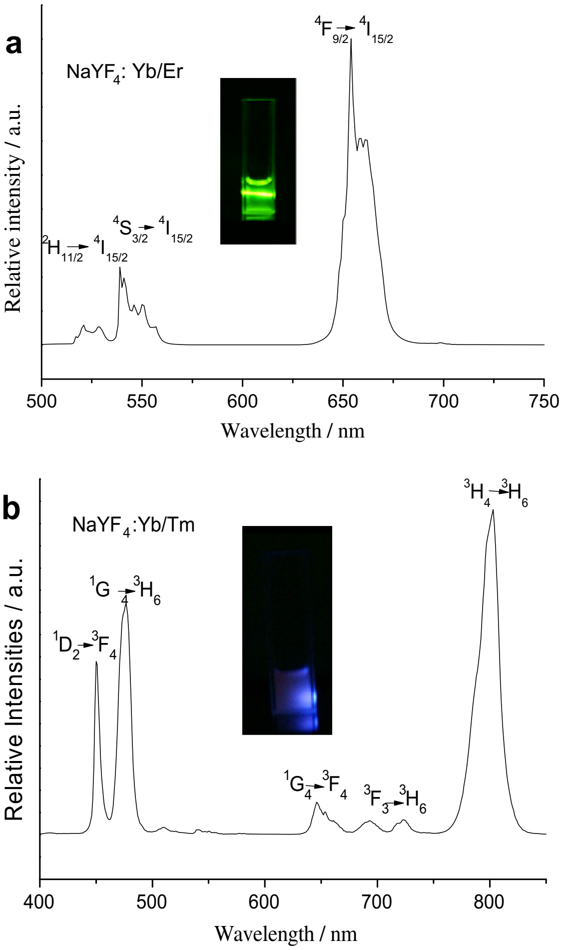

Fig. 4. Up-conversion luminescent spectra and photograph (inset) of $NaYF_4$:Yb^{3+}/Er^{3+} (20/2 mol%) (a), and $NaYF_4$:Yb^{3+}/Tm^{3+} (20/2 mol%) (b) nanocrystals under excitation of 980 nm.

Fig. S4 shows the hydrogel dispersed by Yb^{3+}/Er^{3+} codoped $BaREF_5$ (RE = Y, Lu) nanocrystals, which exhibits bright up-conversion luminescence under the 980 nm excitation. They have similar spectra profile corresponding to the same wavelength positions except for different emission intensities. The spectral peaks can be ascribed to transitions of Er^{3+}:$^{2}H_{11/2} \rightarrow {}^{4}I1_{5/2}$ (~520 nm), $^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ (~540 nm), and $^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ (~655, 664 nm) [24]. Inset of Fig. S4a shows the naked green emission visible to the naked eye. The hydrogel dispersed by Yb^{3+}/Tm^{3+} cooped $BaREF_5$ (RE = Y, Lu) nanocrystals yield blue emission visible to the naked eye under excitation with 980 nm (Fig. S4b). The corresponding up conversion spectra shows a weak emission in the indigo centered at about 450 nm and ascribed to the $^{1}D_{2} \rightarrow {}^{3}F_{4}$ transition, whereas very intense blue emissions are observed centered at 475 nm and are assigned to the $^{1}G_{4} \rightarrow {}^{3}H_{6}$ transition. Up-conversion emission can be also detected in the red and NIR regions of the spectra and assigned to the $^{1}G_{4} \rightarrow {}^{3}F_{4}$ (centered at 650 nm), $^{3}F_{3} \rightarrow {}^{3}H_{6}$ (700 nm) and $^{3}H_{4} \rightarrow {}^{3}H_{6}$ (centered at 800 nm) transitions of Tm^{3+}, respectively [25]. The NIR emission is much more intense than the blue and red up-conversion emissions.

Conclusions

In summary, luminescent hydrogels dispersed with rare earth fluoride nanocrystals codoped with Tm^{3+}/Er^{3+}, Yb^{3+} are prepared by the dispersion and assembly of ion liquid compound (1-chlorohexane-3-methylimidazolium chloride, [C_6mim][Cl]) assisted by agarose. These hydrogels exhibit the characteristic up-conversion luminescence of the corresponding rare earth fluoride nanocrystals. These results provide a strategy to prepare up-conversion luminescent hydrogels with ionic liquid to disperse rare earth fluoride nanocrystals.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.12.071.

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