Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

Silver nanoparticle based highly selective and sensitive solvatochromatic sensors for colorimetric detection of 1,4-dioxane in aqueous media

Anshu Kumar,[a,b] Gaurav Vyas,[a,b] Madhuri bhatt,[a,b] Shreya Bhatt,[a,b] and Parimal Paul[*a,b]

Citrate stabilised silver nanoparticle (Ci-AgNPs) based solvatochromic sensor, which functions as highly selective and sensitive colorimetric probe for 1,4-dioxane in aqueous media is reported. The surface of the AgNPs generates reactive oxygen species, which promote degradation of 1,4-dioxane, assembled at the vicinity of the nanoparticle surface through charge transfer interaction. During this process, Ag^0 is oxidised to Ag^+ and the yellow colour of the solution turned to colourless. This sensor is used for estimation of 1,4-dioxane in ground water and also vapour of 1,4-dioxane diffused in aqueous media.

Solvatochromic property, which is a phenomenon where position of optical absorption bands and thereby colour of the solution can be influenced by surrounding environments such as solvents, has been fairly studied with various organic compounds,[1] organometallic,[2] metal-organic framework,[3] metal complexes[4] and hybrid materials[5]. In this class of compounds, the shifts of the absorbance bands and the colour of the solutions are dependent on polarity of the solvents in which compounds are dissolved,[1] solvents encapsulated in the pores/interlayers,[3,5] interacted at a co-ordinately unsaturated sites[2] and the solvent exchanged at the labile sites.[4] Most of these systems, the absorption bands display broad overlaps, as a result colorimetric differentiation of solvents has been extremely difficult. It is therefore, important to develop solvatochromic sensors for selective detection and quantification of solvents. Only a few examples of this class of sensors are available in the literature, they are a trinuclear Ag(I) pyrazolate based luminescence sensor for selective sensing of benzene,[6] a fluorescent Au(I)@(Ag$_2$/Ag$_3$)-thiolate cluster for sensing of DMSO,[7] and recently a tailor made colorimetric and florescence

[a]Analytical Discipline and Centralized Instrument Facility, CSIR-Central Salt & Marine Chemicals Research Institute, Bhavnagar 364 002, India.
[b]Academy of Scientific and Innovative Research (AcSIR),CSIR-CSMCRI, Bhavnagar, 364002, India.
Electronic Supplementary Information (ESI) available: synthesis, experimental condition and Figs. S1–S13, See DOI: 10.1039/b000000x/

turn-on type solvatochromic sensors that enables selective detection of THF and also can differentiate dichloromethane and chloroform has been reported.[8]

In the present study, we aimed to develop nanoparticle based solvatochromic sensors for selective detection and estimation of carcinogenic hazardous solvent(s). In this context, silver nanoparticles are promising because they have one of the highest visible-region extinction coefficients (10^9 $M^{-1}cm^{-1}$ order) with yellow colour due to surface plasmon resonance (SPR).[9] This SPR band is very sensitive to the particle size, shape and the interparticle distances, the transition of nanoparticles from dispersion to aggregation also exhibit distinct colour change and that property can be used as a tool to monitor the recognition event.[10]

Among various widely used solvents, cyclic ether compounds like 1,4-dioxane has been categorized as carcinogenic hazardous solvent.[11] Inhalation exposure to 1,4-dioxane causes vertigo, drowsiness, headache, anorexia and irritation of the eyes, nose, throat, and lungs in humans.[12] Damage to the liver and kidneys has been observed in rats chronically exposed in their drinking water.[13,14] Tumors have been observed in orally exposed animals and the Environmental Protection Agency (EPA), USA has classified 1,4-dioxane as a Group B2, probable human carcinogen.[15] In recent times, 1,4-dioxane being detected in excessive amount both in ground as well as surface water.[16] 1,4-Dioxane has also been used as a stabilizing agent for chlorinated solvents in the textile and paper industries.[11,17] Therefore, the risk of generating high level 1,4-dioxane contaminated water or processed solvents becomes high so as the detection of 1,4-dioxane becomes very essential. There are sophisticated instrument based methods for detection of 1,4-dioxane,[18] however, these methods involve large and costly instruments, which are not suitable for outdoor use. Therefore, it is necessary to develop a simple, selective, highly sensitive and easy to carry method for the detection of 1,4-dioxane, particularly in aqueous media.

