

Research Article

Raman Spectroscopy Characterization of Dissolved Polysilicon Byproduct SiCl_4 in Ionic Liquids

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Silicon tetrachloride (SiCl_4) is the main byproducts of the polysilicon industries. The dissolution behaviors of SiCl_4 in imidazolium ionic liquid, including [Bmim]OTf, [Bmim]NTf₂, [Hmim]NTf₂, and [Omim]NTf₂, were investigated for recycling Si from SiCl_4 . Raman spectroscopy was used to understand the combination between the ionic liquid and SiCl_4 , and the conductivity of ionic liquids in different conditions was determined. The results indicated that [Bmim]NTf₂ exhibited a better SiCl_4 dissolving capacity compared to [Bmim]OTf, longer alkyl chain lengths in the imidazolium cations of the ionic liquids exhibited a better performance in dissolving SiCl_4 , and [Bmim]NTf₂:PC = 1 : 2 exhibited the best conductivity. In addition, molecular bondings between C-Cl, Si-O-Si, and C-Si were formed between the ionic liquids and SiCl_4 .

1. Introduction

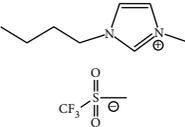
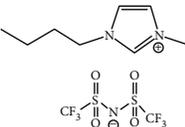
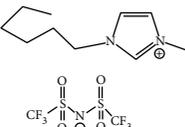
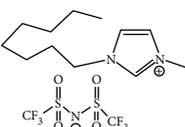
With the rapid development of industries around the world in recent decades, the depletion of nonrenewable fossil fuels may arrive in the near future. As a result, the development of green renewable energy has been given much attention in recent years, especially silicon-based photovoltaics (PV) due to the great progress presented by the photovoltaic industries. According to the target of the Chinese *Solar Photovoltaic Industry Development Plan in 13th Five-Year*, which was released in 2015, industry-leading companies have a polycrystalline silicon (poly-Si) capacity production of 50,000 tons, and the backbone enterprises had a capacity of over 10,000 tons. Silicon tetrachloride (SiCl_4) is one of the main by-products in the production of polycrystalline silicon (poly-Si) by the Siemens process, and it is a highly toxic substance. Polysilicon production generates at least four tons of SiCl_4 for every ton of polysilicon produced. Once SiCl_4 is released, it rapidly forms a dense gas cloud and reacts violently with water vapor in the atmosphere to form a gas cloud consisting of the mixture of silicon tetrachloride,

hydrochloric acid, and silicic acid, which endangers environment and people [1]. Therefore, it is essential to avoid pollution and find alternative recycling processes.

Many companies have developed technologies for recycling SiCl_4 by-products to produce resource-reusable and resource-recyclable processes that generate a great amount of SiCl_4 and simultaneously relieve their economic burdens. There are two main ways for the comprehensive utilization of SiCl_4 internationally: one uses SiCl_4 as a raw material to produce chemicals, such as white carbon black, silicate ester, optical fiber, and organic silicon [2, 3] and the other directly converts SiCl_4 to SiHCl_3 for recycling [4–6].

In recent years, the study of the dissolution of biomass materials, such as cellulose, chitin, chitosan, and the delignification of wood [7–10] in imidazolium-based carboxylate ionic liquids (ILs), has had notable advances. ILs are salts with melting point below 100°C [11]. ILs are powerful solvents that are known for their excellent solubility and low vapor pressures. In addition, ILs are good electrolytes and have a wider electrochemical window than aqueous solutions, which allow them to electrodeposit more reactive

TABLE 1: Ionic liquids used in the study.

Chemical name	Abbreviation	Structure
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	[Bmim]OTf	
1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	[Bmim]NTf ₂	
1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	[Hmim]NTf ₂	
1-Octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	[Omim]NTf ₂	

metals beyond the potential range of aqueous solutions without hydrogen gas production. As a result, the solvent function of ILs has aroused great attention in the chemistry of electrodeposition, and certain studies on the electrodeposition of Si from SiCl_4 dissolved in ILs have been performed. Abedin et al. [12] reported the initial nanoscale electrodeposition of silicon on the room-temperature IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide saturated with SiCl_4 . Gu et al. [13] indicated the presence of crystalline silicon at low temperature in an electrochemical liquid-liquid-solid process, wherein SiCl_4 was dissolved in an electrolyte system. Zhang et al. [14] reported an efficient method to prepare crystalline Si from SiCl_4 at a low temperature of 100°C with IL [N4441]TFSI as the electrolyte. Shah et al. [15] concluded that Si can be electrodeposited as thin film and crystals using ILs [Bmim]NTf₂ and [Bmim]PF₆. However, these studies do not illustrate the dissolution behavior and mechanisms of SiCl_4 in ILs.

