

Research Article

Sensing of Zinc-Containing Nanopollutants with an Ionic Liquid

Michelle Wang,¹ James Wang,² H.-C. Wang,³ Hsin-Liang Huang,⁴ and H.-L. Liu⁵

¹ School of Pharmacy, Ohio State University, Columbus, OH 43210, USA

² Department of Bioengineering, University of Washington, Seattle, WA 98105, USA

³ Division of Chest Medicine, Department of Medicine, Veterans General Hospital-Kaoshiung, Kaoshiung 813, Taiwan

⁴ Department of Safety, Health and Environmental Engineering, National United University, Miao-Li 630, Taiwan

⁵ Department of Medical Sociology and Social Work, College of Health Science, Kaohsiung Medical University, Kaoshiung 800, Taiwan

Correspondence should be addressed to Hsin-Liang Huang, hlhuang@nuu.edu.tw

Received 29 August 2010; Revised 12 November 2010; Accepted 2 December 2010

Academic Editor: Sherine Obare

Copyright © 2010 Michelle Wang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The rapid maturing of nanotechnology and its wide range of applications not bring benefits only, so the downsides are worth noting. Nanopollutants, generally undetectable, are often found as byproducts involved in various chemical or physical reactions. Many nanopollutants are concerned and suspected of causing negative impact on human health due to their unpredictable existence in the environment. Unlike the traditional sensing systems which can detect select gaseous molecules, effective nanoparticle sensing methods are still lacking in the literature. In this paper, sensing of zinc-containing nanopollutants suspended in N₂ with a room-temperature ionic liquid (RTIL) ([C₄mim][PF₆] (1-butyl-3-methyl imidazolium hexafluorophosphate)) has been studied. The sensitivities (R_{IL}/R_{nano}) obtained by determination of the RTIL resistance to the absorbed phosphor fly ash (<200 nm) is 7.0, while the RTIL has higher sensitivity of 11 and 10, respectively, to ZnO and ZnS nanoparticles. By component-fitted X-ray absorption near edge structure (XANES) spectroscopy, it seems that the N-methyl imidazole (mim) complexes are formed during sensing of the phosphor fly ash, ZnO and ZnS nanoparticles with the RTIL. The ¹H and ³¹P NMR observations also suggest that the (mim) behaves as a carrier during sensing of nanopollutants with the RTIL.

1. Introduction

Nanotechnology developments and applications have been growing very rapidly especially in the recent decades. Many nanosize (<100 nm) materials have been widely used in catalysis, photon-electronic devices, and surface treatments. However, the hidden dangers of nanopollutants from the diverse sources may exacerbate the environment and human health on a daily basis [1]. Nanopollutants may diffuse into the deep lung [2]. Unknown diseases caused by nanopollutants existing in the environment have been suspected [1, 2].

Room-temperature ionic liquids (RTILs) are generally nonvolatile, nonflammable, and with high thermal stability at the temperature range of 273–573 K. Therefore, RTILs are also named “Green solvents” [3]. Room-temperature ionic liquids can also be applied in the industrial synthesis, separation, electrochemistry, and catalysis [3–6]. Organic metals (such as Cd, Pb, or Zn dithizonates) could be absorbed in RTILs at a pH value range of 4–8 [7]. Recently,

it was found that Au nanoparticles could be well suspended in the RTIL ([C₄mim][PF₆]) for at least 20 days [8]. Observations referenced above [4–8] implicate the potential applications of the RTIL in sensing of nanopollutants.

Although it is well known that the selected gaseous molecules adsorbed on the semiconductor sensing materials can be detected [9]. The concept of gas sensing is completely different from detection of ultrafine particles in nanometer scales. Effective nanopollutant sensing methods are still lacking in the literature. Thus, a feasibility study for sensing of nanopollutants with a RTIL (i.e., [C₄mim][PF₆]) was carried out in the present work. Specifically, resistances of the RTIL were determined during absorption of zinc nanoparticles as well as environmental zinc-rich nanopollutants.

