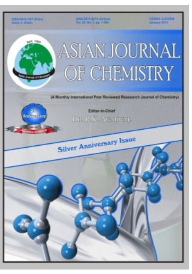
Asian Journal of Chemistry; Vol. 25, No. 3 (2013), 1733-1736

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14354



Facile Synthesis of Cu_2O Nanocubes and Their Enhanced Photocatalytic Property Assisted by H_2O_2

JUNCUI XU[1,2,*], HUI WANG[1], HEYUN GU[1], CHUNYAN ZENG[1] and YUMEI YANG[1]

[1]School of Chemical Engineering and Anhui Key Laboratory of Controllable Chemical Reaction and Material Chemical Engineering, Hefei University of Technology, Hefei 230009, Anhui Province, P.R. China
[2]Department of Chemical and Chemical Engineering, Hefei Normal University, Hefei 230061, Anhui Province, P.R. China

*Corresponding author: Fax: +86 551 2901450; Tel: +86 551 2901450; E-mail: xxjjcz20000214@yahoo.cn

(*Received*: 23 July 2012; *Accepted*: 29 September 2012) AJC-12201

Well-defined and uniform Cu_2O nanocubes with an average edge length of about 170 nm have been successfully synthesized in the absence of any surfactant using home-made CuC_2O_4 as precursor at room temperature. The composition, structure and morphology of the obtained products have been characterized by X-ray powder diffraction, transmission electron microscope and field-emission scanning electron microscopy. The experimental results demonstrate that the Cu_2O nanocubes exhibit enhanced photocatalytic property for high concentration (100 mg/L) of acid fuchsin degradation under UV light in the presence of H_2O_2. The factors affecting the acid fuchsin photocatalytic degradation have been investigated, such as irradiation, photocatalyst concentration and hydrogen peroxide initial concentration.

Key Words: Cu_2O nanocubes, Photocatalytic activity, Acid fuchsin, Hydrogen peroxide.

INTRODUCTION

Over the past decades, controlled synthesis of nanostructured materials has attracted considerable interests due to the fact that the particle size and morphology of nanomaterials greatly influence their properties. Cuprous oxide is a *p*-type semiconductor with a direct band gap of 2.17 eV and displays unique optical and magnetic properties, which makes it a promising material in a wide range of applications for solar energy conversion[1], gas sensing[2], CO oxidation[3], lithium ion batteries[4] and photocatalytic degradation of organic pollutants[5,6]. Recently, much effort has been devoted to the synthesis of cuprous oxide nanocubes[7-9]. Most of the synthetic strategies involve high temperature and/or with surfactants such as cetyltrimethyl ammonium bromide (CTAB), or requiring special conditions and some of the nanocubes could not reach well-defined cubic structures.

Currently, many researchers focus their attention on investigating highly effective photocatalysts. As a photocatalyst, cuprous oxide has been attracted much interests[10] owing to its numerous advantages, such as non-toxicity, low cost, chemical stability and a high absorption coefficient in visible regions[11]. However, electron-hole pairs can easily recombine and the photochemical reaction is possible inhibited when the narrow gap semiconductor (*i.e.*, Cu_2O) is used as a photocatalyst[12]. It is known that the photocatalytic activity closely relates to not only the efficiency of electron-hole (e^-/h^+) separation but also the size, morphology, crystal structure and specific surface area of a photocatalyst. Thus, some researchers have done much work to find a way to improve the photoactivity of Cu_2O nanomaterial[13].

Taking the mentioned concept into account, our aim focuses on the preparation of uniform Cu_2O nanocubes and enhancement of their photocatalytic activity. Herein, a simple and rapid route has been chosen to synthesize the uniform and monodispersed Cu_2O nanocubes with the edge length of about 170 nm. The method does not require the assistance of any organic compounds or surfactants and high temperature and the as-prepared Cu_2O nanocubes are uniform in both shape and size. Furthermore, the photocatalytic activity of Cu_2O nanocubes in presence of H_2O_2 has been investigated for the decomposition of acid fuchsin with high concentration (100 mg/L) under UV at room temperature.

EXPERIMENTAL

All chemicals were of analytical grade and used as received. Distilled water was used throughout.