The present study aims to find the solubility of SiCl_4 dissolved in four different ILs with different anions (trifluoromethylsulfonate (TfO^-) and bis[(trifluoromethyl)sulfonyl]imide (NTf_2^-)) and different cations (1-butyl-3-methylimidazolium [Bmim]⁺, 1-hexyl-3-methylimidazolium [Hmim]⁺, and 1-octyl-3-methylimidazolium [Omim]⁺) and to characterize the dissolution behavior of SiCl_4 dissolved in the given ILs. At the same time, Raman spectroscopy was employed to analyze the possible dissolution mechanism at the molecular level. The study aims to provide basic support for the further research of the electrochemical deposition of Si.

2. Experimental

2.1. Materials and Apparatus. SiCl_4 (analytical reagent) was purchased from Aike Chemical Reagent Co. Ltd. (Chengdu,

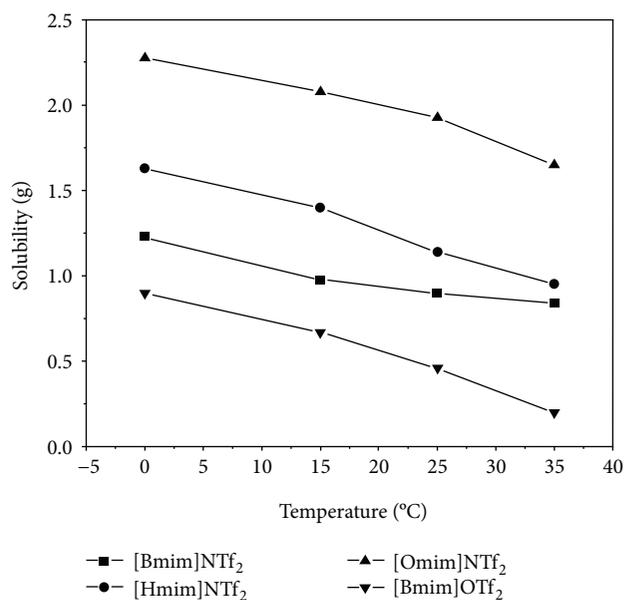


FIGURE 1: Solubility of SiCl_4 in the imidazolium ILs at different temperatures.

China). The ILs were produced by Shanghai Cheng Jie Chemical Co. Ltd. (Shanghai, China), and their full names, abbreviations, and chemical structures are presented in Table 1. All IL samples were exposed to a moderate temperature of 80°C for 48 h in a vacuum drying oven to remove the water content and minimize the presence of volatile compounds.

2.2. Experimental Methods. The solubility of SiCl_4 in ILs was tested by the liquid-liquid phase equilibrium system. SiCl_4