By synchrotron X-ray absorption spectroscopy, molecule-scale data such as bond distance and coordination number (CN) of select elements in the complicated environmental samples can be obtained [5, 10–13]. In addition, reaction paths in catalysis, adsorption, solidification, and

waste recycling can be revealed by component-fitted X-ray absorption near edge structure (XANES) [12–14]. To better understand the fate of zinc compounds absorbed in the RTIL during sensing, the XANES spectroscopic technique was also used in this work.

2. Experimental

Detailed procedures for synthesis of the RTIL were described in previous literature [5]. Briefly, 0.3 moles of 1-chlorobutane (99.4%, TEDIA, USA) and 0.3 moles of 1-methylimidazole (mim) (99%, Fluka) were mixed and refluxed at 343 K for 72 hours. The $[C_4mim]^+$ solution was then mixed with 55.2 g of KPF_6 (>99.0%, SHOWA, Japan). About 30 mL of the RTIL ($[C_4mim]^+[PF_6]$) were prepared for nanopollutant sensing experiments.

The sensing experiments were carried out on a home-made sensing system. About 0.05 mL of the RTIL ($[C_4mim][PF_6]$) was coated onto a glass substrate. Silver wires were used for electrical connections and measurements of the resistances of the RTIL during sensing of nanoparticles. Nanoparticles such as ZnO (21–107 nm) (99.5%, Kanto Chemical), ZnS (20–100 nm) (99.99%, Aldrich), CuO (27–95 nm, Kanto Chemical), or TiO_2 (20–101 nm, Kanto Chemical) suspended (20–40 ng/m^3) in the flowing N_2 gas (200 mL/min) were absorbed by the RTIL. To simulate environmental nanopollutants, phosphor fly ashes (<5000 nm) collected from particulate collection systems (such as bag houses) in the used CRT or TV disassembling processes were filtered to enrich particle sizes in the range of <200 nm. Resistances of the RTIL during absorption of those nanoparticles were monitored with a digital multimeter (HP34401A). The sensitivities of the RTIL to ZnO, ZnS, TiO_2 , and CuO nanoparticles were determined by measuring ratios of resistances of the fresh RTIL to nanoparticles absorbed in RTIL (R_{IL}/R_{nano} (decreasing resistance) or R_{nano}/R_{IL} (increasing resistance)).

XANES spectra of zinc in the phosphor fly ash, ZnO and ZnS nanoparticles and Zn^{2+} -(mim) (prepared by dissolution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (99%, Hanawa Guaranteed Reagent) in (mim)) were recorded on the Wiggler (17C) beam line under the electron storage ring energy of 1.5 GeV at the Taiwan National Synchrotron Radiation Research Center. A Si (111) double-crystal monochromator was used for energy selection with energy resolution ($\Delta E/E$) of 1.9×10^{-4} (eV/eV). Beam energy was calibrated by the absorption edge of a zinc powder at 9659 eV. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. The absorption edge was determined at the half-height (precisely determined by its derivative) of the XANES spectrum after preedge baseline subtraction and normalization to the maximum above-edge intensity [5, 12, 14].

Images and diffraction patterns of the phosphor fly ash absorbed in the RTIL (studied by transmission electron microscopy (TEM) (JEOL, TEM-200CX)) indicate that the nanopollutants were well dispersed in the RTIL during sensing at 298 K. 1H and ^{31}P NMR spectra of the RTIL absorbing the phosphor fly ash, ZnO, and ZnS nanoparticles

TABLE 1: Sensitivities (R_{IL}/R_{nano} (decreasing resistance) or R_{nano}/R_{IL} (increasing resistance)) of the RTIL to 20–40 ng/m^3 of nanoparticles at 298 K.

