ACES Asian Chemical Editorial Society

DOI: 10.1002/asia.201700616

CHEMISTRY AN ASIAN JOURNAL Communication

Silica Nanohybrids

Dual-fluorophore Raspberry-like Nanohybrids for Ratiometric pH Sensing

Isaac Acquah[+],[a, d] Jinkyu Roh[+],[b] and Dong June Ahn*[a, b, c]

Abstract: We report on the development of raspberry-like silica structures formed by the adsorption of 8-hydroxypyrene-1,3,6-trisulfonate (HPTS)@silica nanoparticles (NPs) on rhodamine B isothiocyanate (RBTIC)@silica NPs for ratiometric fluorescence-based pH sensing. To overcome the well-known problem of dye leaching which occurs during encapsulation of anionic HPTS dye in silica NPs, we utilized a polyelectrolyte-assisted incorporation of the anionic HPTS. The morphological and optical characterization of the as-synthesized dye-doped NPs and the resulting nanohybrids were carried out. The pH-sensitive dye, HPTS, incorporated in the HPTS-doped silica NPs provided a pH-dependent fluorescence response while the RBITC-doped silica provided the reference signal for ratiometric sensing. We evaluated the effectiveness of the nanohybrids for pH sensing; the ratio of the fluorescence emission intensity at 510 nm and 583 nm at excitation wavelengths of 454 nm and 555 nm, respectively. The results showed a dynamic response in the acidic pH range. With this approach, nanohybrids containing different dyes or receptors could be developed for multifunctioning and multiplexing applications.

Monitoring pH is vital in many fields such as biomedical sciences and engineering, environmental science. The H^+ distribution in biological media may be non-uniform and thus it might be required that the pH gradient be captured for comprehensive evaluation. In one application, pH changes in the local microenvironments of cell cultures and microbial films was determined by the fluorescence imaging of dye-doped polymeric nanoparticles dispersed in the culture media.[1] The proliferation of cancer cells in tumors creates oxygen-deficient and acidic conditions in tumors. Screening for this acidic pH could provide a means for early detection of cancer.[2] Optical sensors based on fluorescence are popular in pH sensing due to their advantages of reduced interferences, ease of miniaturization, and relatively low cost.[3] Fluorescent-based pH sensors utilize pH-sensitive fluorophores for pH quantification. Though they have the ability to measure pH, the influences of photobleaching, nonspecific quenching and solvatochromic effects detrimentally impact the long-term stability of free fluorophore molecules and thus the accuracy of the resulting sensors.[4,30–32] To circumvent these limitations, particle-based systems incorporating the indicator dye have been developed.[3,5–7] Silica still remains one of the main matrix material for core–shell nanoparticles. The chemical versatility, biocompatibility, stability, size uniformity and tunability of silica nanoparticles (NPs) as matrix material accounts for their ubiquitous applications.[8,9,33,34] Additionally, the high surface-to volume ratio and porous characteristic of silica nano-structures increases the amount of sensor material exposed to analyte for interaction.

Despite the advantages of particulate dye-doped sensing polymers, uneven dye concentration in particles, variations in ambient and exciting laser intensities and photodetector drifts, may render the particles only effective as qualitative sensors.[10–12] Thus, merely quantifying pH based in fluorescence intensity measurements may be unreliable. Ratiometric sensing scheme is a robust method to eliminate these deleterious effects. This sensing scheme integrates an internal pH-insensitive reference dye together with a sensing dye and utilizes the ratio of the fluorescence intensities of the two dyes to quantitatively determine pH. Furthermore, the ratiometric method enhances the reproducibility of sensors by cancelling out uneven concentration effects among sensing particles.

HPTS has been widely used as a pH-sensitive fluorophore due to its high florescence quantum yield, non-toxicity and rapid response.[13–15] In spite of its attractive characteristics, its anionic nature of HPTS poses a great difficulty when embedding in silica. Synthesis of HPTS-doped silica NPs using reverse microemulsion method for pH sensing has been attempted but a significant amount of the dye out of the silica matrix when the NPs were dispersed in aqueous solution.[16] Leaching

[a] I. Acquah,[+] Prof. D. J. Ahn
Department of Biomicrosystem Technology
Korea University
145 Anam-ro, Seongbuk-gu, Seoul 02841 (Republic of Korea)
E-mail: ahn@korea.ac.kr

[b] J. Roh,[+] Prof. D. J. Ahn
Department of Chemical and Biological Engineering
Korea University
145 Anam-ro, Seongbuk-gu, Seoul 02841 (Republic of Korea)

[c] Prof. D. J. Ahn
KU-KIST Graduate School of Converging Science and Technology
Korea University
145 Anam-ro, Seongbuk-gu, Seoul 02841 (Republic of Korea)

[d] I. Acquah[+]
Biomedical Engineering Program
Kwame Nkrumah University of Science and Technology
University Post, PMB, Kumasi (Ghana)

[+] These authors contributed equally to this work.

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/asia.201700616.