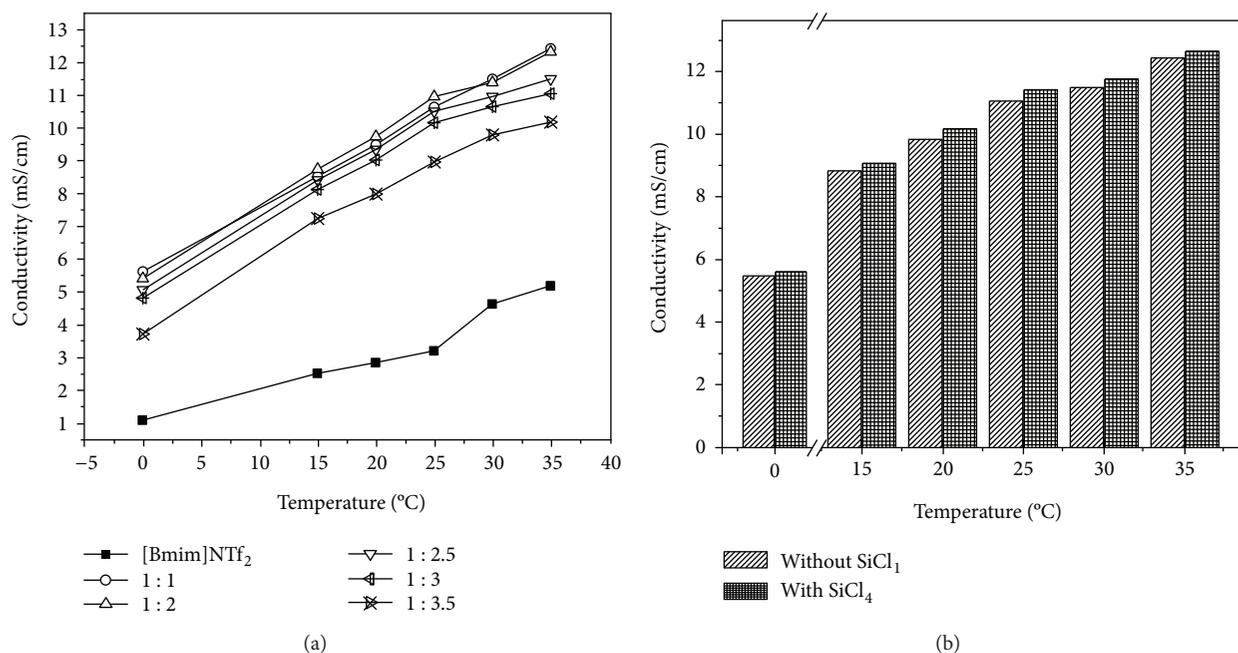


FIGURE 2: (a) Conductivity of [Bmim]NTf₂:PC at different ratios and under different temperatures and (b) conductivity of [Bmim]NTf₂:PC at a ratio of 1:2 and following the dissolution of SiCl₄.

was dripped using a pipette and added into a 10 mL glass equalizer tube that contained 5.0 g dried ILs, after which the tube was sealed with parafilm. The mixture was heated at a certain temperature and mixed for half an hour by a magnetic stirrer at certain speed, and was then left to settle for half an hour to allow the layers to separate. Additional SiCl₄ was added to the sample until a separated layer was observed. The mixture was then cyclically weighed until a constant mixture weight was measured. Characterizing the mass of IL as M_1 and the final balanced weight as M_2 , the solubility of SiCl₄ in the ILs can be calculated as follows:

$$S(g) = \frac{M_2 - M_1}{M_1} \times 100, \quad (1)$$

where (g) represents the amount of SiCl₄ that was dissolved in 100 g ILs.

The Raman spectroscopy was obtained with SENTERRA (Bruker, Germany). The conductivity was investigated using a conductivity meter (FE30 Mettler Toledo FiveEasy™ conductivity benchtop meter, Thermo Fisher Scientific, USA).

3. Results and Discussion

3.1. Solubility Effects of SiCl₄ in ILs at Different Temperatures. The solubility values of SiCl₄ in imidazolium ILs, specifically [Bmim]OTf, [Bmim]NTf₂, [Hmim]NTf₂, and [Omim]NTf₂, were measured at 0°C, 15°C, 25°C, and 35°C, respectively (Figure 1).

3.2. Solubility Effects of SiCl₄ in ILs with Different Anions. The solubility of SiCl₄ in [Bmim]NTf₂ and [Bmim]OTf is presented in Figure 1. [Bmim]NTf₂ exhibited a better capacity in dissolving SiCl₄ than [Bmim]OTf. Considering that [Bmim]NTf₂ and [Bmim]OTf had the same cation, the

presence of different anions in the ILs affected the solubility of SiCl₄, thereby indicating that the anions in bis[(trifluoromethyl)sulfonyl]imide([NTf₂)⁻) exhibited better capacities of dissolving SiCl₄ as compared to the anions in trifluoromethanesulfonate([OTf]⁻). Another possible explanation may be the presence of stronger covalent bonds between SiCl₄ and [NTf₂)⁻, whereas SiCl₄ and [OTf]⁻ had weaker covalent bonds.

3.3. Solubility Effects of SiCl₄ in ILs with Different Alkyl Chain Lengths in the Imidazole. As shown in Figure 1, [Omim]NTf₂ exhibited the best efficiency for dissolving SiCl₄ at any temperature among the investigated ILs. The solubility of SiCl₄ in these ILs generally decreased in the following order at any given temperature: [Omim]NTf₂ > [Hmim]NTf₂ > [Bmim]NTf₂ > [Bmim]OTf.

