



Urea-silica nanohybrids with potential applications for slow and precise release of nitrogen



Madhavi de Silva^{a,1}, Dumindu P. Siriwardena^{a,1}, Chanaka Sandaruwan^{b,1}, Gayan Priyadarshana^c, Veranja Karunaratne^d, Nilwala Kottegoda^{a,*}

^a Department of Chemistry, Center for Advanced Materials Research, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

^b Sri Lanka Institute of Nanotechnology (SLINTEC), Homagama, Sri Lanka

^c Faculty of Technology, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

^d Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

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ABSTRACT

The adoption of nanoparticles as carrier matrices in the production of hybrid functional materials is futuristic in agriculture applications. In this study, a greener, modified *in-situ* sol-gel route was employed to synthesize urea-silica nanohybrids with a high urea loading of 36% (w/w) and a loading efficiency of ~83%. Characterization studies indicated the successful incorporation of urea into silica nanoparticles and the formation of strong bonds between the nanoparticles and urea molecules without any substantial modification to the structure and morphology of silica nanoparticles. Aforesaid observations were further corroborated by the slow and sustained release behavior exhibited by nanohybrids in water for more than ten days. The developed urea-silica nanohybrids could be utilized as a potential candidate for slow-release nitrogen fertilizers.

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1. Introduction

Nanohybrids have gained momentum in the recent past owing to their versatile applications in a wide spectrum of fields. Quantum effects, which originate from the manipulation of matter at a scale of one billionth of a meter, award these nanohybrids special properties in contrast to their macro-scale counterparts [1–3]. There are a multitude of instances where nanohybrids are used for medicinal, energy-related, electronic and construction applications. Ironically, there is a paucity of work in developing novel nanohybrids relating to agriculture.

Over the last years different carrier matrices have been utilized in the synthesis of nanohybrids for efficient delivery of plant nutrients. The development of such efficient nanofertilizers for increased crop yields is of timely importance due to increasing human population and demand for food with limited land availability for farming. Earlier, our group has reported the successful synthesis of urea-hydroxyapatite and urea-layered material nanohybrids as slow-release plant nutrients [3–6]. Wanyika et al has previously described the synthesis of mesoporous silica

nanoparticles as a carrier for urea molecules [7]. However, the major drawbacks of this work is its complex liquid crystal templating synthetic protocol and the low urea loading of 15.5% (w/w) [7]. Therefore, the current study focuses on a novel energy-efficient synthesis of urea-silica nanohybrids with a high nitrogen loading.

Herein, we disclose a relatively greener synthetic approach for the development of urea embellished silica nanoparticles with a urea loading of 35.6% (w/w). Silica nanoparticles play a dual role by acting as the carrier matrix for urea and by supplying silicon which is a micro plant nutrient necessary for the plant growth. Importantly, slow and sustained release behavior exhibited by nanohybrids prevents the premature loss of urea.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS) (Sigma Aldrich, 99.9%), urea (Research Lab, 99.5% w/w), ammonia and reagents used throughout this research were of analytical grade and employed without further purification. Distilled water was used in all solution preparations and as a reagent.

* Corresponding author.

E-mail address: nilwala@sjp.ac.lk (N. Kottegoda).

¹ These authors contributed equally.

2.2. Preparation of urea-silica nanohybrids using modified sol-gel method

A mixture of TEOS (10 cm³) and methanol (50 cm³) was stirred at 400 rpm for 10 min at room temperature until TEOS dissolved completely. Next, distilled water (2 cm³) was added drop wise using a micro burette at a rate of 0.2 cm³/min and the mixture was further stirred for 1.5 h at 50 °C. Ammonia (25%, 4 cm³) was added drop wise at a rate of 0.15 cm³/min with simultaneous addition of 5–6 drops of urea solution (prepared by dissolving 2 g urea of in a minimum amount of methanol). Stirring of the mixture at a rate of 400 rpm continued for 3.5 h at 50 °C. Synthesized gels were

then dried using microwave drying (MW) (1000 W, 2450 MHz) in 10 s cycles for 2 min and conventional oven drying (OD) (60 °C, 48 h) methods to obtain microwave dried silica nanoparticles (S_{MW}) and oven-dried silica nanoparticles (S_{OD}), respectively.