Preparation of copper oxalate precursor: A typical procedure was performed as follows. 100 mL of copper sulfate solution (0.015 M) was put in the 400 mL beaker, then 30 mL oxalic acid solution (0.05 M) was added drop by drop in the solution under constant magnetic stirring at room temperature. A light blue precipitate appeared immediately. After 0.5 h of reaction time, the precipitates in the beaker were collected by centrifugation, washed thoroughly with distilled water and absolute ethanol and finally dried in air for 12 h.

Preparation of Cu_2O nanocubes: Typically, the as-prepared precursor was dispersed in 130 mL of distilled water by ultrasonication and then the mixture was stirred for about 10 min, followed by 30 mL of ascorbic acid (0.05 M) solution and 40 mL of NaOH solution (0.0625 M) added in the solution, stirred for about 30 min in turn. A colour change from light blue to brick red soon took place. Finally, the brick red precipitates were collected and washed with distilled water and absolute ethanol respectively and dried at 50 ºC in oven for 6 h.

Characterization: The as-prepared precursor and sample were characterized by X-ray powder diffraction in a Rigaku D/max-γB X-ray diffractometer with a CuK_α radiation source (λ = 1.5418 Å) operated at 40 kV and 80 mA. Field-emission scanning electron microscopy (FE-SEM) measurement was taken by JEOL-7500B (FEI Sirion-200) and JEOL JSM-6490 (LV) scanning electron microscope. Transmission electron microscopic images were taken with Hitachi H-800 transmission electron microscope performed at an accelerating voltage of 200 kV, respectively.

Photo-catalytic activity evaluation: Acid fuchsin, a common triphenylmethane dye, was selected as the model pollutant to evaluate the photocatalytic activity of the Cu_2O nanocubes as-prepared. The photocatalytic experiments were performed in a photochemical reactor (BD-GHX-II, BD experimental instrument Co. Ltd., Nanjing, China). The ultraviolet light was provided by a high pressure Hg lamp (300 W) with the major emission at 365 nm, which was cooled to room temperature by a circulating water jacket. The distance between the light and the reaction beaker was maintained at 10 cm. In all the experiments, the initial concentration of acid fuchsin aqueous solution was constant (100 mg/L). 50 mg of Cu_2O samples (except the experiments involving variation of catalyst amounts) was dispersed in a beaker, which contained 100 mL of acid fuchsin solution. The degradation reactions were carried out after the establishment of the adsorption/desorption equilibrium by magnetic stirring for 0.5 h in the dark. After that, 0.4-1.2 mL of H_2O_2 (30 %, wt %) was dropped into the above solution. At given time intervals, 1 mL of the mixture solution was pipetted into a volumetric flask and quickly diluted with distilled water to 10 mL prior to analysis. For optical absorption measurements, the diluted solution was immediately centrifuged in order to remove the catalyst particles, which tend to scatter the incident beam. The supernatant solution was analyzed by a Shimadzu UV-2550 ultraviolet-visible (UV-VIS) spectrophotometer at a wavelength of 540 nm (the maximum of the acid fuchsin adsorption wavelength). The decolourization ratio of acid fuchsin solution was calculated according to the equation $C = (A_0 - A)/A_0 \times 100\ \%$, where C stands for the decolourization ratio, A_0 is the initial absorbance of acid fuchsin solution and A is the absorbance of photo-degraded acid fuchsin solution at different time.

RESULTS AND DISCUSSION

The composition and phase purity of samples were examined by XRD. Fig. 1a shows the XRD pattern of as-prepared Cu_2O nanocubes synthesized by direct reaction of aqueous ascorbic acid and CuC_2O_4 precursor for 0.5 h at room temperature without any surfactant in alkaline solution. The CuC_2O_4 precursor (XRD pattern of CuC_2O_4 was shown in Fig. 1a in Supplementary Data) was prepared by using aqueous $CuSO_4$ and $H_2C_2O_4$ solution for 0.5 h of reaction at room temperature. As presented in Fig. 1a that all the peaks match well with those of cubic Cu_2O, with the Pnnm space group Pn3m (224) (JCPDS No. 78-2076).

