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Ionic liquid combined with carbon nanotubes: A soft material for the preconcentration of PAHs

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ABSTRACT

The combination of ionic liquids with carbon nanotubes has opened a new possibility of ionic liquids as modifiers for carbon nanotubes. Upon being ground into ionic liquids, carbon nanotube bundles are untangled, and the resultant fine bundles form a network structure. This is due to the possible specific interaction between the imidazolium ion component and the p-electronic nanotube surface. The resultant soft material has a high capacity to adsorb/absorb analytes from samples. In this work, the soft material was prepared by mixing 15 mg of carbon nanotubes with 300 μL of IL. The soft material was immobilized on cotton fibers to perform the preconcentration of aromatic compounds such as PAHs from river water samples. The most important fact is the synergic effect between the ionic liquid and the carbon nanotubes which results in a high capacity to preconcentrate analytes. In fact, the sorption capacity of 15 mg of the soft material containing 0.55 mg of MWNT and 11 μl of IL is two times higher than the capacity of 15 mg of MWNT and 3.7 times higher than that of 100 μl IL.

1. Introduction

The discovery of carbon nanotubes (CNTs) [1,2] has stimulated intense research activities, leading to remarkable scientific and technological advances in the development of nanostructured materials. This state-of-the-art carbon form consists of a rolled-up graphene sheet with hexagonally arranged sp^2-hybridized carbon atoms [3,4], and can be regarded as an ultimate p-electronic architecture. Since CNTs provide extraordinary mechanical, electrical, and thermal properties, numerous potential applications are expected [5]. However, one major drawback is that CNTs are hard to process due to their poor dispersability. In particular, single-walled CNTs (SWNTs) exist as ropes and bundles [6], which are heavily entangled with each other to form agglomerates. For a better processability of CNTs, many chemical and physical approaches to the modification of the CNT surface have so far been attempted [7,8]. For example, adsorption of organic molecules onto the nanotube surface by means of van der Waals forces and/or p-stacking interactions has been shown to be promising for dispersing CNTs in fluid media, occasionally affording individual nanotubes.

Ionic liquids are characterized by negligible vapor pressure, high chemical and thermal stabilities, high ionic conductivity, and broad electrochemical potential window [9–12]. Due to such unique properties coupled with an ability to dissolve a wide range of organic and inorganic substances, they have drawn increasing attention not only as a new class of electrolytes, but also for recyclable alternatives to conventional organic solvents for wet processes, including chemical syntheses, catalyses, liquid/liquid extractions, and so forth [13–15].

Compared with chemical approaches through covalent functionalization, such noncovalent approaches are easy to perform and have an additional advantage in that they can avoid disruption of the p-electronic conjugation of the CNTs. Recently; imidazolium-ion-based ionic liquids (Fig. 1) as a new class of dispersants for CNTs have been found [16]. Previously reported dispersants include solid substances that are usable only by the combination with appropriate solvents. In contrast, ionic liquids are fluid at room temperature and able to disperse CNTs by themselves, affording readily processible gelatinous substances. This feature gives a great advantage over the known examples, since one can “design” soft composite materials directly from the resulting gels, readily modify their physical properties, incorporate certain functionalities, and even transfer them into other fluid media or solid matrices. This method allows for large-scale processing of CNTs. Furthermore, we and other groups have noticed several unique aspects of the physical gels from ionic liquids and CNTs, referred to as “bucky gels” or “soft materials”. This article is devoted to study the analytical potential of this new material to preconcentrate organic molecules. PAHs have been selected in this paper as a model of aromatic compounds.

2. Experimental section

2.1. Reagents and materials

The ionic liquid (IL) used to obtain the soft material was 1-hexyl-3-methylimidazolium hexafluorophosphate ($HmimPF_6$),

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which was purchased from Merck (Spain) and used as received. The MWNTs were of two different types. MWNT-1 with diameters of 5–20 nm and length of 1–10 μm supplied by Bayer Material Science (Germany) and MWNT-2 with diameters of 10–30 nm and length of 5–15 μm supplied by Nano-Tech Port Co. (NTP, China). The purity was 90–98% and 90–95% by volume, correspondingly. HPLC grade methanol, acetonitrile and hexane were supplied by Panreac (Barcelona, Spain). Finally, purified water (18 mΩ) was obtained from a Millipore Milli-Q water purification system. The Polycyclic Aromatic Hydrocarbons (PAHs) employed as analytes were Acenaphthene (99%), Naphthalene (≥ 99%, GC), Phenanthrene (≥ 97%, HPLC), Benzo (a) pyrene (> 98%, HPLC), pyrene (≥ 99%, GC) and perilene (≥ 99%, GC) from Fluka (Spain). Benz (a) anthracene (≥ 98%, GC/HPLC), fluoranthene (99%) and fluorene (99%) were purchased from Aldrich (Spain).

