Two-photon absorption enhancement induced by aggregation with accurate photophysical data: spontaneous accumulation of dye in silica nanoparticles†

Lin Li,[a] Yupeng Tian,*[ab] Jiaxiang Yang,*[ab] Pingping Sun,[a] Lin Kong,[a] Jieying Wu,[a] Hongping Zhou,[a] Shengyi Zhang,[a] Baokang Jin,[a] Xutang Tao[b] and Minhua Jiang[b]

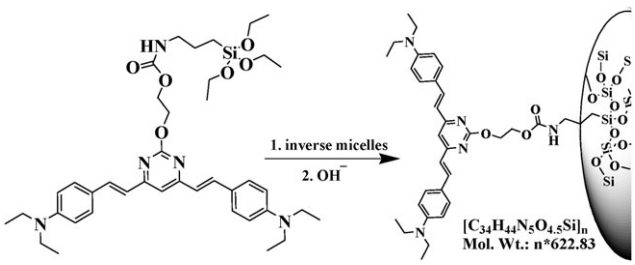
Received (in Cambridge, UK) 11th September 2009, Accepted 11th December 2009
First published as an Advance Article on the web 11th January 2010
DOI: 10.1039/b918841j

The accurate photophysical data of dye-concentrated nanoparticles have been measured by the strategy of constructing ethoxysilane hydrolysis-assisted nanomaterials, which give rise to a large enhancement in two-photon absorption.

In the past decades, researchers have been more interested in seeking novel two-photon absorption (TPA) materials for their promising applications in optical limiting, two-photon laser scanning fluorescence imaging, microfabrication, 3D optical data storage, photodynamic therapy and so on.[1] They have done substantial research on structure–property relationships. Although it is still under exploration, thanks to the effort of scientists, some efficient molecular design strategies were put forward to provide guidelines for the development of materials with large TPA cross-sections.[2] Scaling down these materials has recently afforded an exciting new class of highly tailorable nanomaterials known as dye-concentrated nanoparticles (DCNs), which exhibit enhanced fluorescence and TPA activity by aggregation.

Compared with purely inorganic or organic nanomaterials, new phenomenon can arise in DCNs by the careful selection of organic building blocks and particle species. Cohanoschi *et al.*[3a] observed strong surface plasmon enhancement of TPA of chromophores in solution containing gold colloid. Marder and co-workers[3b,c] also observed strong enhancement of the TPA of organic molecules near silver nanoparticle fractal clusters, and this enhancement effect was manifested in the composite materials with very strong TPA. Prasad and co-workers[4] reported a novel class of dye-concentrated composite nanoparticles with enhanced TPA by nanoaggregation. Our previous work[5] found enhanced TPA by combination of the large organic salt with CdS nanoclusters. This field has been growing rapidly during the past ten years due to the realization of the two-photon-based technologies as mentioned above and improved methods of characterization. All these interesting results are of scientific significance and technical potential. However, up till to now, the photophysical data of DCNs cannot be exactly measured due to the complicated components and dubious molecular weight. In this communication, we devised a novel strategy to construct ethoxysilane hydrolysis-assisted DCNs, which have determinate photophysical data and aggregation-induced enhancement of TPA (Scheme 1).

The functional precursor was synthesized by covalently linking a TPA dye (a pyrimidine derivative) to 3-isocyanatopropyltriethoxysilane (ICTES) and was characterized by MS, NMR and IR (see ESI†). Pyrimidine derivatives exhibit intense single- and two-photon excited fluorescence,[6] and can easily undergo reactions with ICTES. The synthesis of the DCNs was performed in an inverse micelles solvent mixture (THF/1-butanol/water) in the presence of a base (NaOH). The template-directed synthesis followed a procedure similar to that used by Moreau *et al.*,[7] and differed from that used by Prasad and Blanchard-Desce *et al.*[8] since tetraethyloxyl orthosilicate (TEOS) or any other co-polymerized silanes were left out. After hydrolysis, the TEM (Fig. 1(a)) analysis revealed that the resulting solid particles were relatively uniform spheres with diameters of $\sim$5 μm. The magnified SEM image exclusively shows that an individual microsphere is composed of many discrete particles with $\sim$100 nm diameters (Fig. 1(b)). The XRD diffractogram of DCNs is reproduced in Fig. 1(c). The hybrid materials are totally amorphous in the range of $10^\circ \leq n \leq 80^\circ$. Broad signals are observed and it is well known that these broad signals correspond to the existence of a short-range order in the material.[9] The broad peaks centered at 23.00° were ascribed to the coherent diffraction of the siliceous backbone of the hybrids.[10] The absence of any crystalline regions in these samples correlates well with the presence of organic chains in the host inorganic framework.