Field-emission scanning electron microscopy (FESEM) and TEM were used to observe the morphology and structure of the samples. Fig. 1b presents FESEM image of the Cu_2O sample. The FESEM image obviously shows that the sample is composed of well-defined cubic morphology with rough surfaces and uniform sizes. The average diameter is about 170 nm,which is smaller than the average diameter of about 400 nm for Cu_2O cubes reported by our group, which were prepared by reducing a copper citrate complex solution with ascorbic acid at room temperature[14]. The TEM image (Fig. 1c) further confirms the uniform cubic shape of the Cu_2O nanocubes.

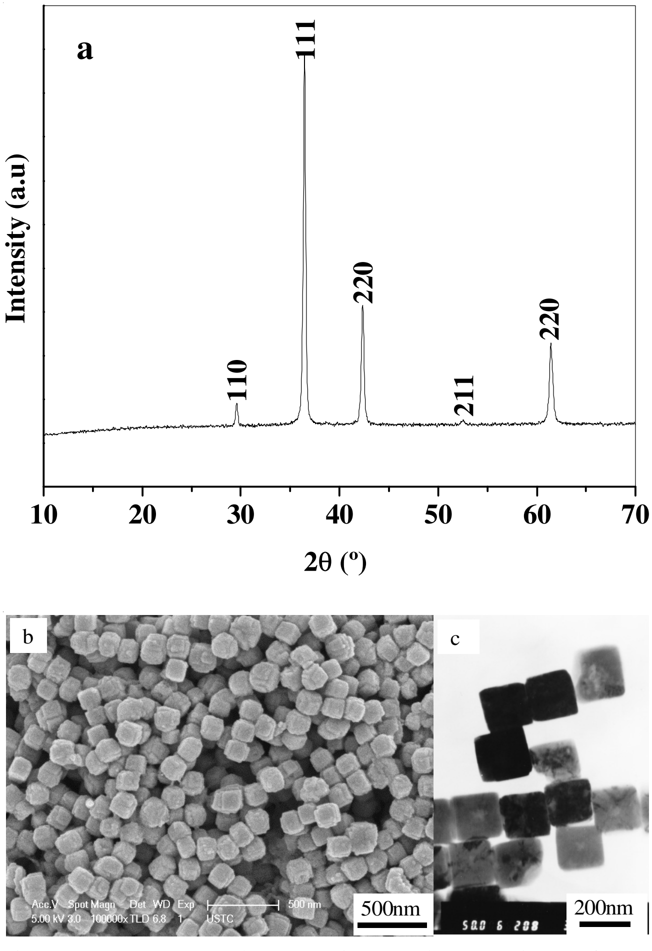


Fig. 1. (a) XRD pattern, (b) FESEM image and (c) TEM image of Cu_2O nanocubes

Here, the photocatalytic activity of the as-synthesized Cu_2O nanocubes was investigated towards the degradation of acid fuchsin at room temperature. The change of the decolourization ratio of acid fuchsin under different conditions is depicted in Fig. 2. As shown in trace 'a', acid fuchsin was hardly degraded (about 5 %) observed at the absence of both catalyst and H_2O_2 under UV light irradiation, suggesting that the dye is photostable. Even under UV light irradiation, acid fuchsin was still difficult to degrade in dispersion with Cu_2O (trace 'b', 15 %) only or in the H_2O_2-only solution (trace 'c', 20 %). The results also demonstrate that in the presence of Cu_2O, the photocatalytic degradation of acid fuchsin is faster than that of without Cu_2O (trace 'a' and 'b'). Observed from trace 'd', acid fuchsin was not completely photodegraded in the presence of both catalyst and H_2O_2 in the dark (below 60 %). However, as shown in trace 'e' (91 %), it was nearly completely degraded under UV light irradiation which suggests that UV light irradiation is essential for the catalytic degradation of dye pollutants. Specially, comparing trace 'b' with 'e', which demonstrated the curves of photodegradation of the acid fuchsin solution without H_2O_2 and with H_2O_2 respectively, we can easily see that upon addition of H_2O_2, the catalyst Cu_2O nanocubes presented considerable enhancement for the degradation of the acid fuchsin solution. It is due to that the hydroxyl radicals ($^•OH$) and superoxide radical anions ($O_2^{•-}$) are the primary oxidizing species in the photocatalytic processes[15]. Therefore, it is important for the excited electron in the conduction band to be scavenged by an external agent to prevent its recombination with the positive hole. Here, H_2O_2 plays two important roles not only as strong oxidant but also as electron scavengers[16], which can enhance the photocatalytic degradation by contribution to the $^•OH$ formation and inhibiting the electron-hole recombination at the semiconductor surface[17].