Nanoparticle	Size (nm)	Sensitivity	
		R_{IL}/R_{nano}	R_{nano}/R_{IL}
TiO_2	20–101	13	
ZnO	21–107	11	
ZnS	<100	10	
CuO	27–95		16
Phosphor fly ash	<200	7.2	
Phosphor fly ash	<5000	1.4	

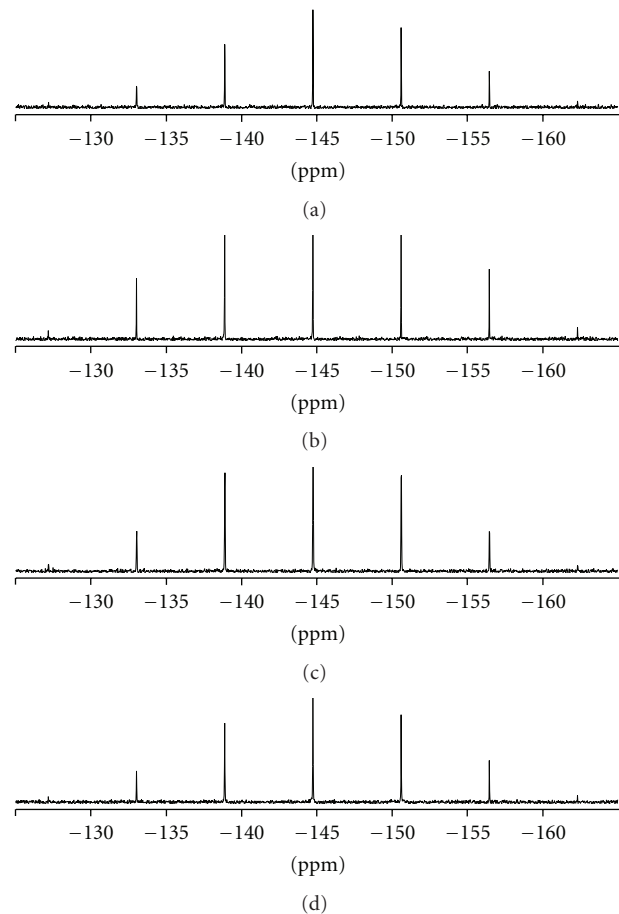


FIGURE 1: ^{31}P NMR spectra of (a) RTIL ($[C_4mim][PF_6]$) and (b) phosphor fly ash, (c) ZnO, and (d) ZnS nanoparticles absorbed in the RTIL.

were also determined on a Bruker Avance 300 spectrometer with tetramethyl silane and triphenyl phosphine as the internal standard (acquisition time = 1.373 s, actual pulse repetition time = 2 sec, number of scans = 32, and excitation pulse-angle = 30°).

3. Results and Discussion

The large phosphor fly ash (200–5000 nm in diameters) which is collected from bag houses in the used CRT or TV