Scheme 1 Schematic representation of the preparation progress of DCNs.

[a] *Department of Chemistry, Anhui University, Hefei, 230039, P. R. China. E-mail: yptian@ahu.edu.cn; Fax: +(86) 551-5107304; Tel: +(86) 551-5108151*
[b] *State Key Laboratory of Crystal Materials, Shandong University, 250100, Jinan, P. R. China*

† Electronic supplementary information (ESI) available: Synthesis procedures and characterization of dye, details of optical spectra. CCDC 752289. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/b918841j

Fig. 1 As-synthesized **DCNs**: (a) TEM image (scale bar = 10 μm); (b) SEM image (scale bar = 2 μm). (c) The XRD diffractogram of the DCNs.

Subsequently, the dye and DCNs were characterized by optical absorption and emission spectroscopy. Steady-state absorption and emission spectra of dilute suspensions (1.0×10^{-6} mol L^{-1}, based on Mol. Wt. of monomer) of the particles in DMF (Fig. 2(a)) reveal the presence of the covalently linking TPA dye inside or outside the particles: the typical dye-related one-photon absorption ($\lambda_{max} \approx 440$ nm) and emission bands ($\lambda_{max} \approx 560$ nm) can be distinguished. The extensive extraction applied, ensures the removal of free dye. No obvious light scattering effect has been observed from the one-photon absorption spectrum of DCNs, but the absorption of the DCNs is slightly blue-shifted compared to the free dye in DMF. More importantly, the emission bandwidth of DCNs is dramatically narrower than that of the fluorescence band of free dye. Both the dye and DCNs show sensitivity to the solvent and exhibit moderate quantum yields, the detailed linear photophysical data can be found in the ESI†. All these provide evidence that immobilization of dyes *via* ethoxysilane hydrolysis-assisted aggregation is a valid strategy and it shows only a minor influence on the linear optical properties of the dye, which is very important for optical applications.[1f]

In time-correlated single-photon counting measurements, the fluorescence of the dye and DCNs both show nonmono-exponential decay. The decay curves can generally be adequately described by the sum of two exponentials, a shorter lifetime (1.57 ns for free dye and 0.86 ns for DCNs, respectively) and a longer lifetime (2.60 ns for free dye and 2.52 ns for DCNs, respectively). Fractional intensities of the longer decay components are 44.5% for the free dye and 65.5% for DCNs. Also, fractional amplitudes of the longer decay components are 32.6% for the free dye and 38.7% for DCNs. Obviously, for either intensity or amplitude based on the calculation of life time, the longer decay components of DCNs are more than those of the free dye. In combination with the slightly higher fluorescence quantum yields of the free dye, this reveals that an efficient interaction occurs in DCNs. Such a feature further confirms the efficient immobilization of the dyes on the silica mesoporous structures.

As shown in the ESI†, the linear dependence on the square of the input laser power of the free dye suggests that it is a two-photon excitation mechanism obviously. The TPA spectra of the free dye and DCNs were determined in detail in the wavelength range (from 720 to 860 nm) by investigating their two-photon-excited fluorescence in DMF with a concentration of 1.0×10^{-3} mol L^{-1} (based on Mol. Wt. of monomer), and are shown in Fig. 2(b). The TPA cross sections (δ) were determined by comparing their two-photon excited fluorescence to that of fluorescein in water (pH = 11).[11] It is worthwhile noting that at the wavelength range (720–860 nm) δ of the free dye is negligible in the absence of DCNs but is strongly enhanced in DCNs (δ = 284 GM, 1 GM = 10^{-50} cm^4 s $photon^{-1}$), thus offering a >1400-fold increase, which seems slightly different from Marder's discussion of nanoparticles as a carrier for large numbers of dyes.[3b] It is worth underlining that this value exceeds that of many fluorophores widely used in biology, including fluorescein, BODIPY, DAPI and GFP.[12,13] The spectra of DCNs display one excitation peak, and this feature is similar to that observed in the linear absorption spectra, except that the optimal excitation wavelengths (830 nm) are roughly doubled.