2.2. Equipment. Instrumentation

Absorption and fluorescence emission spectra were measured on a PTI QuantaMasterTM Spectrofluorometer (Photon Technology International) equipped with a 75 W xenon short arc lamp and the model 814 PTM detection system. FeliX32 software was used for fluorescence data collection and analysis, which also controlled the whole instrument. The slit widths for excitation and emission were both 3 nm. All optical measurements were carried out in 1 cm quartz cuvettes at room temperature under ambient conditions.

Transmission electron microscopy (TEM) experiments were carried out with a Jeol JEM 2010 high-resolution electron microscope to obtain high-resolution images. Samples were prepared by placing one drop of a dilute solution of MWNT onto a copper TEM grid with a Carbowax forward.

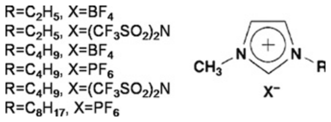

Fig. 1. Molecular formulas and schematic structures of typical imidazolium-ion-based ionic liquids.

2.3. Preparation of the soft material and extraction unit

The soft material was prepared by mixing 15 mg of carbon nanotubes with 300 μL of IL. The suspension formed was then ground in an agate mortar with a pestle. After that the suspension turned viscous, affording a soft material like a gel. Finally to prepare the extraction unit, a cotton fiber with a diameter of 4 mm and a length of 1.3 mm that corresponds to an area of 16.3 mm^2 was used as a support. To impregnate the cotton with the soft material, the cotton was immersed in the gel, excess of gel was removed and the surface was carefully smoothed with the weighing paper.

3. Results and discussion

MWNTs were mixed in a mortar with an ionic liquid such as 1-hexyl-3-methylimidazolium hexafluorophosphate. During this time the suspension turned viscous, affording a gel or soft material. This observation implied that the ionic liquid may interact with the π-electronic surface of the MWNTs by means of cation–π and/or π–π interactions. However, unexpectedly, the gelation was not reproducible. After many trials with magnets, the mixing of ionic liquid with MWNTs in an agate mortar with a pestle was the most reproducible method. The gelation occurs in a variety of imidazolium-ion-based ionic liquids (Fig. 1) upon grinding with 0.5–1 wt% (critical gel concentration) of MWNTs [16].

When MWNTs are ground into ionic liquid in excess with respect to the critical gel concentration, the gel and ionic liquid phases are clearly separated from each other by centrifugation, indicating that the gel can trap a limited amount of the ionic liquid. Bucky gels thus obtained are easy to process into any shape. For example, through extrusion from a needle, one can fabricate a cable-like material that is not easily torn apart even when suspended. Due to the negligible volatility of ionic liquids, bucky gels, in sharp contrast with ordinary organogels and hydrogels, are highly stable and can retain their physical properties even under a reduced pressure.

By means of transmission electron microscopy (TEM), we found that bucky gels contain highly exfoliated MWNT bundles