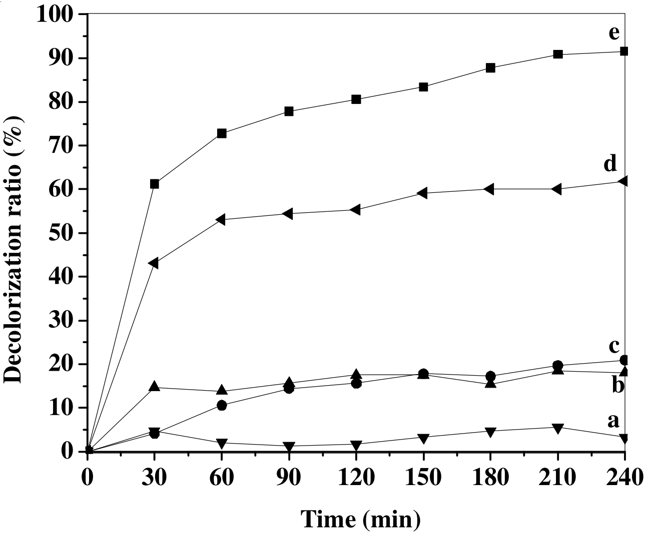


Fig. 2. Decolourization ratio of acid fuchsin solution as a function of degradation time under different catalytic conditions: (a) UV, (b) Cu_2O + UV, (c) H_2O_2 + UV, (d) Cu_2O + H_2O_2 (in the dark) and (e) Cu_2O + H_2O_2 + UV. (Experimental conditions: the initial concentration of acid fuchsin solution,100 mg/L; photocatalyst concentration, 0.5 g/L; the initial concentration of H_2O_2, 0.078 M)

The effect of photocatalyst concentration on the degradation ratio of acid fuchsin was investigated employing different concentrations of the Cu_2O nanocubes varying from 0.3 to 2.0 g/L, as shown in Fig. 3. When the content of Cu_2O nanocubes was in the range of 0.30-1.0 g/L, the decolourization ratio increased from 82.2 to 96.6 % with increase in catalyst concentration (Fig. 3a, b and c). However, increase of the catalyst concentration more than 1 g/L results in the decrease of degradation rate (Fig. 3d, about 93 %). The reason is due to that at the beginning, the increase in the concentration of catalyst increases the availability of active sites on the photocatalyst surface, which in turn increases the number of hydroxyl and superoxide radicals[18]. However, when the concentration of the catalyst increases above the optimum value, the degradation rate decreases, which is due to increased light scattering of the catalyst particles causing a reduction of light penetration in the solution[17]. Moreover, the decrease in the percentage of degradation at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules[19]. Therefore, there is a limit of catalyst concentration that must be used for the photodegradation of a particular pollutant in wastewater. This optimum loading of photocatalyst is found to be dependent on the initial solute concentration[20].

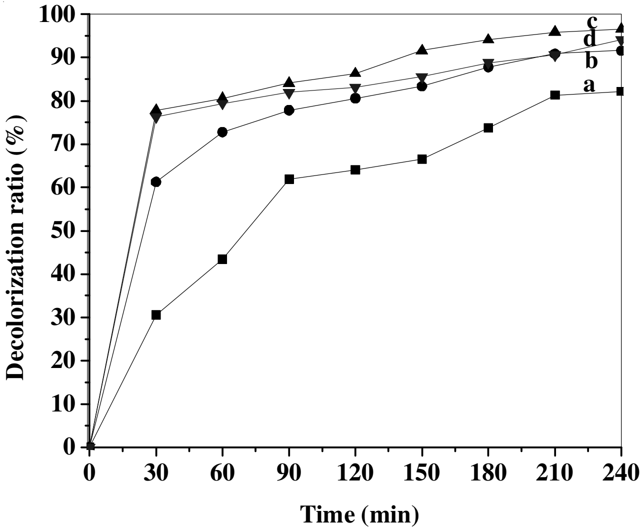


Fig. 3. Decolourization ratio of acid fuchsin solution as a function of degradation time with cuprous oxide as the catalyst under different initial concentrations: (a) 0.3 g/L, (b) 0.5 g/L, (c) 1.0 g/L, (d) 2.0 g/L. (Experimental conditions: the initial concentration of acid fuchsin solution, 100 mg/L; UV; the initial concentration of H_2O_2, 0.078 M)

