Luminescent Nanoparticles of Silica-Encapsulated Cadmium – Tellurium (CdTe) Quantum Dots with a Core – Shell Structure: Preparation and Characterization

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Dedicated to Prof. *Jean-Claude Bünzli* on the occasion of his 65th birthday

Water-soluble thioglycolic acid (TGA)-capped CdTe quantum dots (QDs) were synthesized in aqueous medium, and then encapsulated in a silica nanosphere by copolymerization of the TGA-capped CdTe conjugated with (3-aminopropyl)triethoxysilane (APS-CdTe conjugate), free (3-aminopropyl)-triethoxysilane (= 3-(triethoxysilyl)propan-1-amine; APS), and tetraethyl orthosilicate (TEOS) in a H_2O-in-oil reverse microemulsion consisting of *Triton X-100*, octanol, cyclohexane, and H_2O in the presence of aqueous NH_3 solution. The characterizations by transmission electron microscopy (TEM) and luminescence spectroscopy shows that the luminescent nanoparticles are monodisperse, spherical, and uniform in size, *ca.* 50 nm in diameter with a regular core – shell structure. In addition, primary amino groups directly introduced to the nanoparticle's surface by using free APS in the nanoparticle preparation enable the nanoparticles to be used easier as a biolabel. The effects of pH and metal cations on the luminescence of the nanoparticles also suggest that the new nanoparticles could be useful probes for luminescent sensings of pH and Cu^{2+} ion.

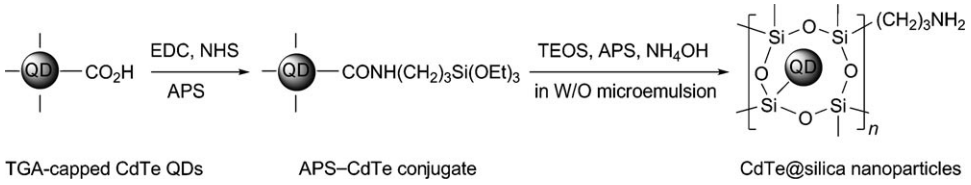
Introduction. – In recent years, much attention has been paid to the surface modification of luminescent quantum dots (QDs) for improving their properties for biotechnology applications [1]. As biolabeling materials, silica-encapsulated luminescent-QD nanoparticles display some advantages compared with free QDs. The silica shell of the nanoparticles can not only impede electron, proton, and oxygen diffusion to the QD's surface resulting in the improvement of chemical and photochemical stabilities of QDs, but also prevent aggregation of the QDs in aqueous systems [2]. In addition, the silica shell can provide good biocompatibility for avoiding the toxic effect of the precursor on cells [3], and is easier to be modified for bioconjugation thus bypassing the tedious surface-modification procedures [4].

There are two established methods for the encapsulation of luminescent QDs within a silica shell. The first one is known as '*Stöber*' approach. *Nann* and *Mulvaney* have demonstrated that single or multiple QDs could be encapsulated in a silica sphere by this method [5], but the size distribution of the prepared QDs@silica nanoparticles was broad and ranged from 30 to 120 nm. The second one is the reverse microemulsion approach. *Murase* and co-workers demonstrated that this method could be used to prepare luminescent CdTe – silica particles with no core – shell structure [6]. More recently, *Yang* and *Gao* [2] and *Su* and co-workers [7] reported that QDs could be incorporated in silica nanoparticles by this method.

In comparison with the previous reports, a covalent binding–copolymerization method was established to prepare amino-surface-modified luminescent CdTe@silica nanoparticles in this work. The new approach is based on the copolymerization of the CdTe conjugate with (3-aminopropyl)triethoxysilane (= 3-(triethoxysilyl)propan-1-amine); APS), free APS, and tetraethyl orthosilicate (TEOS) by the catalysis with aqueous NH_3 solution in a H_2O-in-oil (W/O) reverse microemulsion. Characterizations by transmission electron microscopy (TEM) and luminescence spectroscopy indicate that the new nanoparticles are monodisperse, spherical, and uniform in size with a regular core–shell structure, and show selective luminescence responses to pH and Cu^{2+} ion. These results suggest that the new nanoparticles could be used as luminescent probes for biolabeling and pH and Cu^{2+} sensings.