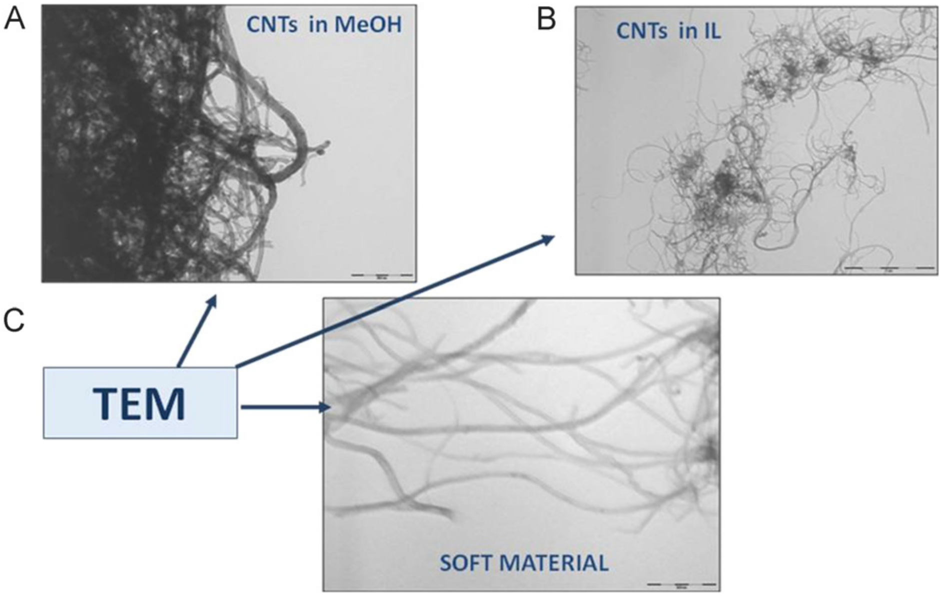

Fig. 2. TEM micrographs of MWNTs (A) received from a commercial source and dispersed in methanol, (B) dispersed in [Hmim][PF$_6$], deposited on the grid and washed with methanol to remove the IL and (C) the soft material located on the grid and washed with methanol to remove the IL.

(Fig. 2). As observed by electronic absorption and Raman spectroscopy, MWNTs are not chemically disrupted, indicating that the gelation is induced only physically. Meanwhile, the rheological properties of the bucky gels suggested that the gel involves an elastic network.

Raman spectroscopy has been used to assess the integrity of MWNTs in HmimPF$_6$ and to provide information about the interaction between the CNTs and the ionic liquid. Fig. 3 depicts the Raman spectra obtained for the bundled MWNTs studied. The spectra exhibit the typical bands of MWNTs, namely the G-band (1597 cm^{-1}), which comprises several tangential modes due to stretching vibrations in MWNT sidewall C–C bonds, the D-band (ca. 1287 cm^{-1}), which is assigned to disordered carbon, and its second-order harmonic (the G-band, ca. 2582 cm^{-1}). The D-band is associated with disordered sp^3-hybridized carbon present as impurities and MWNT defects. The G/D ratio, which increases with increasing graphite crystallite size, is a measure of purity. We thus ascribed the increased G/D ratio obtained to the sample treatment removing carbonaceous impurities from the CNT surface. The Raman bands of the MWNT can be better observed in the difference spectrum, which was calculated following baseline correction and normalization to the 2978 cm^{-1} band for the ionic liquid. A blue-shift of the G-band was observed in the dispersions. The magnitude of this shift ranged from 8 to 12 cm^{-1} and depended on the concentration of MWNTs. Such interactions lead to the formation of a new system, IL-coated MWNTs, which consist of isolated or weakly interacting MWNTs. The extent of formation of the π-complex depends on the degree of overlap between pz orbitals in the carbon atoms or, in others words, on the cylindrical shape of the MWNTs. It is important to remark that the same behavior and analytical response were obtained for the two types of nanotubes studied in this work. However, considering that the soft material was easy to prepare with MWNT-1 and that the obtained soft material presented a higher mechanical stability, it was selected to study the analytical response to a preconcentration. This higher capacity to form the gel was attributed to a minor content in amorphous carbon material.