The results indicated the effects of the alkyl chain length in the imidazole cation on the solubility of SiCl₄ given that longer alkyl chain lengths exhibited stronger advantages in dissolving SiCl₄.

3.4. Conductivity of [Bmim]NTf₂/PC/SiCl₄ at Different Temperatures. The conductivity of pure IL [Bmim]NTf₂, [Bmim]NTf₂/PC, and [Bmim]NTf₂/PC/SiCl₄ was measured at different temperatures. The results are presented in Figure 2.

As shown in Figure 2(a), the conductivity increased following an increase in temperature given that ion activities strengthen at higher temperatures. At the same time, the pure IL [Bmim]NTf₂ exhibited a lower conductivity at any given temperature due to the lower dynamic viscosity of the pure IL. The results also indicated an ideal [Bmim]NTf₂:PC dissolution conductivity ratio of 1:2. The conductivity of SiCl₄ that was dissolved in [Bmim]NTf₂/PC at a ratio of 1:2 is

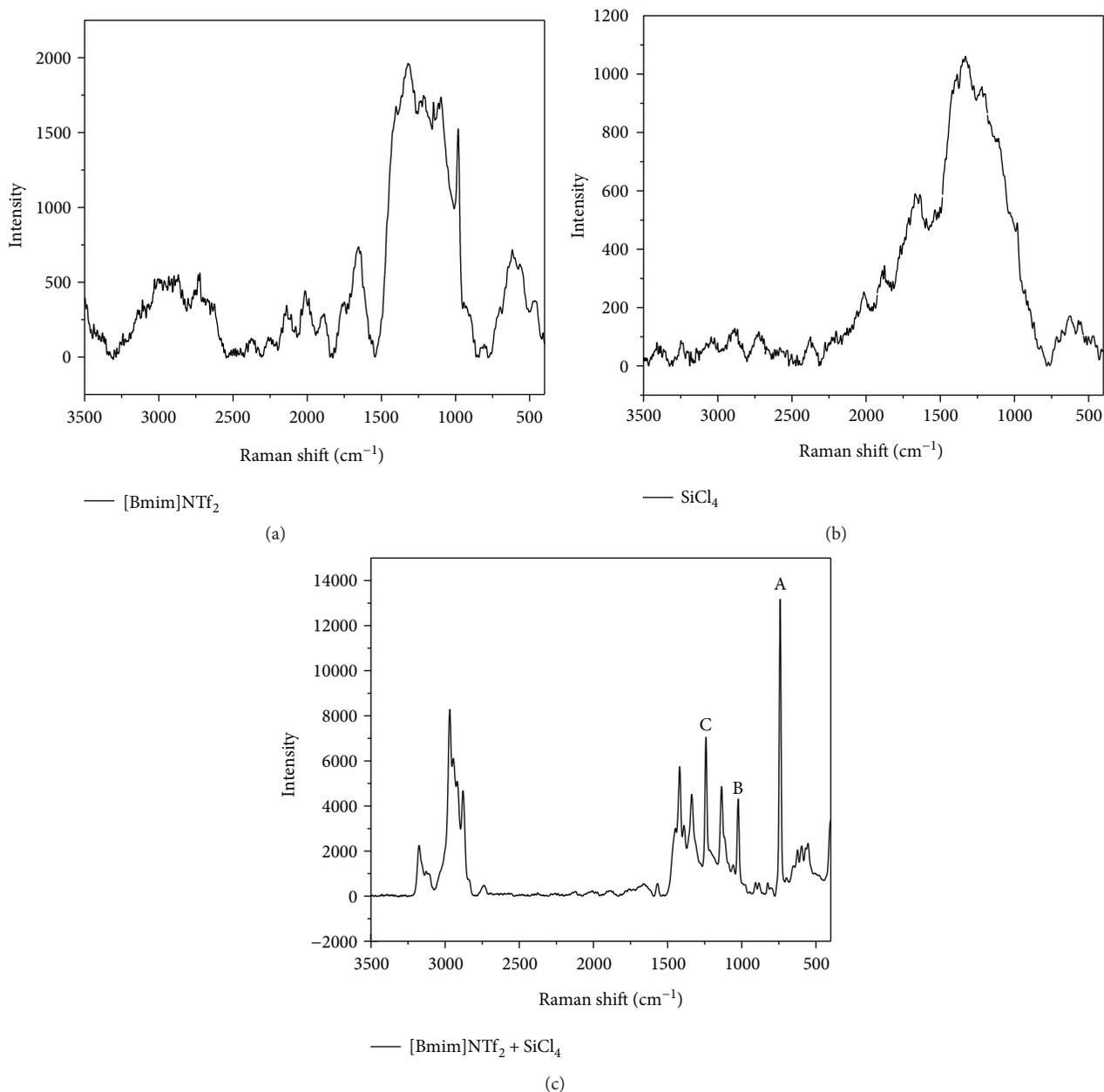


FIGURE 3: Raman spectra of the original ILs and the ILs dissolved SiCl₄.

presented in Figure 2(b), wherein the results indicated an increase in the dissolution conductivity following the dissolution of SiCl₄, though SiCl₄ exhibited very minimal effects.

3.5. Characterization by Raman Spectroscopy. To clearly define the combination of SiCl₄ with ILs at the molecular level, [Bmim]NTf₂ were characterized by Raman spectroscopy, of which the Raman spectra of original ILs and their solutions with SiCl₄ are presented in Figure 3, wherein no apparent peaks were observed in the spectra of the original ILs and SiCl₄ (Figures 3(a) and 3(b)). However, some new peaks were observed in the spectra of the ILs that were dissolved SiCl₄ (Figure 3(c)), thereby indicating that new molecular bonds were formed between the ILs and SiCl₄. The Raman shift at 740 cm⁻¹ (a) in Figure 3(c) represents C-Cl

stretching vibration, which is a strong band, whereas the observation of a new shoulder at 1024 cm⁻¹ (b) represents the presence of Si-O-Si stretching vibration. In addition, the presence of C-Si vibration at a high wavenumber 1241 cm⁻¹ (c) was observed in Figure 3(c).