In conclusion, we have demonstrated that ethoxysilane hydrolysis-assisted DCNs result not only in a significant increase in the TPA cross sections but also a solid holding of the linear optical properties of the dye, which demonstrates the utility of using the silica particles as a tool for concentrating

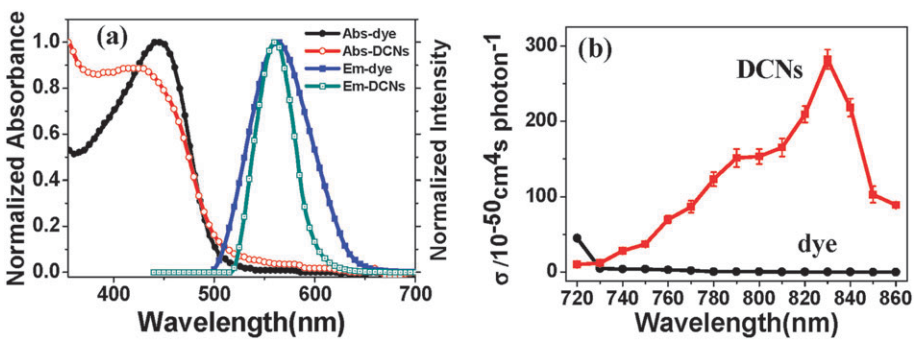


Fig. 2 (a) Normalized UV-vis absorption and PL spectra of **dye** and **DCNs** in DMF. The fluorescence was excited at 445 nm for the **dye** and 431 nm for **DCNs**, respectively; (b) TPA cross section of **dye** and **DCNs** in DMF *versus* excitation wavelengths from 720 nm to 860 nm in DMF.

dyes. This approach is not limited to the design of more efficient TPA materials but should be applicable to a broad range of modified fluorophores widely used in biology.

This work was supported by a grant for the National Natural Science Foundation of China (20771001, 50873001, 20875001, 50703001,20775001 and 50532030), the Team for Scientific Innovation Foundation of Anhui Province (2006KJ007TD), and the Natural Science Foundation of Anhui Province (070414188).

Notes and references

1 (*a*) B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I. Y. S. Lee, D. McCord-Maughon, J. Q. Qin, H. Rockel, M. Rumi, X. L. Wu, S. R. Marder and J. W. Perry, *Nature*, 1999, **398**, 51–54; (*b*) P. A. Bouit, G. Wetzel, G. Berginc, B. Loiseaux, L. Toupet, P. Feneyrou, Y. Bretonniere, K. Kamada, O. Maury and C. Andraud, *Chem. Mater.*, 2007, **19**, 5325–5335; (*c*) S. Kawata, H. B. Sun, T. Tanaka and K. Takada, *Nature*, 2001, **412**, 697–698; (*d*) G. S. He, J. D. Bhawalkar, C. F. Zhao and P. N. Prasad, *Appl. Phys. Lett.*, 1995, **67**, 2433–2435; (*e*) H. M. Kim, C. Jung, B. R. Kim, S. Y. Jung, J. H. Hong, Y. G. Ko, K. J. Lee and B. R. Cho, *Angew. Chem., Int. Ed.*, 2007, **46**, 3460–3463; (*f*) G. S. He, L. S. Tan, Q. D. Zheng and P. N. Prasad, *Chem. Rev.*, 2008, **108**, 1245–1330; (*g*) H. M. Kim and B. R. Cho, *Chem. Commun.*, 2009, 153–164; (*h*) Y. H. Gao, J. Y. Wu, Y. M. Li, P. P. Sun, H. P. Zhou, J. X. Yang, S. Y. Zhang, B. K. Jin and Y. P. Tian, *J. Am. Chem. Soc.*, 2009, **131**, 5208–5213.

2 (*a*) D. Beljonne, W. Wenseleers, E. Zojer, Z. Shuai, H. Vogel, S. J. K. Pond, J. W. Perry, S. R. Marder and J. L. Brédas, *Adv. Funct. Mater.*, 2002, **12**, 631–641; (*b*) G. P. Bartholomew, I. Ledoux, S. Mukamel, G. C. Bazan and J. Zyss, *J. Am. Chem. Soc.*, 2002, **124**, 13480–13485; (*c*) O. Mongin, L. Porrès, M. Charlot, C. Katam and M. Blanchard-Desce, *Chem.–Eur. J.*, 2007, **13**, 1481–1498; (*d*) Q. D. Zheng, G. S. He and P. N. Prasad, *Chem. Mater.*, 2005, **17**, 6004–6011; (*e*) Y. P. Tian, L. Li, Y. H. Zhou, P. Wang, H. P. Zhou, J. Y. Wu, Z. J. Hu, J. X. Yang, L. Kong, G. B. Xu, X. T. Tao and M. H. Jiang, *Cryst. Growth Des.*, 2009, **9**, 1499–1504; (*f*) H. M. Kim, B. R. Kim, M. J. An, J. H. Hong, K. J. Lee and B. R. Cho, *Chem.–Eur. J.*, 2008, **14**, 2075–2083; (*g*) N. Tian and Q. H. Xu, *Adv. Mater.*, 2007, **19**, 1988–1991.