In this communication, we report citrate coated AgNPs as a novel solvatochromic sensors for 1,4-dioxane in aqueous media. It has also been applied for quantitative estimation of 1,4-dioxane in vapour as
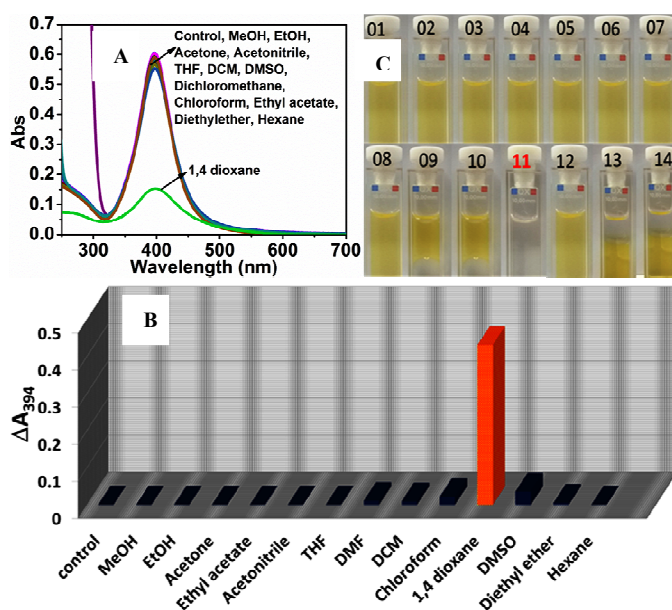
Fig 1 (A) Absorption spectral change of ci-AgNPs (3.2 nM) after interaction with 13 different solvents, (B) plot of the change in absorption intensity at 394 nm (ΔA_{394}) of ci-AgNPs (pH 8) in the absence (01) and presence of different solvents (02-14) for 5 min. (C) photograph showing no colour change was observed for solvents other than 1,4-dioxane.
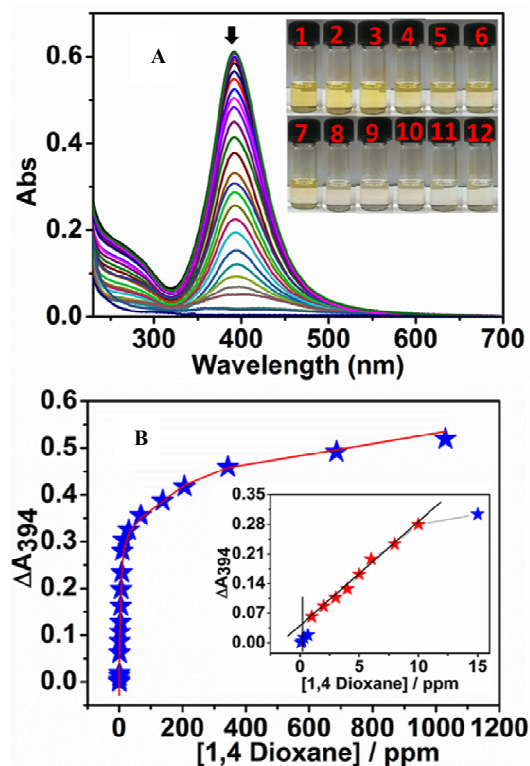

Fig. 2 (A) Absorption spectral change of ci-AgNPs (3.2 nM, pH 8) upon addition of different amounts of 1,4-dioxane (0-1000 ppm) with 5 min incubation and instant photographs showing the colorimetric change is inserted, (B) The plot of ΔA_{394} as a function of the concentration of 1,4-dioxane and the linear relationship in the concentration range 1-10 ppm (inserted).

well as in ground water. To the best of our knowledge this is the first report to use citrate coated AgNPs as solvatochromic sensors and also to use for selective detection of 1,4-dioxane.

Citrate stabilized silver nanoparticles (Ci-AgNPs) were prepared by the reaction of silver nitrate and sodium borohydride in aqueous media at room temperature in presence of trisodium citrate (ESI for details). The Ci-AgNPs exhibits characteristic absorption band at 394 nm (Fig. S1) due to surface plasmon resonance, which confirmed the formation of silver nanoparticles.[19] The transmission electron microscopic (TEM) images exhibited that the Ci-AgNPs are highly dispersed and uniform in aqueous solution (Fig. S2) with particle size of 5 to 7 nm.