Therefore, according to the molecular structures of [Bmim]OTf and [Bmim]NTf₂ in Table 1, the molecular structure of [Bmim]NTf₂ exhibited two oxygen atoms as compared to the one oxygen atom of [Bmim]OTf. The presence of Si-O bonding between the IL and SiCl₄ enhanced the SiCl₄ dissolving capacity of [Bmim]NTf₂ as compared to [Bmim]OTf, as presented in Figure 1. According to the discussions above, the molecular bondings of C-Cl and C-Si also enhanced the dissolution of the ILs and SiCl₄, thereby increasing the possibility for ILs with longer alkyl chain lengths to combine with

SiCl_4 . Based on this reason, the dissolving capacity of $[\text{Hmim}]\text{NTf}_2$ was better than that of $[\text{Bmim}]\text{NTf}_2$ at the same temperature.

4. Conclusions

- (1) The ILs had a better capacity for dissolving SiCl_4 at a lower temperature. At a temperature of 0°C , the average solubility of SiCl_4 in the ILs was measured as follows: $S([\text{Bmim}]\text{OTf}) = 0.180$; $S([\text{Bmim}]\text{NTf}_2) = 0.246$; $S([\text{Hmim}]\text{NTf}_2) = 0.326$; and $S([\text{Omim}]\text{NTf}_2) = 0.455$.
- (2) The alkyl chain length of the imidazolium cation markedly affected the solubility of SiCl_4 . The solubility of SiCl_4 in the ILs generally decreased in the following order: $[\text{Omim}]\text{NTf}_2 > [\text{Hmim}]\text{NTf}_2 > [\text{Bmim}]\text{NTf}_2$. The $[\text{Bmim}]\text{NTf}_2$ and PC exhibited the highest conductivity at a $[\text{Bmim}]\text{NTf}_2$:PC ratio of 1:2, and the change in conductivity was not apparent following the dissolution of SiCl_4 .
- (3) The formation of new molecular bondings were observed between the ILs and SiCl_4 , all of which were generated by the combinations of C-Cl, Si-O-Si, and C-Si. According to the molecular structure of the ILs, $[\text{Bmim}]\text{NTf}_2$ exhibited a better SiCl_4 dissolving capacity compared to $[\text{Bmim}]\text{OTf}$ due to the existence of Si-O-Si. In addition, the presence of C-Cl and C-Si, specifically the alkyl chain length, had a large effect on the dissolving capacity. As a result, the dissolving capacity of $[\text{Hmim}]\text{NTf}_2$ was better than that of $[\text{Bmim}]\text{NTf}_2$ at the same temperature.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