Results and Discussion. – *Preparation and Characterization of the CdTe@silica Nanoparticles.* The *Scheme* shows the preparation principle of the CdTe@silica nanoparticles. Before the preparation, the TGA-capped CdTe QDs (TGA = thioglycolic acid = 2-mercaptoacetic acid) were covalently coupled to APS by reacting the carboxylic acid group of TGA-coated CdTe with APS in the presence of *N*-hydroxysuccinimide (NHS) and 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide (EDC) [8][9] in a carbonate buffer of pH 9.5 to form a functionalized precursor, APS–CdTe conjugate. *Fig. 1* shows the FT-IR spectra of the TGA-capped CdTe QDs and the APS–CdTe conjugate, respectively. The peaks at 2974 and 2931 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of CH_2 and Me groups, and the peaks at 1649 and 1555 cm^{-1} can be assigned to the characteristic absorptions of the CO–NH–R group.

Scheme. *Preparation Principle of the Core–Shell-Type CdTe@Silica Nanoparticles*



The core–shell-type CdTe@silica nanoparticles were prepared by hydrolytic copolymerization of the precursor with TEOS and APS in a W/O microemulsion containing *Triton X-100* (surfactant), octanol (cosurfactant), cyclohexane, and H_2O, catalyzed by aqueous NH_3 solution. As described previously [10][11], in the W/O microemulsion, the aqueous phase containing the precursor formed innumerable nanodroplets (water pools) by the action of the surfactant and cosurfactant. There each nanodroplet acted as a nanoreactor for the synthesis of nanoparticles, and the nanoparticles were formed undergoing the hydrolysis and polymerization reactions of TEOS.

In the present reverse microemulsion system, cyclohexane was used as a continuous oil phase, in which APS and TEOS were dissolved, and the microscale water pools

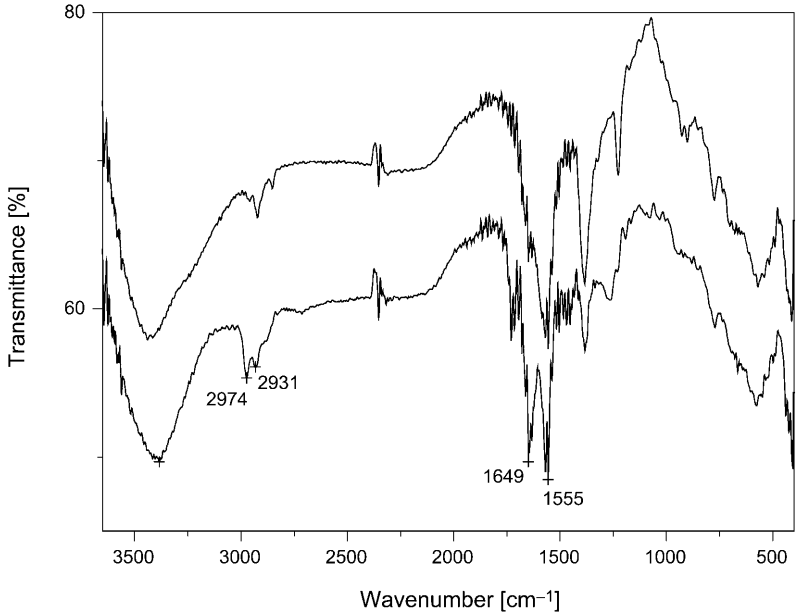


Fig. 1. *FT-IR Spectra of the TGA-capped CdTe QDs* (top) *and the APS–CdTe conjugate* (bottom)

containing luminescent APS–CdTe conjugate were dispersed and stabilized by *Triton X-100* and octanol. The formation of the silica shell was initiated by hydrolyzing APS and TEOS at the oil/H_2O interface in the presence of aqueous NH_3 solution. Thus, the CdTe@silica core–shell structure was formed by the following processes: the hydrolyzed silica species, formed in the initial stage of the reaction, were bound onto the surface of the CdTe QDs to form a silica monolayer, and then the silica layer grew up *in situ* by adsorbing the subsequently hydrolyzed APS and TEOS. With this method, uniform CdTe@silica nanoparticles with a regular core–shell structure, 48 ± 3 nm in diameter, were obtained (*Fig. 2*).

