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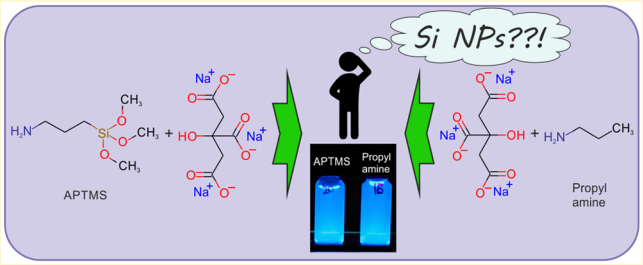
Are Fluorescent Silicon Nanoparticles Formed in a One-Pot Aqueous Synthesis?

Bohdan V. Oliinyk,*[†,‡] Dmytro Korytko,[†] Vladimir Lysenko,[§,∥] and Sergei Alekseev[†]

[†]Chemistry Department, Taras Shevchenko National University of Kyiv, Volodymyrska Street, 64, 01601 Kyiv, Ukraine
[‡]Institute of Analytical Sciences, UMR-5280, Claude Bernard University of Lyon, 5 rue de la Doua, 69100 Villeurbanne, France
[§]Lyon Institute of Nanotechnology, UMR-5270, INSA Lyon, 7 avenue Jean Capelle, 69621 Villeurbanne, France
[∥]Light Matter Institute, UMR-5306, Claude Bernard University of Lyon, 2 rue Victor Grignard, 69622 Villeurbanne, France

Supporting Information

ABSTRACT: Critical analysis of the data reported by Zhong et al. (*J. Am. Chem. Soc.* **2013**, *135* (22), 8350−8356) is carried out. In particular, one of the main results of Zhong et al. concerning the formation of photoluminescent silicon nanoparticles (Si NPs) in an aqueous solution of (3-aminopropyl)trimethoxysilane (APTMS) and trisodium citrate dihydrate (Na_3Cit) under microwave heating is impugned. These results are reconsidered here because of what appear to be significant inaccuracies and misinterpretations that have been spread through a wide number of other subsequent publications.



Being stable, environmentally benign, and inexpensively synthesized, silicon-based nanomaterials have versatile and wide-ranging optical, electronic, and biocompatible/biodegradable properties.[2−4] In particular, due to their unique optical characteristics, silicon-based colloidal nanoparticles (NPs) are well-known to be extremely promising for various multidisciplinary applications, such as bioimaging,[5,6] drug delivery,[7] photoinduced therapy,[8] and many others.[9−12] A variety of physical, chemical, physicochemical, and electrochemical techniques have been developed to produce dispersions of luminescent nanometer sized silicon crystallites.[13,14]

In 2013, a new aqueous synthetic approach based on one-pot synthesis of fluorescent Si NPs, using of (3-aminopropyl)-trimethoxysilane (APTMS) as the silicon source and trisodium citrate dihydrate (Na_3Cit), was reported by Zhong et al.[1] This work has attracted a great deal of attention from the scientific community since 2013 and has accumulated 227 citations according to Google Scholar (June 6, 2019), 203 citations according to Scopus (May 18, 2019), and 191 citations according to SciFinder (June 6, 2019). Among all these papers, special attention should be paid to those that specifically mention use of the approach described in this paper for the basis of or jumping off point for their own work.[15−51] At first inspection, the proposed technique seems to have many advantages in comparison with most other approaches reported earlier. Of these advantages, one can emphasize in particular the following: (i) water is used as a solvent, (ii) short reaction times are sufficient (15 min), (iii) low temperatures are needed (160 °C), and (iv) inexpensive precursors work well. However, taking into account common accepted knowledge in the field of silicon chemistry,[52−54] low temperature formation of crystalline Si^0 nanoparticles (as reported by Zhong et al.) from the water solutions of alkoxysilanes seems very doubtful. Indeed, it remains entirely unclear which reactants in the reaction mixture are remotely capable of reducing a silicon atom bound to oxygen. Moreover, silicon nanoparticles of the claimed size are extremely difficult to passivate and would be very rapidly oxidized to SiO_2 under the action of water.[5] If the reported reduction of the Si−O bonds by citrate were reproducible by other groups, the impact of this discovery would be much more important than just an easy and scalable method for preparation of Si NPs for biological applications. It would represent a new page of silicon chemistry that opens the door to the preparation of inexpensive silicon and silicon-based materials manufacturing. Thus, it deserves to be further investigated to avoid any incorrect speculation on that theme.