2.3. Characterization of nanohybrids

Morphological studies of nanohybrids were conducted using Hitachi SU 6600 Scanning Electron Microscope and JEOL JEM-2100 Transmission Electron Microscope. Nicolet IS 10 FTIR spectrophotometer was used to analyze solid samples using diffuse reflection mode (500–4000 cm⁻¹) and Bruker Vertex 80 FTIR spec-

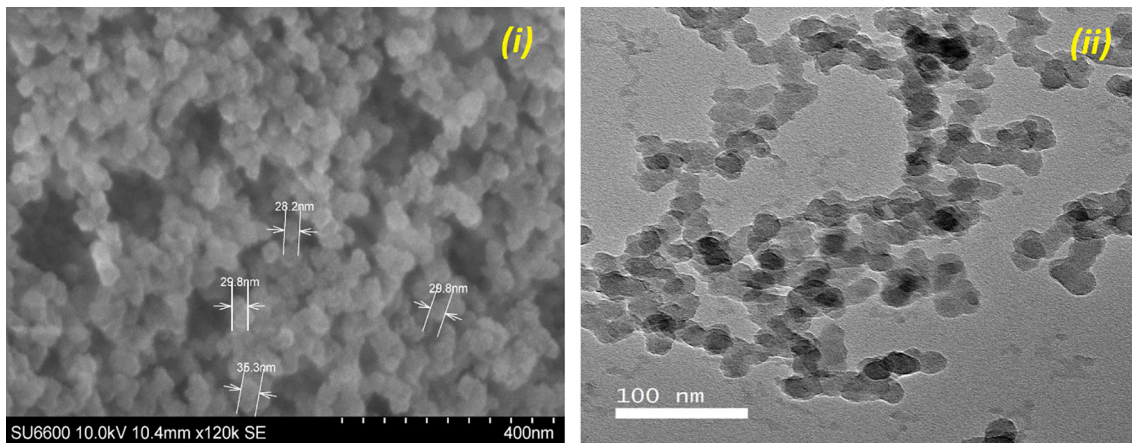


Fig. 1. (i) SEM, (ii) TEM images of S_{MW}.

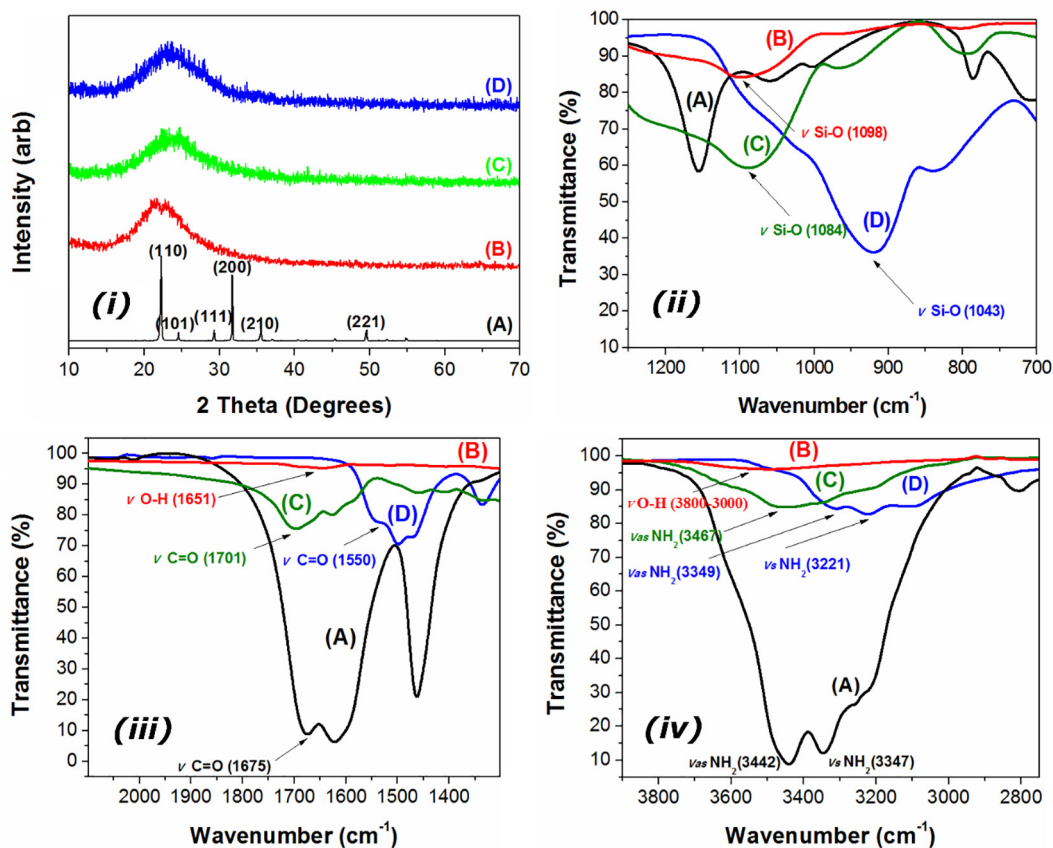


Fig. 2. (i) PXRD patterns, FTIR spectra of (ii) NH₂ (iii) C=O (iv) Si-O regions of (A) urea (B) silica nanoparticles (C) S_{OD} (D) S_{MW}.