In our method, free APS was used for the nanoparticle preparation to introduce primary amino groups onto the surface of the nanoparticles [12–15]. The effect of the APS amount in the preparation system on the shape and size of the nanoparticles was investigated. *Fig. 3* shows the TEM images of five kinds of nanoparticles prepared with 2, 3.5, 5, 8, and 10 mg of APS; as shown, the size of the nanoparticles is increased with the increase of the APS amount from 2 to 5 mg, and further increase of the APS amount from 5 to 10 mg causes the nanoparticles to become irregular. This phenomenon might be due to the faster hydrolysis of APS than that of TEOS, which forms a layer of amino groups on the surface of the nanoparticles, and thus the further formation of Si–O–Si bonds on the nanoparticle's surface is obstructed. This result indicates that higher APS concentration in the preparation system is unfavorable for obtaining smaller and uniform nanoparticles.

Fig. 4 shows the absorption and emission spectra of the free CdTe QDs and the emission spectrum of the CdTe@silica nanoparticles in distilled H_2O. The solution of

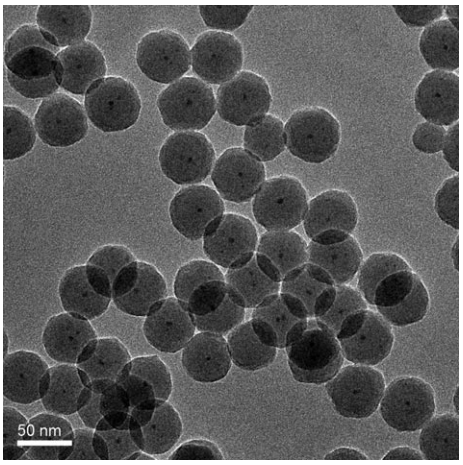


Fig. 2. *TEM Image of the luminescent CdTe@silica nanoparticles with a core–shell structure*

free CdTe QDs shows an absorption band centered at 525 nm and an emission band centered at 577 nm at room temperature. In comparison with the free CdTe QDs, the maximum emission wavelength of the CdTe@silica nanoparticles is shifted by 15 nm toward shorter wavelengths (562 nm). This might be caused by the structure change of the capping reagent (TGA) on the surface of the CdTe QDs after forming the CdTe@silica nanoparticles.

Effects of pH and Metal Ions on the Luminescence of the CdTe@Silica Nanoparticles. The effect of pH on the luminescence of the CdTe@silica nanoparticles in 0.05M phosphate buffers of different pHs (pH 2 to 13) was investigated. As shown in *Fig. 5*, the luminescence intensity of the nanoparticles is linearly increased with the increase of pH from 2 to 8, and remains stable from pH 8 to 11. This result suggests that the nanoparticles could be a useful luminescent probe for pH sensing ($pH < 8$), and the luminescence detection should be carried out in a buffer of $pH > 8$ if the nanoparticles are used as a biolabel.

Fig. 6 shows the effects of metal ions on the luminescence of the free CdTe QDs and the CdTe@silica nanoparticles. It was found that the luminescence of the free CdTe QDs could be strongly quenched by Cu^{2+}, with a 92% decrease of luminescence intensity in the presence of 15 μM Cu^{2+} ion. This result is in agreement with the previously reported result [16], showing that the free CdTe QDs are unsuitable to be used as a luminescence biolabel for the Cu^{2+}-containing samples. However, after forming the CdTe@silica nanoparticles, the luminescence-quenching effect of Cu^{2+} ion is remarkably reduced. The luminescence intensity of the CdTe@silica nanoparticles is decreased by 76% in the presence of 15 μM Cu^{2+} ion. It was also found that the quenching effects of other metal ions including Mg^{2+} (not shown), Ca^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, and Ni^{2+} on the luminescence of both the free CdTe QDs and the CdTe@silica nanoparticles are weaker. The selective quenching of Cu^{2+} ion on the luminescence of the free CdTe QDs and the CdTe@silica nanoparticles suggests that these materials could be used as luminescent sensing probes for the Cu^{2+} ion.