First of all, the TEM micrographs presented by Zhong et al. (Figure 1a) as well as a similar image from ref 17 show (i) a number of spherical particles without any evidence of crystallinity at a 5 nm scale and (ii) a single obviously crystalline particle at a 1 nm scale. However, if the lattice fringes are clearly visible at a 1 nm scale, they should be also visible at a 5 nm scale at least for a few particles having the correct orientation with respect to the incident electron beam (e.g., see Figure 1b). Furthermore, taking into account the

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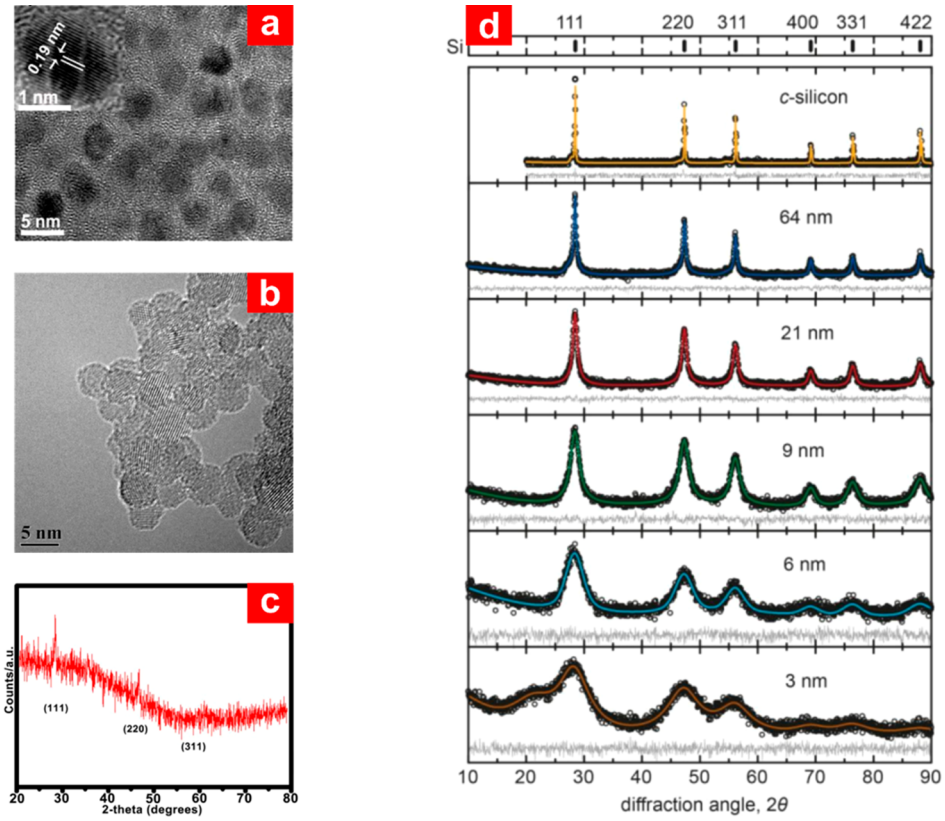

Figure 1. (a) HRTEM images of the Na_3Cit + APTMS reaction product. Reprinted with permission from ref 1. Copyright 2013 American Chemical Society. (b) HRTEM images of plasma synthesis Si NPs. Reprinted with permission from ref 56. Copyright 2009 American Chemical Society. (c) Powder XRD patterns of the Na_3Cit + APTMS reaction product. Reprinted with permission from ref 1. Copyright 2013 American Chemical Society. (d) Powder XRD patterns of crystalline Si and H-terminated Si NPs of different sizes. Reprinted with permission from ref 57. Copyright 2019 American Chemical Society.

scale bar (1 nm) in Figure 1a, the lattice spacing cannot correspond to 0.19 nm as is indicated, but rather to 0.057 nm, which seems doubtful for Si NPs.

An XRD pattern of the particles prepared by Zhong et al. (Figure 1c) differs significantly from typical XRD patterns of Si NPs (Figure 1d). Indeed, no characteristic broad peaks inherent to the nanoscale crystallites[55] can be seen on Figure 1c. The narrow and barely visible peaks at $2\theta = 28$ and 47° in Figure 1c can be related rather to traces of some crystalline admixtures (inorganic salts, for example), residual peaks from the "zero-background sample holder made of monocrystalline silicon plate"[1] or other artifacts. Furthermore, no data regarding the X-ray source is given in the original paper. Thus, the XRD data does not provide solid evidence of the formation of the 204 nm crystalline Si NPs.

Finally, according to the best practices of NP characterization,[58] provision of XPS data is absolutely necessary. Indeed, it could shed light on the oxidation state of silicon atoms in the particles. However, no thorough XPS analysis was provided in this publication, and thus, the compositional identity of the NPs is still questionable.

