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Molecular interactions between carbon nanotubes and ammonium ionic liquids and their catalysis properties

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ABSTRACT

A new catalytic method has been developed for the synthesis of aza/thia-Michael addition reactions of amines/thiols, which provide higher product yields. This catalyst is a combination of multi-walled carbon nanotubes (MWCNT) with triethylammonium hydrogen phosphate (TEAP) ionic liquid (IL), commonly referred to as bucky gel. In order to gain insight into the interactions involved between IL and MWCNT, we utilised Raman spectroscopy for our analysis. The interactions between MWCNT with TEAP were clearly evidenced by the increasing intensity ratios and spectral shift in the wavelength for the Raman D and G bands of MWCNT. The morphological studies of the resulting composite materials of TEAP and MWCNT (bucky gel) were carried out using scanning electron microscopy (SEM). The key advantage of using bucky gel as a catalyst is that higher product yield is obtained in reduced reaction time for Michael reactions.

1. Introduction

Ionic liquids (ILs) and carbon nanotubes (CNTs) represent very interesting class materials due to their unique properties and wide range of applications [1–16]. Recently, the interactions between carbon nanotubes and active materials such as inorganic metal oxides render the enhanced catalytic performance [17–20]. However, there has been significant curiosity to explore the properties and interactions of ILs with CNTs [21–27]. These bucky gels are found to be of great usage in chemical, physical and biological applications [26]. Fukushima et al. [21] were the first to report that imidazolium based ILs, such as 1-butyl-3-methylimidazolium tetrafluoroborate can form a gel called "bucky gels" by grinding them with single-walled carbon nanotubes (SWCNTs). Later, Wang et al. [28] studied the dispersion mechanism of SWCNTs in imidazolium-based ILs. In order to boost the applicability of bucky gel in organic reactions, we explored the Michael reactions. The Michael reaction has also been studied for more than one century [29]. It has been used extensively in the synthesis of pharmaceutical intermediates, peptide analogues, antibiotics, and other biologically active molecules and drugs [29–33]. Unfortunately, the reaction is suffering from many limitations, such as the use of expensive reagents, harsh conditions, etc. All these limitations enforced us to explore a new, more efficient catalyst with limited drawbacks. In light of the above considerations, we have explored the combination of IL (triethylammonium dihydrogen phosphate (TEAP)) and MWCNT as a catalyst system for organic reactions commonly known as bucky gel. We also examined the interactions between MWCNT and TEAP using Raman spectroscopy. We were further motivated to carry out morphological studies of the resulting composite materials of TEAP and MWCNT using scanning electron microscopy (SEM). In addition, the synthesis of aza/thia-Michael reaction products was carried out using this bucky gel as a catalyst system.

2. Materials and methods

2.1. Materials

CNTs were obtained from Sigma-Aldrich (USA). All the reagents used were of analytical grade. Melting points were determined using a Thomas Hoover melting point apparatus. ^{1}H (400 MHz) and ^{13}C (75 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Jeol 400 NMR spectrometer in $CDCl_3$ (with tetramethylsilane (TMS) for ^{1}H and chloroform-*d* for ^{13}C as internal references).

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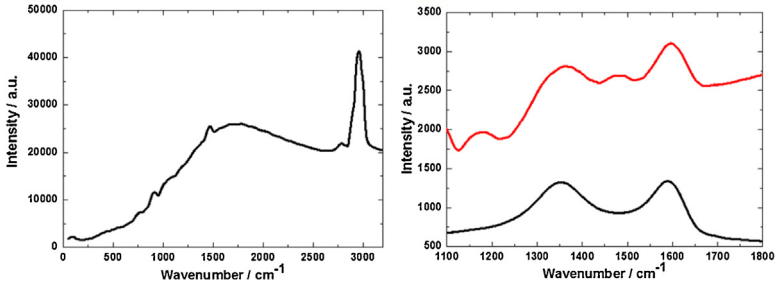