The sensing property of Ci-AgNPs towards various solvents was investigated by spectrophotometric method. The UV-vis spectral changes of the aqueous solution of Ci-AgNPs (3.2 nM) were recoded upon addition of MeOH, EtOH, acetone, ethyl acetate, acetonitrile, THF, DMF, DCM, CHCl$_3$, 1,4-dioxane, DMSO, diethyl ether, and hexane with 0.0166 ($V_{solvent}/V_{total}$) volume ratio and after incubated of 5 min at room temprature. The spectral change is shown in Fig. 1A, the change in absorption intensity at 394 nm (λ_{max}) in the form of a bar diagram is shown in Fig. 1B and the corresponding colour change is shown in Fig. 1C. It may be noted that except 1,4-dioxane no other solvent exhibits any spectral as well as colour change. For optimization of the experimental conditions, concentration (Fig. S3), incubation time (Fig. S4) and pH (Fig. S5) dependent experiments for the interaction of 1,4 dioxane with Ci-AgNPs were carried out. Depending on the results of these experiments, the optimum conditions used for the subsequent experiments are, 3.2 nM concentration of Ci-AgNPs, 5 min incubation time and 8.0 pH. To find out the concentration range, in which 1,4-dioxane can be estimated quantitatively, UV-vis titration was carried

out upon addition of increasing amount of 1,4-dioxane (0 to 1000 ppm), the spectral change, corresponding colour change and the plot ΔA_{394} vs. concentration of 1,4-dioxane are shown in Fig. 2. It may be noted that with increasing the amount of 1,4-dioxane added, the intensity of the yellow colour of the solution decreased and finally turned to colourless. The ΔA_{394} vs. concentration plot exhibits linear relationship in the range of 1-10 ppm, which suggests that 1,4-dioxane can be estimated if concentration is within this range.

The absorption band at 394 nm is the characteristic peak of Ag^0 nanoparticles due to LSPR and any changes occurring on the surface of ci-AgNPs is expected to cause colour change with shift of this band towards either blue or red. However, the intensity of the 394 band is reduced gradually without any shift upon addition of 1,4-dioxane and ultimately intensity became zero. This observation indicates that in presence of 1,4-dioxane, the crystalline core of Ci-AgNPs nanoparticles progressively releases Ag$^+$ ions, as the yellow colloidal solution tuned to almost clear and colourless (noted in the videography and Fig. S12, ESI).[20] The dispersed particles of ci-AgNPs dissolved in aqueous medium indicating that the Ag^0 in the form of nanoparticles oxidised to Ag$^+$ forming soluble complexes.[21] This is not unusual as it is well-known that Ag^0 is not stable in aqueous medium and its oxidation to Ag$^+$ is thermodynamically favourable at room temperature (ΔG^0_{298} = -11.25 kJ/mol).[22] The ES-mass spectrum, recorded after addition of 1,4-dioxane, exhibited peaks (m/e) corresponding to various degradation products of 1,4-dioxane, such as 2-hydroxyacetic acid, ethane-1,2-diol, 1,4-dioxan-2-olate etc. and Ag$^+$ complexes of a few of them (Fig. S6-

S9). The degradation products observed are similar to those generally produced by reactive oxygen species (ROS) such as super oxide (O_2^-), singlet oxygen ($^1O_2$), hydroxyl radical (OH^-) and hydrogen peroxide (H_2O_2).[22-24] The mass peaks corresponding to the Ag^+-complexes supports the formation of Ag^+ ion.