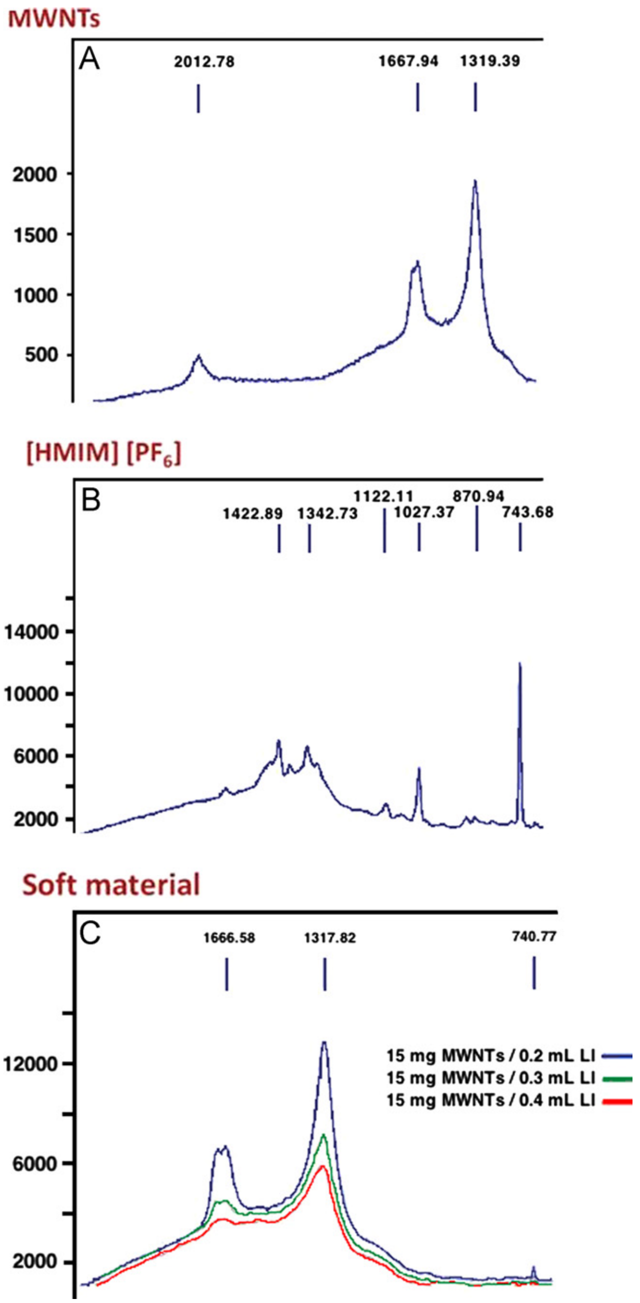

Fig. 3. Raman spectrum (A) MWNTs, (B) ionic liquid and (C) soft material at three different MWNT/IL ratios.

From the chemical point of view, one interesting characteristic of the soft material is its chemical stability. When the material is introduced in different solvents, a part of the ionic liquid is solubilized in the solvent. In general the solubility of the ionic liquid was clearly lower in the presence of the carbon nanotubes in spite of the excess of the ionic liquid in the soft material. Fig. 4 compares the native intrinsic native fluorescence of the IL in different solvents. The native fluorescence of the IL was measured at 435 nm by exciting the system at 395 nm. As can be seen, the intensity of fluorescence was significantly reduced. It will be then possible to desorb the analytes with organic solvents preserving the integrity of the soft material. In addition, direct spectroscopic fluorimetric measurements of desorbed analytes will be possible without the interference of IL.

Fig. 5 shows the isotherms obtained for the preconcentration of naphthalene. As can be seen, two linear ranges are observed. This means that the sorption of analytes is the result of the combination of adsorption but also absorption mechanism. The most important aspect or characteristics of this material is the synergic effect that exists of the IL with the MWNTs. We suppose that this synergic effect is the result of the special orientation of the MWNT in the soft material. This special orientation allows the lateral interaction of carbon nanotubes probably through the π system. Because the π system is stabilized and presents a energy level similar to the energy level of the π system of the organic aromatic compound. This facilitates the interaction. As can be seen in Fig. 6, the sorption capacity of 15 mg of the soft material is two times higher than the capacity of 15 mg of MWNT and 3.7 times higher than that of 100 μl IL. However 15 mg of soft material only contain 0.55 mg and 11 μL of IL. Although, as an example the result of naphthalene was presented, the same effect was obtained for all the PAHs analyzed. In order to demonstrate the analytical potential of this method, several river water samples obtained from the Guadalquivir were analyzed. Because no positive samples were obtained, spiked samples were also analyzed. For that, 11 samples were spiked in the range 5–60 μg/L with different PAHs. Standards and spiked samples were analyzed at the same concentration level. The Fig. 7 shows the result of the representation of fluorescence of spiked samples in front of the fluorescence of standard samples. As can be seen, the graph was statistically comparable with the theoretical graph of slope 1 and intercept 0. The recovery was in the range from 87–105% and the precision, measured as relative standard deviation of the analysis of 15 consecutive samples at the limit of quantification, was 5.7%.