trophotometer with ATR attachment was used to analyze liquid samples. Powdered urea-silica nanohybrids were analyzed using Rigaku Powder X-Ray diffractometer within the range of 5° to 70° 2θ angle at a step size of 0.02° using Cu $K\alpha$ radiation. Perkin Elmer 2400 CHNS/O Series II System analyzer was utilized for elemental analysis.

2.4. Urea release studies in water

The urea release behavior of the synthesized nanohybrids in water was studied by quantifying the amount of nitrogen released in water according to the method described by Kottegoda et al [3]. An amount of 0.60 g of each nanohybrid was used for the study and pure urea (0.13 g) as the control. Elutes were collected in 24 h intervals for 11 days and analyzed using FTIR.

2.5. Kinetic models

The results obtained from the urea release studies were fitted into previously described kinetic models such as zero-order kinetics, first-order kinetics, Higuchi and Korsmeyer-Peppas to obtain rate constants and R^2 values to investigate and identify the urea release mechanism.

3. Results & discussions

Morphological, structural and behavioral patterns of the nanohybrids were studied in order to investigate their suitability as a potential plant nutrient. Scanning and transmission electron micrographs (Fig. 1) showed that even after the urea surface mod-

ification, silica nanoparticles were able to retain their original spherical shape below ~ 50 nm. The slow addition of urea along with other reagents provides sufficient time for silica nanoparticles to grow along the z-axis direction resulting in a definite nanoscale spherical shape. A urea loading efficiency of $\sim 83\%$ was achieved for both nanohybrids. C: H: N elemental compositions of both the S_{MW} and S_{OD} nanohybrids were identical at 6: 3: 12.

PXRD patterns (Fig. 2 (i)) of the synthesized nanohybrids (S_{MW} and S_{OD}) exhibit a remarkable resemblance to the diffractogram obtained for pure silica nanoparticles which leads to the conclusion that the encapsulation of urea has not considerably modified the structure of silica nanoparticles. However, we noticed the absence of crystalline peaks originating from urea in the diffractogram. This indicates the loss of crystalline nature of pure urea during the encapsulation process attributable to interactions that occurred with silica nanoparticles.

Interestingly, in the FTIR spectrum of S_{MW} nanohybrid (Fig. 2 ii, iii, iv) all major peaks including N-H stretching, C=O stretching, Si-O asymmetric stretching, Si-O-Si stretching have undergone significant shifts to lower wavelengths compared to that of pure urea and silica nanoparticles. Peak broadening and ~ 80 cm^{-1} shift observed in asymmetric N-H stretching vibrations of urea could be attributed to the formation of large amounts of new hydrogen bonds and other new non-electrostatic forces. Similarly, C=O stretching vibration frequency has shifted by 125 cm^{-1} and the peak intensity has also decreased further confirming the presence of hydrogen bonds. The electron flexibility of the C=O bond has reduced by virtue of the silica nanoparticle matrix and the existing hydrogen bond network. A shift of 55 cm^{-1} was observed in the Si-O asymmetric stretching frequency arising from the hydrogen