It has been demonstrated that silver nanoparticles can produce ROS,[25] which are highly reactive and can cause degradation of 1,4-dioxane in aqueous media.[24] The 1,4-dioxane molecule is non-planer and polar in its chair conformation in aqueous media, and therefore the oxygen atom of the 1,4-dioxane with δ^+ charge can approach towards the electron rich surface of the Ci-AgNPs making layer(s) around the nanoparticles through charge transfer interaction.[26] The ROS under such a condition can interact with the activated 1,4-dioxane resulting in its degradation forming various compounds as mentioned above. The ES-mass peaks (m/e) clearly demonstrated the formation of these degradation products of 1,4-dioxane and the Ag^+ complexes of 2-hydroxyacetic acid. The disappearance of SPR band, dissolution of Ag^0 nanoparticles in water, colour change from yellow to colourless and the appearance of number of strong mass peaks corresponding to Ag^+-complexes are strongly support the formation of Ag^+ from its nanoparticles (Ag^0). The formation of Ag^+ ion does not significantly affect the stability of Ag^0 nanoparticles as its surface is coated by citrate, which provides the stability of the nanoparticles.[27] The generated Ag^+ ions also stabilized by forming complexes with 1,4-dioxane degraded product 2-hydroxyacetic acid, which also prevented interaction of the Ag^+ ion with the nanoparticles to affect its stability. If the Ci-AgNPs in aqueous media under aerobic condition is kept for long time, the yellow colour of the solution becomes faint with time and intensity of the 394 band is also reduced. It indicates that the formation of ROS in solution under aerobic condition is a continuous but slow process,[28] it becomes fast in presence of a suitable substrate with which ROS can react and in this case the substrate is 1,4 dioxane.

The SEM images (Fig. S10), TEM images (Fig. S11) and EDX (Fig. S12) of the Ci-AgNPs and that of the intermediate and final stages after addition of 1,4-dioxane were recoded. The TEM images, corresponding colour of the solution and schematic illustration of the aggregation of nanoparticles are shown in Fig. 3. It may be noted that the nanoparticles of Ci-AgNPs is highly dispersed and immediately after addition of 1,4-dioxane they have aggregated increasing the size of the nanoparticles of 7 nm to 50 nm, which further aggregated forming large sizes chain type polymeric network. We propose that the Ci-AgNPs in presence of ROS, preferably O_2^-, and 1,4-dioxane in chair form (polar) aggregated, which after degradation of 1,4-dioxane formed polymeric Ag^+ complexes using the degradation products as bridging unit(s), as shown in Fig. 4. In the ES-mass, the presence of peaks (m/e) of the Ag^+ complexes of the degradation products supports the proposed mechanism.

We also conducted experiments for real sample analysis, both in gas phase and in ground water. For sensing in gas phase, 1,4-dioxane has taken in a closed diffusion cell-like vessel and Ci-AgNPs solution was placed in it in a separate container. The vapour of 1,4-dioxane diffused in the solution of Ci-AgNPs, the colour change was visualised and the UV-vis spectra of the solution was recorded at different time interval. Fig. S13 shows the spectral changes and shows the decrease of intensity of absorption with time and from this data the concentration of 1,4-dioxane diffused in the solution was estimated with the help of standard plot (linear portion) obtained from known concentration of 1,4-dioxane (Fig. 5A) and inserted figure shows that the alginate bead exhibited similar color changes from yellow to colourless. For ground water, it was spiked with known concentration of 1,4-dioxane and from the intensity of the absorbance band at 394 corresponding to each concentration, the concentration of 1,4-dioxane
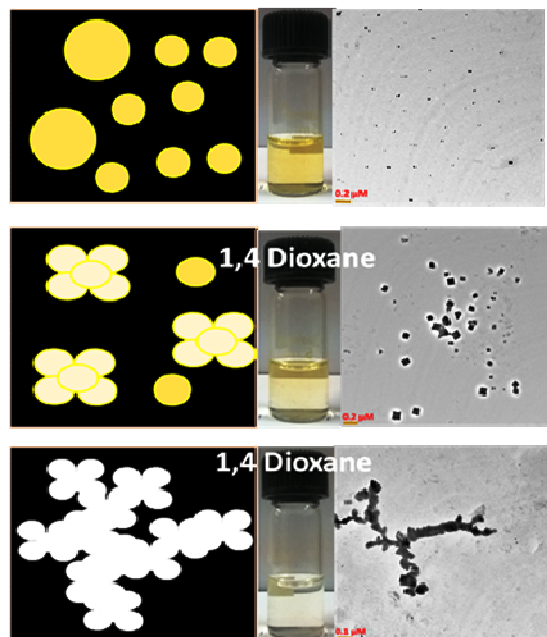