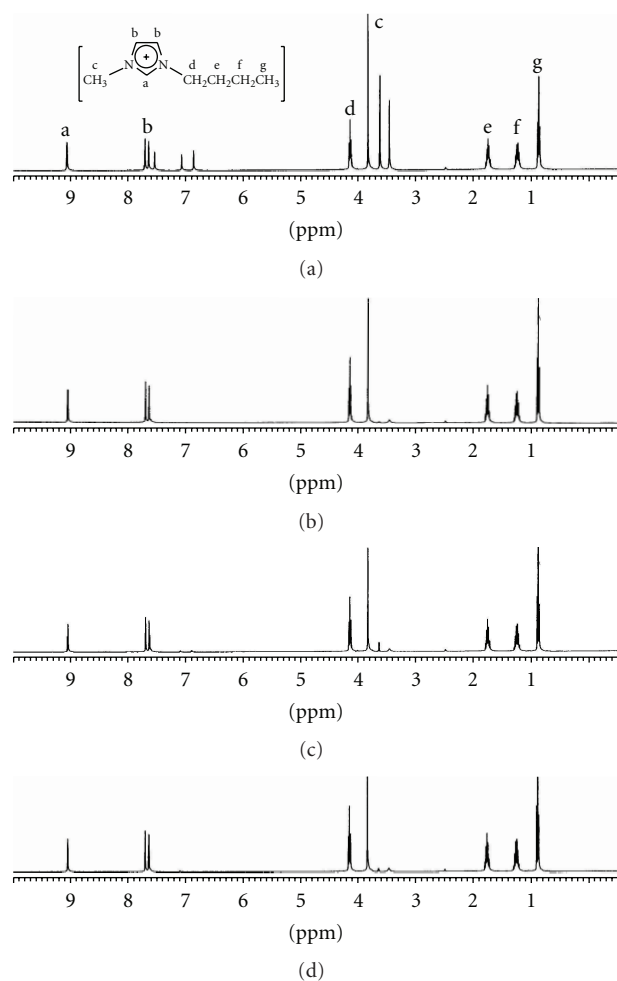


FIGURE 2: ^1H NMR spectra of (a) RTIL ($[\text{C}_4\text{mim}][\text{PF}_6]$) and (b) phosphor fly ash, (c) ZnO, and (d) ZnS nanoparticles absorbed in RTIL.

disassembling processes could not be absorbed effectively in the RTIL ($[\text{C}_4\text{mim}][\text{PF}_6]$). In Table 1, within a response time of four minutes, a very low sensitivity ($R_{\text{IL}}/R_{\text{nano}} = 1.4$ (having a decreasing resistance)) of the RTIL to 20–40 ng/m^3 of the large phosphor fly ash. Is detected for the small phosphor fly ash in the micron-to-nanosize range ($<200\text{ nm}$), the sensitivity ($R_{\text{IL}}/R_{\text{nano}}$) of the RTIL is increased to 7.2. Since zinc is the main element in the phosphor fly ash, sensitivities of the RTIL to ZnO (21–107 nm) and ZnS ($<100\text{ nm}$) nanoparticles (20–40 ng/m^3) were also determined. In Table 1, the RTIL has desired sensitivities ($R_{\text{IL}}/R_{\text{nano}} = 10\text{--}11$) to the ZnO and ZnS nanoparticles. A greater sensitivity (13) of the RTIL to the nanosize TiO_2 (20–101 nm) particles is also found. It seems that the RTIL can absorb nanoparticles with a good selectivity.

To better understand how the absorbed nanoparticles interact with the RTIL, chemical structure of the anions $[\text{PF}_6]$ in the RTIL during sensing of the phosphor fly ash, ZnO, and ZnS nanoparticles was studied by ^{31}P NMR (shown in Figure 1). It is clear that the $[\text{PF}_6]$ is not perturbed during