Since hydroxyl radicals appear to play an important role in the photocatalytic degradation, as electron acceptors, hydrogen peroxide was added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit the electron/hole (h^+_{VB}/e^-_{CB}) pair recombination[21]. The effect of change in H_2O_2 concentration on degradation efficiency for acid fuchsin is depicted in Fig. 4. Interestingly, the initial hydrogen peroxide concentration in the solution has a very similar effect on the decolourization ratio to that of Cu_2O nanocubes. When the concentration of H_2O_2 was increased from 0.039 to 0.078 M (Fig. 4a and b), the photocatalytic performance of the nanocubes reached a peak (Fig. 4b), which is attributed to incremental $^•OH$ radical produced by reacting with e^-_{CB} and superoxide radical anion of oxygen[22]. However, further increasing the concentration of H_2O_2, the photocatalytic activity didn't yield further improvements (Fig. 4c and d). The result is consisted with Coleman's group, who degraded 1,4-dioxane in water using TiO_2 photocatalysis in the presence of H_2O_2 under UV irradiation[23]. The decrease may be a combination of formation of less reactive hydroperoxyl radicals and also due to competition of hydrogen peroxide with the contaminants for conduction band electrons. Hydrogen peroxide has been found to consume hydroxyl radicals[24]. Finally, the catalyst Cu_2O could also be oxidized by H_2O_2 with high concentration to form CuO, which is a semiconductor with a narrow band gap of about 1.4 eV and its photocatalytic efficiency is poor due to its serious recombination and weak redox ability of those excited electrons and holes compared with Cu_2O[5]. Therefore, the proper addition of hydrogen peroxide could enhance the photocatalytic activity of Cu_2O nanocubes.

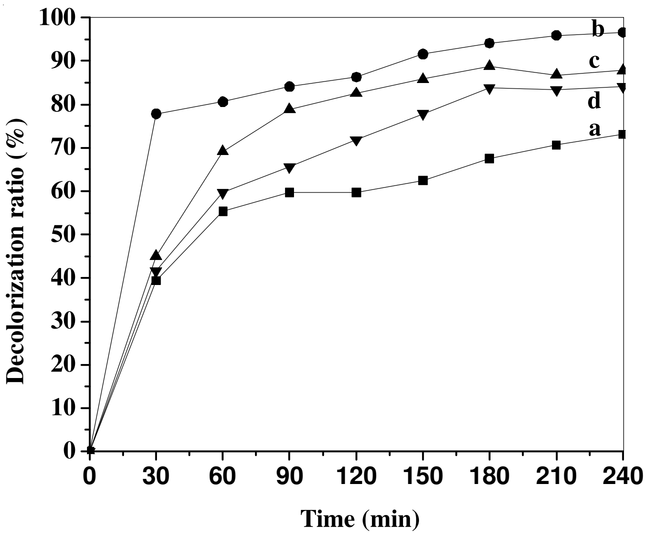


Fig. 4. Decolourization ratio of acid fuchsin solution as a function of photocatalytic degradation time in the presence of hydrogen peroxide under different initial concentrations: (a) 0.039 M, (b) 0.078 M, (c) 0.098 M, (d) 0.117 M. (Experimental conditions: the initial concentration of acid fuchsin solution, 100 mg/L; UV; photocatalyst concentration, 1.0 g/L)

The stability of Cu_2O particles after the photocatalytic process was also studied. The X-ray diffraction analysis of Cu_2O nanoparticels after irradiation of 4 h indicates that no other phase such as CuO and $Cu(OH)_2$ could be found except cubic Cu_2O, which proves that the Cu_2O nanocubes are photostable and not oxidized even though in the presence of H_2O_2 throughout the photocatalysis process. Similar results have also been shown in previous studies for photocatalytic degradation of methyl orange[11].