Fig 3 Schematic illustration of ci-AgNPs and TEM images at different stages approaching towards the solvatochromic sensing of 1,4 dioxane with colour change in aqueous media.
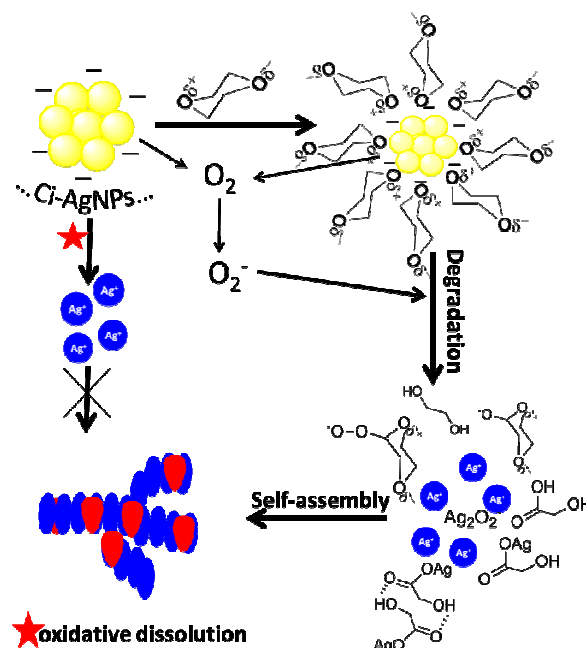

Fig. 4 Schematic diagram showing the degradation process of 1,4-dioxane by ci-AgNPs (Ag(0)) and the generation of Ag^+.
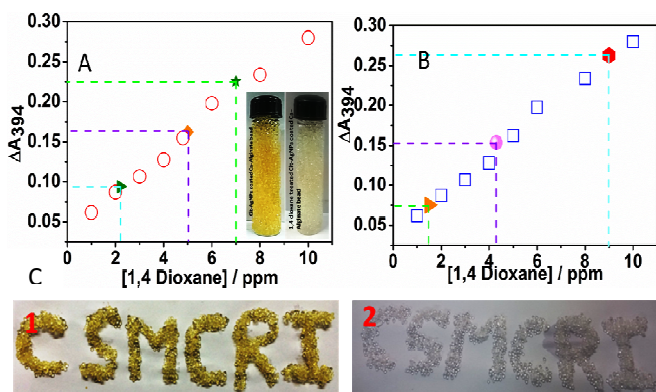
Fig. 5 (A) Determination of unknown concentration of 1,4-dioxane in gas phase by standard plot and the inserted photograph is showing sharp colour change of ci-AgNPs loaded calcium alginate bead. (B) Determination of unknown concentration of 1,4-dioxane in ground water by standard plot and (C) the photographs are showing sharp colour change of ci-AgNPs loaded calcium alginate bead in absence (1) and in presence (2) of 1,4 dioxane (200 ppm).

was evaluated with the help of the standard plot (Fig. 5B) and Fig. 5C shows the alginate beads exhibited similar color changes from yellow (1) to colourless (2) in presence of 1,4 dioxane (200 ppm).

In conclusion, a Ci-AgNPs based solvatochromic sensor has been developed, which selectively senses 1,4-dioxane out of 14 solvents tested in this study. The sensing of 1,4 dioxane induces visible colour change of the solution from yellow to colourless and the lower detection limit determined is 1 ppm. The reactive organic species generated by the surface of the ci-AgNPs under aerobic condition, promoted degradation of 1,4 dioxane etching out Ag^+ from Ag^0 resulting in colour change and decrease in intensity of absorption band. This new sensor is used for quantitative estimation of 1,4-dioxane in ground water and also vapour of 1,4-dioxane diffused in aqueous media. To the best of our knowledge, this is the first example for selective colorimetric detection and estimation of 1,4-dioxane using a solvatochromic sensor.

References and Notes

1   E. Benedetti, L. S. Kocsis, and K. M. Brummond, *J. Am. Chem. Soc.*, 2012, 134, 12418–12421.

2   L. T. -S. Lo, S. -W. Lai, S. -M. Yiu, & C. -C. Ko, *Chem. Commun.*, 2013, **49**, 2311–2313.

3   Z. –Z. Lu, R. Zhang, Y.-Z. Li, Z. -J. Guo, & H. -G. Zheng, *J. Am. Chem. Soc.*, 2011, **133**, 4172–4174

4   H. Hosokawa, Y. Funasako, and T. Mochida, *Chem. Eur. J.*, 2014, **20**, 15014 – 15020

5   K. Schreiter, K. Schreiter, K. Hofmann, A. Seifert, A. Oehlke, K. Ladewig, T. Rüffer, H. Lang and S. Spange, *Chem. Mater.*, 2010, **22**, 2720–2729.