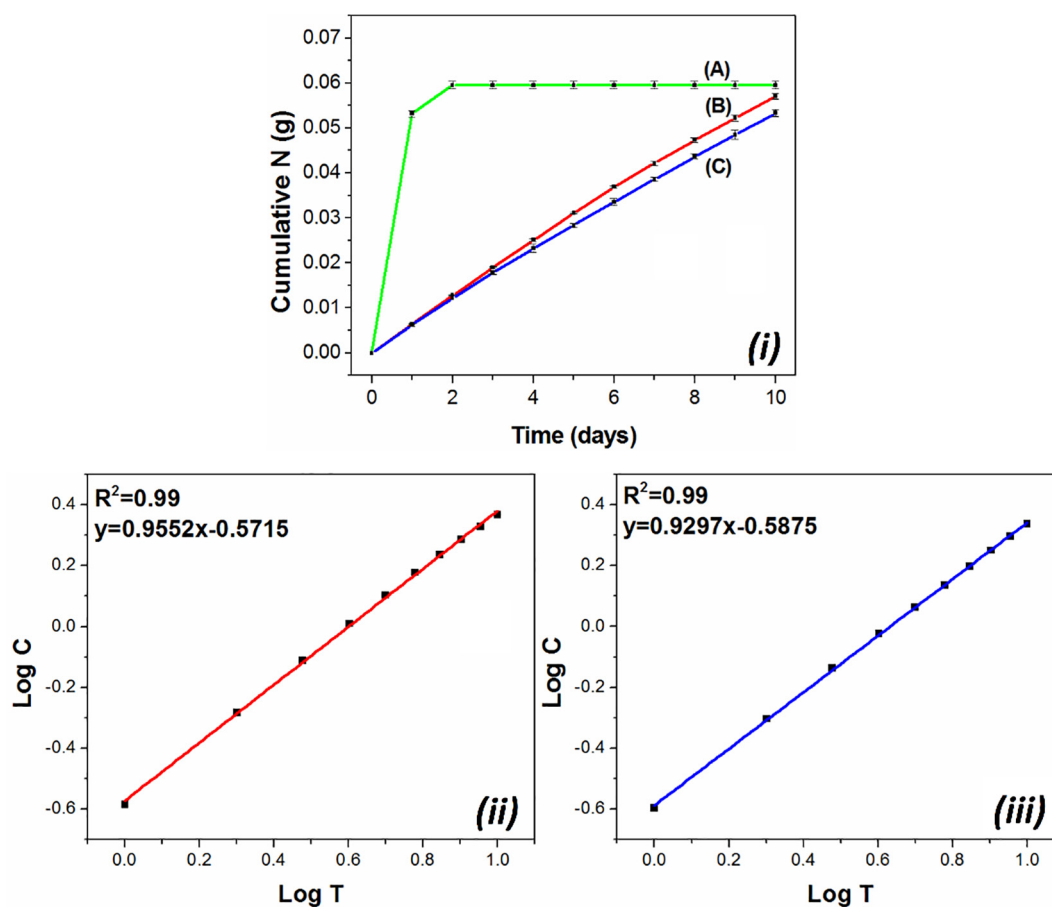


Fig. 3. Comparison of (i) release behavior of (A) Urea (B) S_{OD} (C) S_{MW} and release kinetics for Korsmeyer-Peppas model of (ii) S_{OD} and (iii) S_{MW} .

bonding with urea molecules or solvent molecules remaining in the final solid product. Peak intensity Si-O-Si stretching vibration has decreased suggesting the reduction of the number of Si-O-Si bonds. The formation of new hydrogen bonds in the silica nanoparticle matrix was observed by the 20 cm^{-1} peak shift. The above-mentioned permutations contribute to evidence that urea is acting as a spacer molecule and that it has been successfully encapsulated within the silica nanoparticle matrix. The FTIR spectrum of S_{OD} was also investigated. However, it did not exhibit stronger hydrogen bond formation and peak shifts compared to that of S_{MW} .

A small, visibly slower and sustained release of nitrogen was observed over a period of more than 10 days in the synthesized nanohybrids compared to that of the quick and rapid release of all the nitrogen in urea (Fig. 3. (i)). Commonly, the release of urea from the nanohybrids showed a burst release in the beginning. Although, in both S_{OD} and S_{MW} , there was no significant burst release, they appeared to release steadily with precision over a ten day period, with S_{OD} nanohybrid showing a comparably higher urea release. This behavior demonstrates the weak bonding between urea and silica nanoparticles in the oven-dried nanohybrid compared to the microwave dried nanohybrid which was also illustrated by the FTIR data. The release behavior of both S_{MW} and S_{OD} nanohybrids fitted in alignment with Korsmeyer–Peppas model (Fig. 3. (ii,iii)) accompanied by R^2 values of 0.99 and 0.99 accordingly, expressing that the release rate of urea is controlled by the diffusion rate of urea via the silica nanoparticle matrix.

4. Conclusions

A novel nitrogen slow-release material with comparatively high nitrogen loading was developed by the surface modification of silica nanoparticles with urea via a greener synthetic procedure. Urea had interacted with the surface hydroxyl groups of silica nanoparticles through carbonyl and amine groups by forming H-bonds without causing any substantial adjustment to the structure of nanoparticles. The developed nanohybrids exhibited a slow and sustained release behavior of urea for more than ten days. This behavior was in alignment with the Korsmeyer–Peppas model implying that the release rate of urea is controlled by the diffusion rate of urea via the silica nanoparticle matrix in which urea has been bound. Thus, we can claim the suitability of Urea-Silica Nanohybrids as a slow-release plant nutrient formulation for the effective and precise delivery of nitrogen and silica to plants.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2020.127839>.

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