In order to check the assumption expressed by Zhong et al. regarding the formation of Si NPs, the following control reactions between sodium citrate and organic amine (one containing silicon, APTMS, and one without silicon, *n*-propylamine) have been carried out.

The reaction conditions were chosen to be the closest to those by Zhong et al., as described here. In particular, 5 mmol of amine was added to 10 mL of deionized water. Then, 5 mmol of trisodium citrate was added. In the case of *n*-$C_3H_7NH_2$, 15 mmol of methanol was added to simulate the same conditions as in the case of APTMS, which hydrolyzes in water to produce methanol. At this point, the solutions were transferred into 25 mL PTFE-lined stainless steel autoclaves. The sealed autoclaves were heated to 180 °C in an electric oven and left for an additional 5 h at this temperature. The final solutions were centrifuged at 10 000 rpm for 5 min, but no precipitate was observed to form, as had been reported.

Products of the reactions of Na_3Cit with both Si-containing APTMS and Si-free *n*-$C_3H_7NH_2$ appeared as yellowish (colorless upon dilution) clear solutions with bright blue photoluminescence (PL) under UV excitation (Figure 2a). Steady-state PL and absorption spectra were collected using an Edinburgh Instruments Ltd. FLS920 spectrometer with a Xe lamp (150W, Hamamatsu) as the excitation source. The PL, PL excitation, and optical absorbance spectra were found to be identical (Figure 2b,c), independent of the presence or absence of silicon in the organic amine. Furthermore, the general appearance and the spectral properties of the "Si NPs sol" described by Zhong et al. are also identical to those shown here in Figure 2.

In addition, to further confirm the similarity of the reaction products, time-resolved PL and PL photostability experiments were carried out. A picosecond pulsed laser EPL-375 (λ_{em} = 377.2 nm, 76.4 ps pulse width) was used as an excitation source for the time-resolved PL measurements. Figure 3a shows time-resolved PL of the both samples. The degree of the similarity between the two samples is obvious, and indeed

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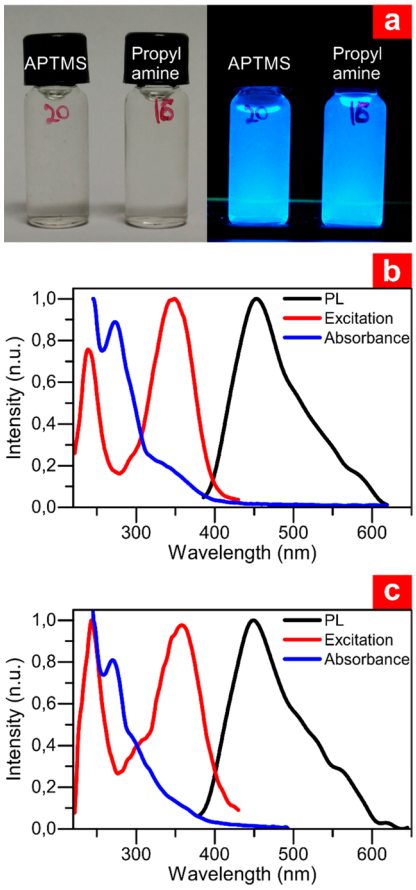

Figure 2. (a) Appearance of the reaction products under ambient light (left) and 365 nm irradiation (right). PL, PL excitation, and absorbance spectra of (b) Na_3Cit + n-$C_3H_7NH_2$ and (c) Na_3Cit + APTMS reaction products ($\lambda_{excitation}$ = 365 nm and $\lambda_{emission}$ = 450 nm).

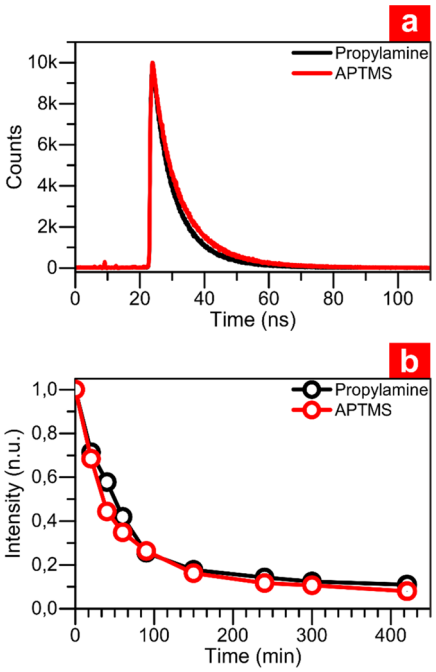

Figure 3. (a) Time-resolved fluorescence and (b) PL photostability of Si-containing (APTMS) and Si-free (n-$C_3H_7NH_2$) reaction products.

fitting with a single exponent ($y = y_0 + Ae^{-x/\tau}$) yields close PL lifetimes: 7 and 8 ns for n-$C_3H_7NH_2$ and APTMS derived samples, respectively. Such low and similar PL lifetimes suggests a common molecular nature of the luminescent species.