Fig. 1. Raman spectra of (a) TEAP IL, and (b) pure MWCNT (black) and MWCNT–TEAP (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

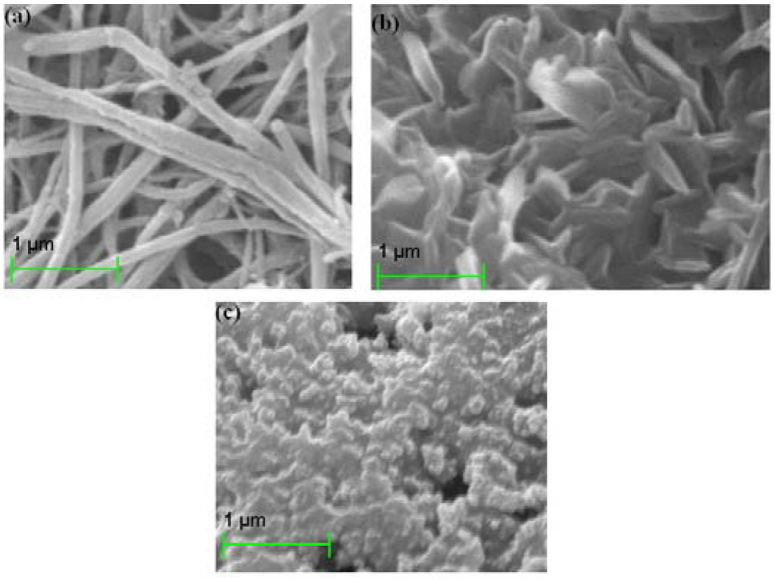


Fig. 2. SEM image of (a) pure MWCNT, (b) TEAP IL and (c) MWCNT–TEAP composite.

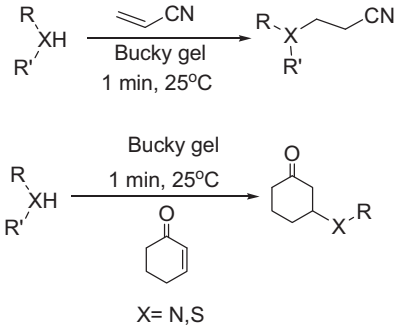
CNTs could be easily dispersed in the TEAP based room temperature IL by mechanical milling, forming a thermally stable bucky gel as discussed below [21,27,28].

2.2. General procedure for the preparation for aza/thia-Michael reaction

A solution of 1 mmol amine/thiol and 1.2 mmol α,β-unsaturated nitriles or carbonyl compounds was added to bucky gel (0.1 mmol) and the mixture was stirred at 25 °C for 1 min. Likewise, the completion of the reaction was monitored using TLC. The product formed in the one-phase system, was further extracted with ether. In the same way as in the above preparation, the resulting organic phase extract was washed with a saturated solution of $NaHCO_3$, water, and dried over Na_2SO_4. After removal of the solvent, the residue was further purified by recrystallization or silica gel chromatography. The reaction products were then analyzed using ^1H and ^{13}C NMR spectroscopy.

3. Results and discussion

Our present investigation has revealed a new catalyst system (bucky gel) for the synthesis of Michael reaction products. We have utilized the Raman spectroscopy to ascertain the interactions between TEAP and CNTs during the formation of bucky gel. Raman spectroscopy (Renishaw Raman spectroscopy, of 514 nm) proves to be a powerful tool for the structural characterization of CNTs. The Raman spectra of TEAP IL is as displayed in Fig. 1a and its comparison with that of MWCNT (black curve) and MWCNT–TEAP composite (red curve) is well exhibited in Fig. 1b. The curvature and the graphene like sheet character in the MWCNTs is better exemplified by the characteristic D and G bands of MWCNTs as depicted by all the curves. The Raman



Scheme 1. The conjugate addition of amines and thiols to α,β-unsaturated nitriles and carbonyl compounds using the bucky gel.