3 (*a*) I. Cohanoschi and F. E. Hernandez, *J. Phys. Chem. B*, 2005, **109**, 14506–14512; (*b*) F. Stellacci, C. A. Bauer, T. Meyer-Friedrichsen, W. Wenseleers, S. R. Marder and J. W. Perry, *J. Am. Chem. Soc.*, 2003, **125**, 328–329; (*c*) W. Wenseleers, F. Stellacci, T. Meyer-Friedrichsen, T. Mangel, C. A. Bauer, S. J. K. Pond, S. R. Marder and J. W. Perry, *J. Phys. Chem. B*, 2002, **106**, 6853–6863.

4 (*a*) M. Lal, L. Levy, K. S. Kim, G. S. He, X. Wang, Y. H. Min, S. Pakatchi and P. N. Prasad, *Chem. Mater.*, 2000, **12**, 2632–2639; (*b*) S. Kim, H. E. Pudavar and P. N. Prasad, *Chem. Commun.*, 2006, 2071–2073; (*c*) S. Kim, Q. D. Zheng, G. S. He, D. J. Bharali, H. E. Pudavar, A. Baev and P. N. Prasad, *Adv. Funct. Mater.*, 2006, **16**, 2317–2323; (*d*) F. Erogbogbo, K. T. Yong, I. Roy, G. X. Xu, P. N. Prasad and M. T. Swihart, *ACS Nano*, 2008, **2**, 873–878.

5 X. J. Zhang, Y. P. Tian, F. Jin, J. Y. Wu, Y. Xie, X. T. Tao and M. H. Jiang, *Cryst. Growth Des.*, 2005, **5**, 565–570.

6 (*a*) L. Li, Y. P. Tian, J. X. Yang, P. P. Sun, J. Y. Wu, H. P. Zhou, S. Y. Zhang, B. K. Jin, X. J. Xing, C. K. Wang, M. Li, G. H. Cheng, H. H. Tang, W. H. Huang, X. T. Tao and M. H. Jiang, *Chem.–Asian J.*, 2009, **4**, 668–680; (*b*) Z. J. Liu, P. Shao, Z. L. Huang, B. Liu, T. Chen and J. G. Qin, *Chem. Commun.*, 2008, 2260–2262; (*c*) Z. J. Liu, T. Chen, B. Liu, Z. L. Huang, T. Huang, S. Y. Li, Y. X. Xua and J. G. Qin, *J. Mater. Chem.*, 2007, **17**, 4685–4689; (*d*) B. Liu, H. L. Zhang, J. Liu, Y. D. Zhao, Q. M. Luo and Z. L. Huang, *J. Mater. Chem.*, 2007, **17**, 2921–2929.

7 J. J. E. Moreau, L. Vellutini, M. W. C. Man and C. Bied, *Chem.–Eur. J.*, 2003, **9**, 1594–1599.

8 (*a*) S. Kim, T. Y. Ohulchanskyy, H. E. Pudavar, R. K. Pandey and P. N. Prasad, *J. Am. Chem. Soc.*, 2007, **129**, 2669–2675; (*b*) V. Lebret, L. Raehm, J. O. Durand, M. Smaïhi, C. Gerardin, N. Nerambourg, M. H. V. Werts and M. Blanchard-Desce, *Chem. Mater.*, 2008, **20**, 2174–2183.

9 (*a*) G. Cerveau, R. J. P. Corriu, E. Framery and F. Lerouge, *Chem. Mater.*, 2004, **16**, 3794–3799; (*b*) B. Yan and H. F. Lu, *Inorg. Chem.*, 2008, **47**, 5601–5611.

10 (*a*) L. D. Carlos, V. D. Z. Bermudez, R. A. S. Ferreira, L. Marques and M. Assuncao, *Chem. Mater.*, 1999, **11**, 581–588; (*b*) S. S. Nobre, P. P. Lima, L. Mafra, R. A. S. Ferreira, R. O. Freire, L. S. Fu, U. Pischel, V. D. Bermudez, O. L. Malta and L. D. Carlos, *J. Phys. Chem. C*, 2007, **111**, 3275–3284.

11 C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481–491.

12 A. Picot, A. D'Aléo, P. L. Baldeck, A. Grichine, A. Duperray, C. Andraud and O. Maury, *J. Am. Chem. Soc.*, 2008, **130**, 1532–1533.

13 C. Xu, W. Zipfel, J. B. Shear, R. M. Williams and W. W. Webb, *Proc. Natl. Acad. Sci. U. S. A.*, 1996, **93**, 10763–10768.