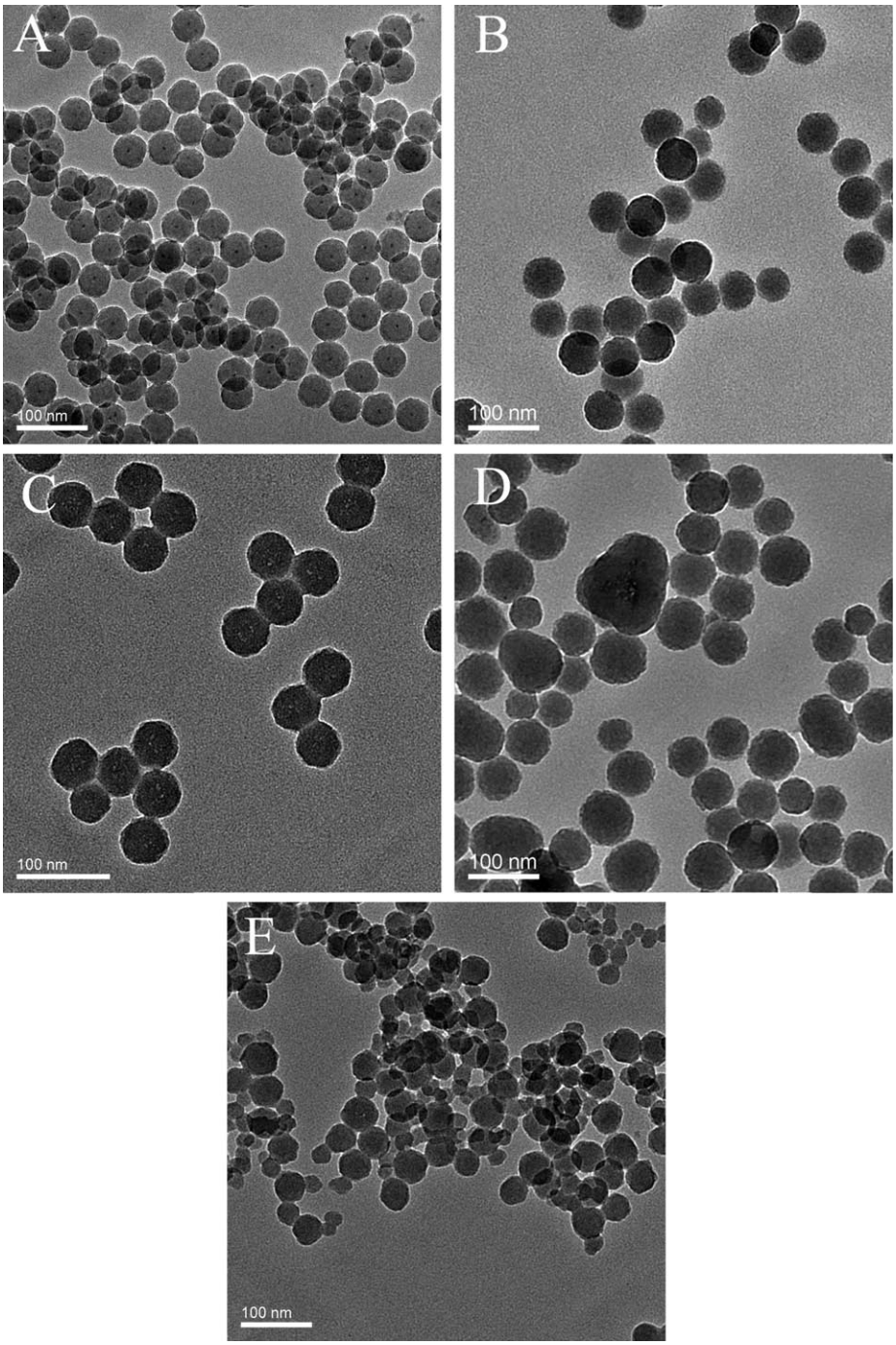


Fig. 3. *TEM Images of the core–shell-type CdTe@silica nanoparticles prepared with different amounts of APS* (A: 2 mg of APS, 48 ± 3 nm in diameter; B: 3.5 mg of APS, 52 ± 5 nm in diameter; C: 5 mg of APS, 52 ± 3 nm in diameter; D: 8 mg of APS, irregular; E: 10 mg of APS, irregular)