A 100 W Hg lamp (UVP, Blak-Ray B-100AP, 21,700 μW/cm^2 at 2 in.) with a 365 nm bandpass filter was used for illumination of the samples to study their PL photostability. Aqueous solutions (15 mL) of both samples with similar PL intensities were mounted in the center of the lamp beam, with a distance of 5 cm from the lamp filter (effective radiated cross-sections of the tubes were ~15 cm^2). Samples were collected, and their PL spectra were measured at certain time moments. As one can see in Figure 3b, the observed photobleaching dynamics are identical for both samples. The results of comparative analysis of time-resolved PL and photobleaching behavior are in good agreement with the other optical properties described above. All these experimental data strongly emphasize the similarity of the products obtained during the reactions between sodium citrate and organic amines, which of course includes the sample containing APTMS (the Si-containing amine) and the silicon-free sample that only has n-propylamine.

Thus, we can conclude with some certainty that silicon is not responsible for the optical properties of the obtained reaction products. Of course, Si atoms could be introduced into the structure of the (Na_3Cit + APTMS) reaction product, but their impact on the resulting optical properties is negligible. Considering the experiments described earlier, as well as taking into account the general chemical properties of silicon, it seems reasonable to assume that the formation of Si NPs (with a Si^0 crystalline core) under the hydrothermal conditions of ref 1 seems rather doubtful and improbable.

As for the data of Zhong et al. as it pertains to the optical properties, the observations may be simply attributed to organic carbon-containing particles and/or molecular fluorophores formed as a result of multiple chemical transformations (predominantly, condensation reactions). Indeed, the PL properties reported by Zhong et al. are similar to those of different carbon nanoparticles and organic dyes. Furthermore, numerous papers devoted to the synthesis of photoluminescent carbon nanoparticles from different amino-containing silanes (e.g., APTMS, APTES, etc.) and miscellaneous organic compounds (e.g., polybasic carboxylic acids, carbohydrates, etc.) have been published.[59−61] According to the described findings, the aminosilane serves as the nitrogen source and as the surface modifier. Thus, the obtained carbon nanoparticles have alkoxysilane-covered surfaces and could be involved in further transformations.

Finally, according to the literature, citrate or citric acid reacts with amine-containing compounds under elevated temperature with formation of brightly luminescent products.[60−72] Their chemical structures are very diverse, changing dramatically upon synthesis conditions. Particularly, the reaction of citric acid with ethanolamine[72] or ethylenediamine[73] under hydrothermal treatment results in the formation of either brightly luminescent molecular compounds of well-defined structure or small noncrystalline carbon-based nanoparticles. The particles of this type could be prepared from different molecular precursors using thermal, hydrothermal, or solvothermal routes (see comprehensive reviews[74,75]). Thus, the most acceptable statement is that the reaction of citrate with APTMS and n-

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$C_3H_7NH_2$ under hydrothermal conditions leads to formation of carbon-based nanoparticles and/or molecular fluorophores.

In conclusion, the perfect similarity of the optical properties of the chemical products obtained in the reactions between sodium citrate and organic amines (Si-containing APTMS and Si-free *n*-propylamine) ferments doubt that the results can be attributed to Si NPs. Proof of Si NPs formation, delivered by Zhong et al., is insufficient for them to be confident in their conclusions. Indeed, formation of Si nanocrystallites in the hydrothermal conditions used by Zhong et al. (especially with the relatively low energy budget) is rather improbable from all viewpoints, including a chemical standpoint. One of the most important goals of this article is to prevent a huge wave of misinterpretations caused by the article of Zhong et al. However, the remarkable photoluminescent properties of the synthesized chemical species may provide access to useful organic carbon-containing particles that can be successfully used for numerous interdisciplinary applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.9b01067.

Synthesis details (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*(B.V.O.) E-mail: oliinykb@gmail.com.

ORCID

Bohdan V. Oliinyk: 0000-0002-1895-3980

Sergei Alekseev: 0000-0003-4190-8528

Author Contributions

B.V.O., D.M.K., S.A., and V.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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