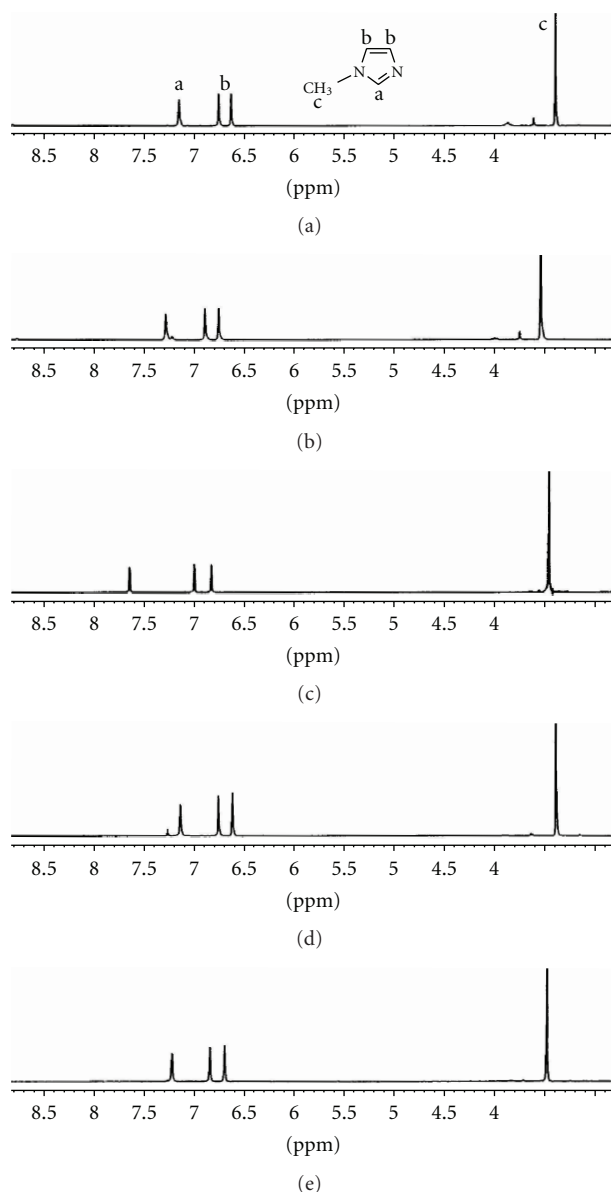


FIGURE 3: ^1H NMR spectra of the (a) 1-methylimidazole ((mim)), (b) Zn-(mim) and (c) phosphor fly ash, (d) ZnO, and (e) ZnS nanoparticles absorbed (mim).

sensing of the nanoparticles. By pulsed-field gradient spin-echo NMR, it was found in the separate experiments [15] that the nanosize (13 nm) Cu@C particles might interact selectively with the RTILs. The cavity sizes in the matrix of the RTIL are in the range of 0.1–1.0 nm [5], providing enough space to confine nanoparticles as large as 10 nm in diameter.

The ^1H NMR spectra in Figure 2 indicate that perturbation of the $[\text{C}_4\text{mim}]$ cations in the RTIL are not observed during sensing of the phosphor fly ash, ZnO and ZnS nanoparticles. Nevertheless, a small amount (2%–5%) of (mim) (at 6.69 and 7.07 ppm) in the RTIL can be found. Perturbation of the nanoparticles with (mim) in the RTIL especially near the (mim) ring is clearly observed