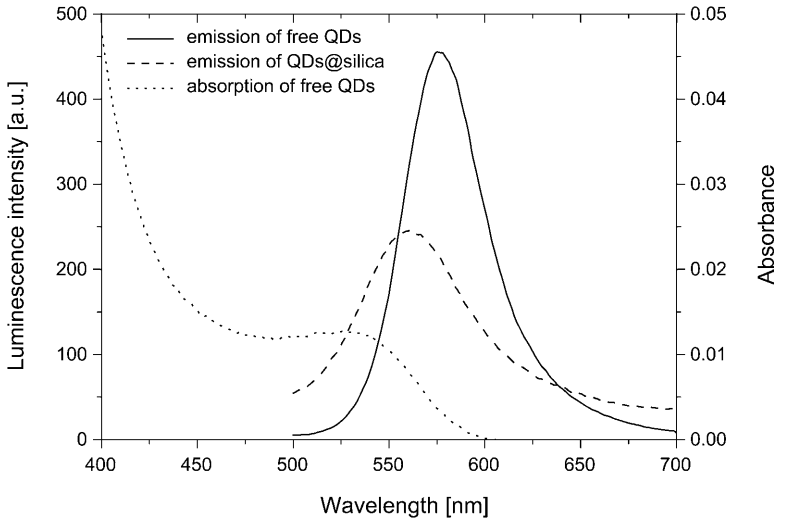


Fig. 4. *Absorption spectrum* (400–600 nm) *of free CdTe QDs and emission spectra* (500–700 nm) *of free CdTe QDs and of the CdTe@silica nanoparticles in distilled* H_2O

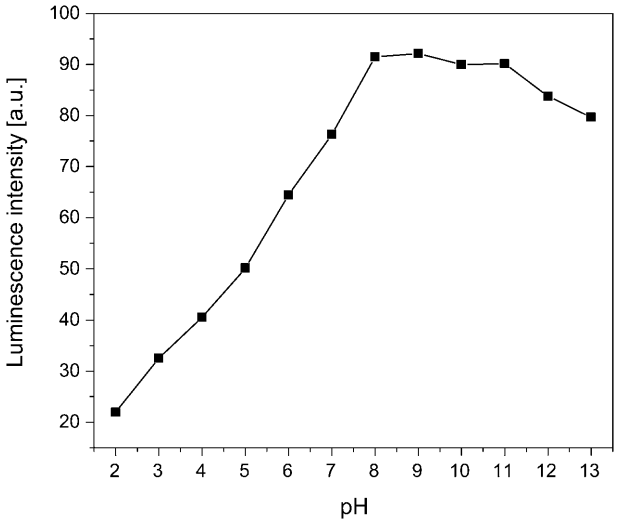


Fig. 5. *Effect of pH on the luminescence intensity of the CdTe@silica nanoparticles' solution*

Conclusion. – In this work, a covalent binding–copolymerization method was developed for the preparation of luminescent nanoparticles of silica-encapsulated CdTe QDs. The new nanoparticles are monodisperse, and uniform in size with a regular core–shell structure. The primary amino groups on the surface of the nanoparticles allow the nanoparticles to be more conveniently used as a luminescence biolabel. In addition, because the luminescence of the new nanoparticles is pH-dependent and can