- [1] Z. Jianwen, Y. Xinxin, X. Yanan, Z. Jian, Z. Xiaoping, and J. Chunming, "Numerical investigation on three-dimensional dispersion and conversion behaviors of silicon tetrachloride release in the atmosphere," *Journal of Hazardous Materials*, vol. 288, pp. 1–16, 2015.
- [2] P. Li and T. Wang, "Thermodynamic analysis of manufacturing polysilicon from SiHCl_3 , SiCl_4 , and H_2 ," *Chinese Journal of Chemical Engineering*, vol. 23, no. 4, pp. 681–688, 2015.
- [3] Q. Chen, H. Chen, and C. Man, "Progress in research of hydrogenation of silicon tetrachloride," *Chlor-Alkali Industry*, vol. 46, no. 6, pp. 27–30, 2010.
- [4] J. Song, Z. B. Cao, L. I. Hui-Peng, Z. K. Jiang, and Y. B. Zhu, "The utilization of silicon tetrachloride which is a by-product in the production of polysilicon," *Chemistry and Adhesion*, vol. 33, pp. 57–62, 2011.
- [5] C. Wang, T. Wang, P. Li, and Z. Wang, "Recycling of SiCl_4 in the manufacture of granular polysilicon in a fluidized bed reactor," *Chemical Engineering Journal*, vol. 220, pp. 81–88, 2013.
- [6] W. J. Ding, J. M. Yan, and W. D. Xiao, "Hydrogenation of silicon tetrachloride in the presence of silicon: thermodynamic and experimental investigation," *Industrial & Engineering Chemistry Research*, vol. 53, no. 27, pp. 10943–10953, 2014.
- [7] H. Wang, G. Gurau, and R. D. Rogers, "Ionic liquid processing of cellulose," *Chemical Society Reviews*, vol. 41, no. 4, pp. 1519–1537, 2012.
- [8] O. Stolarska, A. Pawlowska-Zygarowicz, A. Soto, H. Rodriguez, and M. Smiglak, "Mixtures of ionic liquids as more efficient media for cellulose dissolution," *Carbohydrate Polymers*, vol. 178, pp. 277–285, 2017.
- [9] A. Xu, Y. Zhang, Z. Yang, and J. Wang, "Cellulose dissolution at ambient temperature: role of preferential solvation of cations of ionic liquids by a cosolvent," *Carbohydrate Polymers*, vol. 92, no. 1, pp. 540–544, 2013.
- [10] M. E. Zakrzewska, E. Bogellukasik, and R. Bogellukasik, "Solubility of carbohydrates in ionic liquids," *Energy & Fuels*, vol. 24, no. 2, pp. 737–745, 2010.
- [11] A. E. Visser, N. J. Bridges, and R. D. Rogers, *Ionic Liquids: Science and Applications*, American Chemical Society, Washington, DC, USA, 2012.
- [12] S. Abedin, N. Borissenko, and F. Endres, "Electrodeposition of nanoscale silicon in a room temperature ionic liquid," *Electrochemistry Communications*, vol. 6, no. 5, pp. 510–514, 2004.
- [13] J. Gu, E. Fahrenkrug, and S. Maldonado, "Direct electrodeposition of crystalline silicon at low temperatures," *Journal of the American Chemical Society*, vol. 135, no. 5, pp. 1684–1687, 2013.
- [14] J. Zhang, S. Chen, H. Zhang, S. Zhang, X. Yao, and Z. Shi, "Electrodeposition of crystalline silicon directly from silicon tetrachloride in ionic liquid at low temperature," *RSC Advances*, vol. 6, no. 15, pp. 12061–12067, 2016.
- [15] N. K. Shah, R. K. Pati, A. Ray, and I. Mukhopadhyay, "Electrodeposition of Si from an ionic liquid bath at room temperature in the presence of water," *Langmuir*, vol. 33, no. 7, pp. 1599–1604, 2017.



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