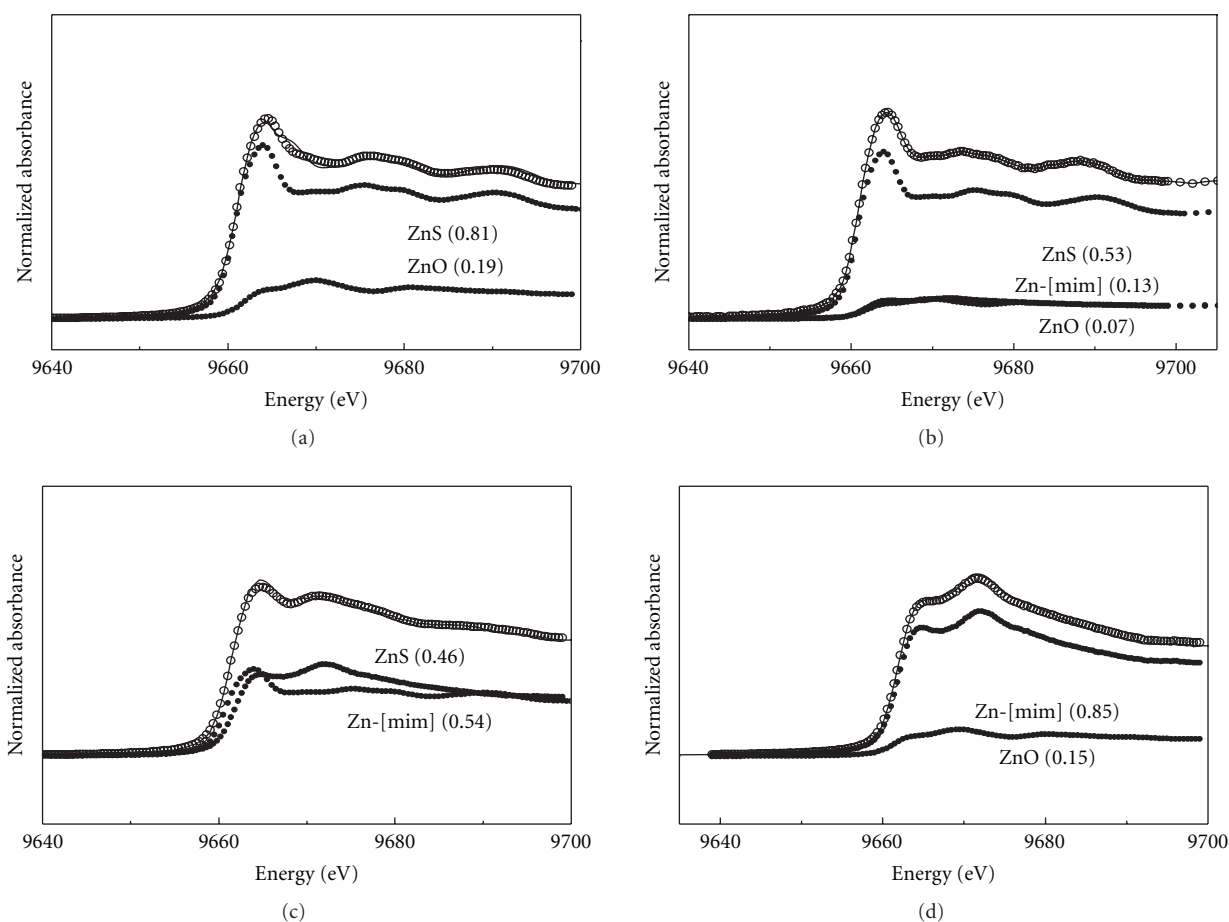


FIGURE 4: Component-fitted XANES spectra of zinc in the phosphor fly ashes having sizes of (a) <5000 nm and (b) <200 nm and nanosize (c) ZnS, and (d) ZnO absorbed in RTIL.

(see Figure 3). Without (mim) in the RTIL, absorption of nanoparticles was found to be not very effective. It seems that (mim) may behave as a carrier to assist transportation of nanoparticles into the RTIL matrix, a similar observation to the previous work [5]. It is also noted in Figure 3 that the high sensitivity ($R_{\text{nano}}/R_{\text{IL}}$) of the RTIL to ZnO or ZnS nanoparticles may be associated with formation of Zn-(mim) complexes during sensing. The (mim) is barely observed, suggesting that chemical interactions between (mim) and nanoparticles may exist.

XANES can provide information such as the oxidation state of an excited atom, coordination geometry, and bonding of local environment in the complex matrix via comparison with model compounds. The XANES spectra are expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range of 9640–9700 eV. Figure 4 shows the XANES spectra of zinc-containing nanoparticles absorbed in the RTIL. The white-line peak at 9667 eV can be attributed to electronic transition of 1s-to-4p. The feature at 9672 eV may be associated with zinc interacting with the RTIL (Figures 4(b) and 4(d)). The least-square fitted XANES spectra of zinc in the phosphor fly ash, ZnO, and ZnS nanoparticles, absorbed in RTIL are also shown in Figure 4. The main zinc species in the phosphor fly

ash are nanosize ZnS (81%) and ZnO (19%). The Zn-(mim) complex is also found in the nanoparticles absorbed by RTIL. It seems that the sensitivity of the RTIL to the nanoparticles is dependent on the amount of the Zn-(mim) complex in the RTIL during sensing.

4. Conclusions

The sensitivity of the RTIL to the phosphor fly ash (<200 nm) is 7.0, while the RTIL has higher sensitivities of 11 and 10, respectively, to ZnO and ZnS nanoparticles. By component fitted XANES spectroscopy, it seems that the Zn-(mim) complex is formed and assists sensing of the phosphor fly ash, ZnO and ZnS nanoparticles with the RTIL. By ^1H and ^{31}P NMR, it is found that the sensitivity of the RTIL to the nanoparticles is associated with the presence of the Zn-(mim) complex in the RTIL during sensing. The (mim) may act as a carrier of the nanopollutants to be more accessible during sensing with the RTIL.