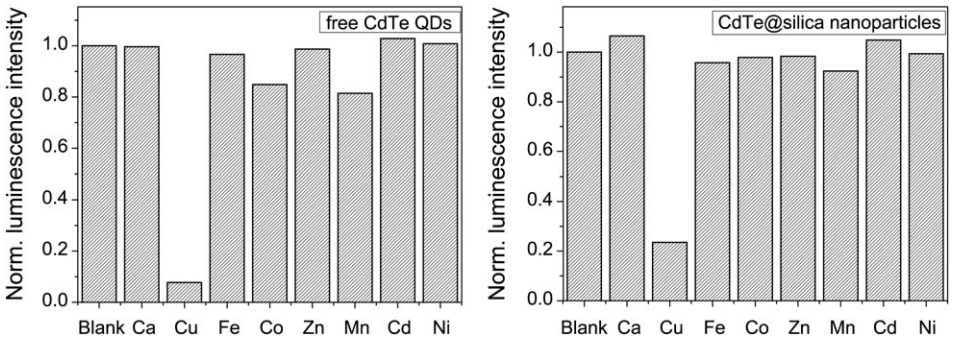


Fig. 6. *Effects of different metal ions on the luminescence intensities of the free CdTe QDs and the CdTe@silica nanoparticles* ($5 \cdot 10^{-5}$ M for Ca^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, and Ni^{2+}, and $1.5 \cdot 10^{-5}$ M for Cu^{2+})

be selectively quenched by Cu^{2+} ion, this kind of luminescent materials is also expected to be useful as luminescent sensing probes for pH and Cu^{2+} ion.

This work was financially supported by grants from the *National Natural Science Foundation of China* (No. 20835001) and the *Specialized Research Fund for the Doctoral Program of Higher Education of China* (No. 200801410003).

Experimental Part

1. *Materials and Reagents.* Tellurium powder (99.999%) was purchased from *Sinopharm Chemical Reagent Co., Ltd.*, and TGA (> 97%) from *Alfa Aesar*. TEOS, APS, *Triton X-100*, NHS, and EDC · HCl were from *Acros Organics*. Unless otherwise stated, all chemicals were of anal. grade, purchased from commercial sources and used without further purification.

2. *Instrumentation.* UV/VIS and Luminescence Spectra: *Perkin-Elmer-Lambda-35* UV/VIS spectrophotometer and *LS-50B* luminescence spectrometer, resp. TEM: *FEI-Tecnai-G220* transmission electron microscope (determination of the shape and size of the nanoparticles). FT-IR Spectra: *Nicolet-Avatar-360* FT-IR spectrometer; KBr pellets. All optical measurements were carried out at r.t. under ambient conditions.

3. *Water-Soluble CdTe QDs.* The H_2O-soluble CdTe QDs were synthesized according to a previously reported method [2]. Briefly, after a NaHTe soln. was synthesized in an O_2-free aq. soln. by reacting $NaBH_4$ with tellurium powder at a molar ratio of 2 : 1, the fresh NaHTe soln. was added to Ar-saturated aq. $1.25 \cdot 10^{-3}$ M $CdCl_2$ soln. at pH 11.2 in the presence of TGA as a stabilizing agent. The molar ratio Cd^{2+}/TGA/HTe^- was fixed at 1 : 2.4 : 0.5. The resulting mixture was then refluxed under stirring to allow the formation of the CdTe nanocrystals. The CdTe QDs of different sizes were synthesized under different refluxing conditions. The TGA-capped CdTe QDs with the maximum emission wavelength at 577 nm and a luminescence quantum yield of 25% at r.t. were used for the silica encapsulation.

4. *CdTe@Silica Nanoparticles.* The APS – CdTe conjugate was prepared before the nanoparticle preparation. To a soln. of EtOH (80 µl) and 0.05M carbonate buffer of pH 9.5 (20 µl) were added CdTe QDs (4 mg), NHS (6.2 mg), and EDC · HCl (2.0 mg). After the mixture was stirred for 1 h at r.t., APS (2 µl) was added, and then the soln. was stirred for 2 h to form the APS – CdTe conjugate soln.

The CdTe@silica nanoparticles were prepared as follows: to a W/O microemulsion consisting of *Triton X-100* (1.89 g), octanol (1.48 g), cyclohexane (5.84 g), and H_2O (480 µl) was added the above-prepared APS – CdTe conjugate soln. After the soln. was stirred for 30 min at r.t., TEOS (100 µl) and APS (2 mg) were added. The copolymerization reaction was initiated by adding conc. aq. NH_3 soln. (60 µl), and the reaction was allowed to continue for 24 h at r.t. The nanoparticles were isolated from the

microemulsion by adding acetone (20 ml), centrifuging, and washing with EtOH and H_2O several times to completely remove surfactant and unreacted materials. The obtained nanoparticles were redispersed in dist. H_2O for the further characterizations.

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Received April 29, 2009