Conclusion

In summary, highly uniform and monodispersed Cu_2O nanocubes with the edge length of about 170 nm have been synthesized by reducing CuC_2O_4 precursor with ascorbic acid at room temperature. The photocatalytic activity of Cu_2O nanocubes prepared can be efficiently enhanced by adding proper concentration of H_2O_2 into the system under UV light irradiation. The reason can be attributed to the formation of more $^{\bullet}OH$ and inhibiting the electron-hole recombination at the semiconductor surface by addition of H_2O_2. In comparison with other methods with the absence of H_2O_2, this method can more effectively degrade pollutants with higher concentration and with smaller H_2O_2 consumption. Therefore, the present study provides a potential approach for wastewater treatment with Cu_2O nanocubes as the photocatalyst.

ACKNOWLEDGEMENTS

The authors are grateful to the financial supports of the National Natural Science Foundation of China (NSFC Grants 20871038, 20876031 and 20976033), the Fundamental Research Funds for the Central Universities (2010HGZY0012), the Education Department of Anhui Provincial Government (TD200702), and the Natural Science Foundation of the Education Departmentof Anhui Province (KJ2012B146 and KJ2012Z323).

REFERENCES

1. R.A. Briskman, *Sol. Energy Mater. Solar Cells*, **27**, 361 (1992).
2. J.T. Zhang, J.F. Liu, Q. Peng, X. Wang and Y.D. Li, *Chem. Mater.*, **18**, 867 (2006).
3. B. White, M. Yin, A. Hall, D. Le, S. Stolbov, T. Rahman, N. Turro and S. O'Brien, *Nano Lett.*, **6**, 2095 (2006).
4. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J.M. Tarascon, *Nature*, **407**, 496 (2000).
5. C.H. Kuo, C.H. Chen and M.H. Huang, *Adv. Funct. Mater.*, **17**, 3773 (2007).
6. H.L. Xu, W.Z. Wang and W.J. Zhu, *J. Phys. Chem. B*, **110**, 13829 (2006).
7. L.F. Gou and C.J. Murphy, *Nano Lett.*, **3**, 231 (2003).
8. Y.Q. Wang, W.S. Liang, A. Satti and K. Nikitin, *J. Cryst. Growth*, **312**, 1605 (2010).
9. Y. Xu, H. Wang, Y.F. Yu, L. Tian, W.W. Zhao and B. Zhang, *J. Phys. Chem. C,* **115**, 15288 (2011).
10. L. Huang, F. Peng, H. Yu and H.J. Wang, *Solid State Sci.*, **11**, 129 (2008).
11. J. Li, L. Liu, Y. Yu, Y. Tang, H. Li and F. Du, *Electrochem. Commun.*, **6**, 940 (2004).
12. Y.L. Du, N. Zhang and C.M. Wang, *Catal. Commun.*, **11**, 670 (2010).
13. W. Sun, W.D. Sun, Y.J. Zhuo and Y. Chu, *J. Solid State Chem.*, **184**, 1638 (2011).
14. W.X. Zhang, Z.X. Chen and Z.H. Yang, *Phys. Chem. Chem. Phys.*, **11**, 6263 (2009).
15. M. Saquib and M. Muneer, *Dyes. Pigm.*, **56**, 37 (2003).
16. K.B. Dhanalakshmi, S. Anandan, J. Madhavan and P. Maruthamuthu, *Mater. Solar Cells*, **92**, 457 (2008).
17. O. Carp, C.L. Huisman and A. Reller, *Solid State Chem.*, **32**, 33 (2004).
18. U.G. Akpan and B.H. Hameed, *J. Hazard. Mater.*, **170**, 520 (2009).
19. J.J. Teo, Y. Chang and H.C. Zeng, *Langmuir*, **22**, 7369 (2006).
20. J.M. Hermann, *Catal. Today*, **53**, 115 (1999).
21. M. Saquib, M.T. Abu, M. Faisal and M. Muneer, *Desalination*, **219**, 301 (2008).
22. N. Shimizu, C. Ogino, M.F. Dadjour and T. Murata, *Ultrason. Sonochem.*, **14**, 184 (2007).
23. H.M. Coleman, V. Vimonses, G. Leslie and R. Amal, *J. Hazard. Mater.*, **146**, 496 (2007).
24. V. Kavitha and K. Palanivelu, *Water Res.,* **39**, 3062 (2005).