Acknowledgment

The financial support of the Taiwan National Science Council is gratefully acknowledged.

References

- [1] D. A. Lauffenburger and J. L. Linderman, *Receptors: Models for Binding, Trafficking and Signaling*, Oxford University Press, New York, NY, USA, 1993.
- [2] H. L. Karlsson, J. Gustafsson, P. Cronholm, and L. Möller, "Size-dependent toxicity of metal oxide particles-A comparison between nano- and micrometer size," *Toxicology Letters*, vol. 188, no. 2, pp. 112–118, 2009.
- [3] T. Welton, "Room-temperature ionic liquids. Solvents for synthesis and catalysis," *Chemical Reviews*, vol. 99, no. 8, pp. 2071–2083, 1999.
- [4] H. L. Huang, H. P. Wang, E. M. Eyring, and J. E. Chang, "Recovery of nanosize zinc from phosphor wastes with an ionic liquid," *Environmental Chemistry*, vol. 6, no. 3, pp. 268–272, 2009.
- [5] H. L. Huang, H. P. Wang, G. T. Wei, I. W. Sun, J. F. Huang, and Y. W. Yang, "Extraction of nanosize copper pollutants with an ionic liquid," *Environmental Science and Technology*, vol. 40, no. 15, pp. 4761–4764, 2006.
- [6] H. L. Huang, H. P. Wang, YU. L. Wei, I. W. Sun, and H. L. Chen, "Extraction of copper in ZSM-5 with a RTIL," *Electrochemistry*, vol. 77, no. 8, pp. 748–750, 2009.
- [7] J. S. Wilkes, "A short history of ionic liquids—from molten salts to neoteric solvents," *Green Chemistry*, vol. 4, no. 2, pp. 73–80, 2002.
- [8] G. T. Wei, Z. Yang, C. Y. Lee, H. Y. Yang, and C. R. C. Wang, "Aqueous-organic phase transfer of gold nanoparticles and gold nanorods using an ionic liquid," *Journal of the American Chemical Society*, vol. 126, no. 16, pp. 5036–5037, 2004.
- [9] H. M. Lin, S. J. Tzeng, P. J. Hsiau, and W. L. Tsai, "Electrode effects on gas sensing properties of nanocrystalline zinc oxide," *Nanostructured Materials*, vol. 10, no. 3, pp. 465–477, 1998.
- [10] K. S. Lin and H. P. Wang, "Rate enhancement by cations in supercritical water oxidation of 2-chlorophenol," *Environmental Science and Technology*, vol. 33, no. 18, pp. 3278–3280, 1999.
- [11] M. C. Hsiao, H. P. Wang, and Y. W. Yang, "EXAFS and XANES studies of copper in a solidified fly ash," *Environmental Science and Technology*, vol. 35, no. 12, pp. 2532–2535, 2001.
- [12] C. H. Huang, H. P. Wang, J. E. Chang, and E. M. Eyring, "Synthesis of nanosize-controllable copper and its alloys in carbon shells," *Chemical Communications*, no. 31, pp. 4663–4665, 2009.
- [13] K. S. Lin and H. P. Wang, "Shape selectivity of trace by-products for supercritical water oxidation of 2-chlorophenol effected by CuO/ZSM-48," *Applied Catalysis B: Environmental*, vol. 22, no. 4, pp. 261–267, 1999.
- [14] E. A. Stern, M. Newville, B. Ravel, Y. Yacoby, and D. Haskel, "The UWXAFS analysis package: philosophy and details," *Physica B*, vol. 208–209, pp. 117–120, 1995.
- [15] F.-L. Chen, A. Letortu, C.-Y. Liao et al., "Cu@C nanoparticles dispersed RTILs used in the DSSC electrolyte," *Nuclear Instruments and Methods in Physics Research A*, vol. 619, no. 1–3, pp. 112–114, 2010.