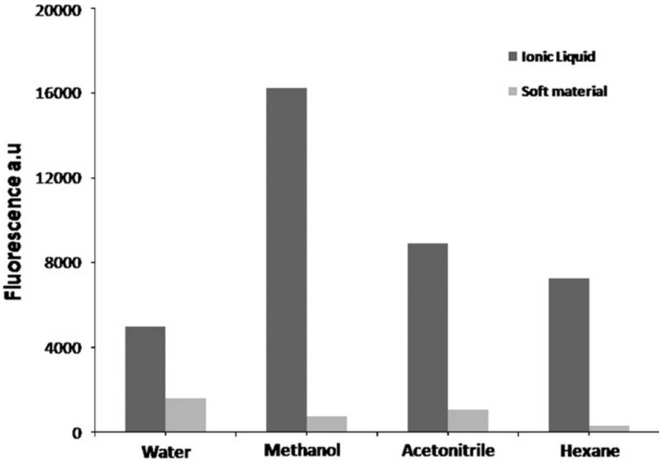

Fig. 4. Comparison of native fluorescence of IL in different solvents obtained after introducing the IL or soft material in the respective solvent.

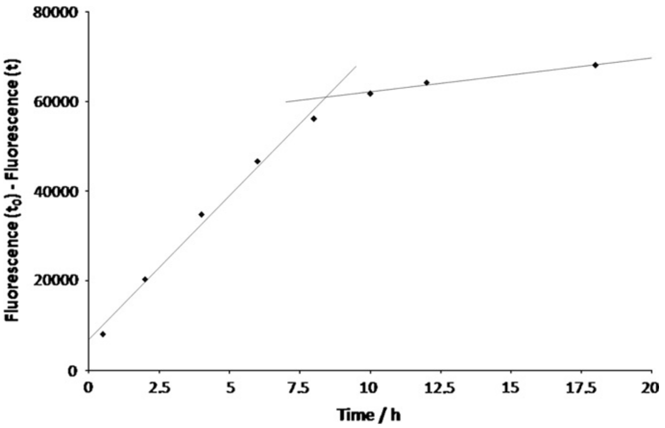

Fig. 5. Characteristic isotherm: evolution of the preconcentration with time.

4. Conclusion

In this work, the use of soft materials obtained from the combination of ionic liquid with carbon nanotubes as sorbent material for the preconcentration of organic compounds such as PAHs has been described. Compared with IL or free MWNTs, the sorption capacity of the soft material was clearly higher pointing out the synergic effect produced by the orientation of the carbon nanoparticles in the soft material.

This result open up new possibilities to the use of soft materials in analytical chemistry to perform sample cleanup and treatment.

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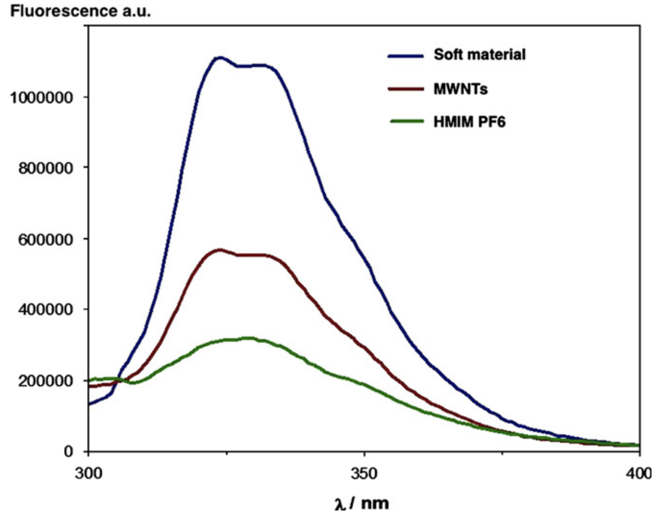

Fig. 6. Comparison of sorption capacity of 15 mg of soft material versus 15 mg of MWNTs and 100 μL of IL.

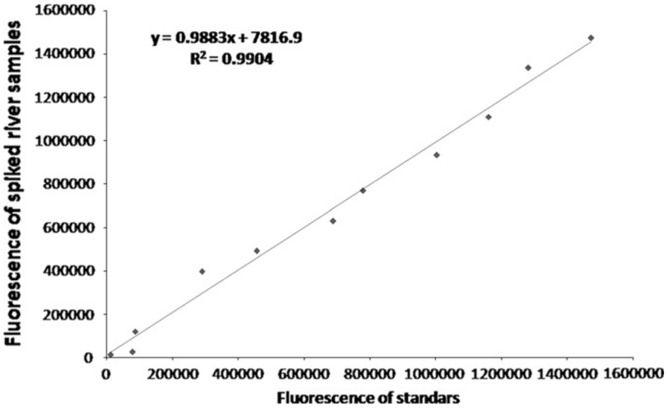

Fig. 7. Recovery of the analysis of spiked river samples. Representation of the concentration found versus concentration added.

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