6   M. A. R. -Omary, M. D. Rashdan, S. Dharanipathi, O. Elbjeirami, P. Ramesh and H. V. R. Dias, *Chem. Commun.*, 2011, **47**, 1160–1162

7   M. Ganguly, C. Mondal, J. Jana, A. Pal, and T. Pal, *Langmuir,* 2014, **30**, 348−357

8   J. Lee, H. T. Chang, H. An, S. Ahn, J. Shim & J. M. Kim, *nature communications*, 2013, **4**, 1-9

9   D. Paramelle, A. Sadovoy, S. Gorelik, P. Free, J. Hobley and D. G. Fernig, *Analyst*, 2014, **139**, 4855–4861

10   C. Noguez, *J. Phys. Chem. C*, 2007, **111**, 3806-3819

11   R. Sekar and T. J. DiChristina, *Environ. Sci. Technol.*, 2014, **48**, 12858−12867.

12   E.J. Calabrese and E.M. Kenyon. Air Toxics and Risk Assessment. *Lewis Publishers, Chelsea, MI.* 1991.

13   U.S. Environmental Protection Agency. p-Dioxane Health Advisory. *Office of Drinking Water, Washington, DC.* 1987.

14   M. I. Stefan, J. R. Bolton, *Environ. Sci. Technol.*, 1998, **32**, 1588-1595.

15   (a) U.S. Environmental Protection Agency. toxicological review of 1,4-dioxane, EPA/635/R-11/003F . (b) U.S. Environmental Protection Agency. 1,4-Dioxane (1,4-Diethyleneoxide) 123-91-1, *Hazard Summary*-Created in April 1992; Revised in January 2000

16   S. –Y. D. Chiang, R. Mora, W. H. Diguiseppi, G. Davis, K. Sublette, P. Gedalanga and S. Mahendra, *J. Environ. Monit.*, 2012, **14**, 2317-2326.

17   (a) A. Abe, *Sci. Total Environ.*, 1999, **227**, 41−47.

18   P. Grimmett, J. Munch, *J. of Chromatographic Science*, 2009, **47**, 31-39.

19   D. Xiong, M. Chen and H. Li, *Chem. Commun.*, 2008, 880–882.

20   K. Fujiwara, G. A. Sotiriou, and S. E. Pratsinis, *Langmuir*, 2015, **31**, 5284−5290.

21   K. Loza, J. Diendorf, C. Sengstock, L. R. -Gonzalez, J. M. G. -Calbet, M. Valle-Regi, M. Kollerb and M. Epple, *J. Mater. Chem. B*, 2014, **2**, 1634–1643.

22   C. Levard, E. M. Hotze, G. V. Lowry, and G. E. Brown, Jr, *Environ. Sci. Technol.*, 2012, **46**, 6900−6914.

23   H. Barndoka, D. Hermosillaa, C. Hanb, D. D. Dionysioub, C. Negroa, Á. Blanco, *Applied Catalysis B: Environmental*, 2016, **180**, 44–52.

24   H. –S. Son, J. –K. Im, K. –D. Zoh, water research, 2009, 4 3, 1457–1463.

25   O. Chol and Z. HU, *Environ. Sci. Technol.*, 2008, 42, 4583–4588.

26   (a) A. Heiland, K. Christmann, *Surface Science*, 1996, **355**, 31-46. (b) A. Chaudhari, *International Journal of Quantum Chemistry*, 2010, **110**, 1092–1099.

27   F. –F. An, J. Ye, J. –F. Zhang, Y. –L. Yang, C. –J. Zheng, X. –J. Zhang, Z. Liu, C. –S. Leeb and X. –H. Zhang, *J. Mater. Chem. B*, 2013, **1**, 3144–3151.

28   Z. –M. Xiu, J. Ma, and P. J. J. Alvarez, *Environ. Sci. Technol.* 2011, **45**, 9003–9008.

ChemComm Accepted Manuscript