DOI 10.31489/2019Ch4/72-76

UDC 544.42+519.242.7

N.V. Khan[1], M.M. Burkitbayev[1], F. Kh. Urakaev[2]

[1]Al-Farabi Kazakh National University, Almaty, Kazakhstan;
[2]V.S. Sobolev Institute of Geology and Mineralogy of the Russian Academy of Sciences, Novosibirsk, Russia
(E-mail: natasha.khan.v@gmail.com)

Development of the synthesis technology of S@AgCl−Ag_2S nanocomposite in aqua medium

This research work is devoted to the development of the synthesis technology of nanocomposite based on sulfur, silver chloride and silver sulfide. The components which included in this nanocomposite make it possible to use it in various fields of science and technology: from biomedicine to agriculture.S@AgCl−Ag_2S nanocomposite was synthesized in aqua medium by two stages: 1) separate obtaining of each component; 2) mixing of all systems (products of reactions). The first stage is based on the interaction of aqueous solutions of silver nitrate with sodium chloride and sodium thiosulfate (in excess) with hydrochloric acid. Each of these reactions was carried out separately. At the second stage there was formation of silver sulfide and directly the S@AgCl−Ag_2S nanocomposite, under interaction of all products of the first stage. The physic-chemical characteristics of the samples were determined by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDAX). The results of XRD and Raman spectroscopy of the samples showed that nanocomposite represented by silver chloride, silver sulfide and sulfur. EDAX analysis identified the presence of silver, chlorine and sulfur. Meanwhile SEM analysis revealed that investigated material has range of particles size from micro to nano ones. Morphology of particles mostly represented by oval and spherical forms, and smooth surface.

Keywords: nanocomposite, nanoparticles, sulfur, silver halides, silver chloride, silver sulfide, aqua medium, aqueous solution.

Introduction

Nowadays nanomaterials are made a big breakthrough in science and technology. By turns nanomaterials can be obtained by various methods from mechanochemical synthesis to liquid phase synthesis [1, 2]. It is known that nanocomposites are multicomponent materials and each individual component must have useful properties. Combining of different elements and their compounds can give a new material with enhanced properties.

There are a lot of researches devoted to the study of silver and silver chloride, its antimicrobial and photocatalytic properties [2–5]. Silver sulfide is a functional material which has semiconductor, thermoelectric and photoluminescence properties [6, 7] also in the study [8] it is assumed that this compound may show some biological activity. As for sulfur it is widely applied as fungicide, fertilizer in agriculture and in production of Li-S batteries [9, 10].

It is obvious that the production of nanocomposite based on the above elements and compounds can lead to the creation of a universal material with a set of features applicable in various fields. At the initial stage of investigation it was important to get the final product corresponding to the claimed composition. Therefore, the aim of this study was development of the synthesis technology of the nanocomposite with S@AgCl−Ag_2S composition.

Experimental

The synthesis proceeded in two stages: 1) separate obtaining of each component; 2) mixing of all systems. The first stage included interaction between aqueous solutions of silver nitrate and sodium chloride. The solutions were poured drop by drop with constant stirring. During this reaction there was obtained silver chloride. Then, through the interaction of aqueous solutions of hydrochloric acid with excess of sodium thiosulfate under conditions similar to previous reaction, there was formation of sulfur.

The second stage included the mixing of solutions with the products which were obtained on the first stage. Silver sulfide is formed in the process of mixing of all solutions. The formation of silver sulfide was observed not only visually (black precipitate), but also subsequently confirmed by a number of physic-chemical methods of analysis. The formation can be explained by the next scheme [11]:

$$Na_2S_2O_3 + 2AgNO_3 = Ag_2S_2O_3 + 2NaNO_3$$

$$Ag_2S_2O_3 = Ag_2SO_3 + S$$

$$Ag_2SO_3 + S + H_2O = Ag_2S + H_2SO_4$$

After mixing the solutions, the excess of sodium thiosulfate reacts with silver nitrate, which is not all amount reacted with sodium chloride at the first stage. As a result, silver sulfide is formed according to the scheme described above and after some time the system comes to balance and forms a composite S@AgCl−Ag_2S.

Further, the solid precipitate is precipitated using a centrifuge ROTINA 380 R, for 15 minutes and at a speed of 4000 rpm. Eventually the samples had been dried at 45 ºC, for 12–16 hours.

Results and Discussion

The phase composition of the sample was identified by XRD using X-ray difractometer Rigaku MiniFlex 600. Identification of the sample was carried out using the databases PDF Card № 00–014–0072 for silver sulfide and PDF Card № 01–085–1355 for silver chloride. The results of analyses (Fig. 1) showed that investigated material represented by clear peaks of silver sulfide and silver chloride and correspond to standard data. On the Fig. 1 spectrum with red color is investigated sample, blue columns are standard peaks of silver sulfide and green columns are standard peaks of silver chloride. Sulfur could not be found. The explanation may consist of that sulfur present in amorphous state; therefore, the XRD analyzer was unable to fix it. Consequently, Raman spectroscopy was performed to detect sulfur and confirm the presence of silver chloride and silver sulfide in the sample.

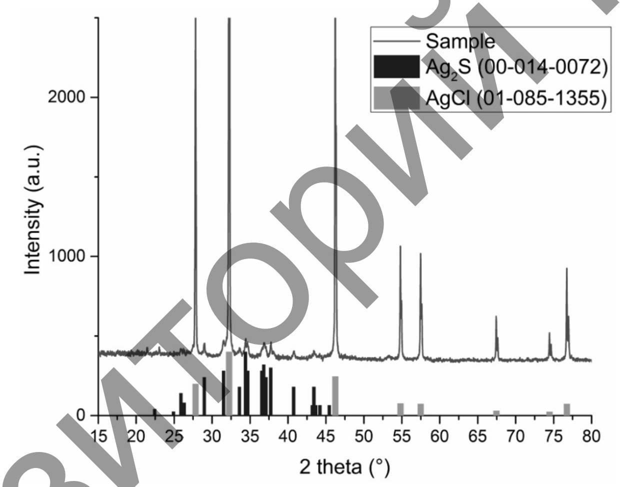


Figure 1. XRD patterns of the sample. Characteristic peaks of the silver sulfide and silver chloride

Raman spectra were excited by a He-Ne laser with a wavelength of 633 nm and recorded by a Raman spectrometer Solver Spectrum (NT-MTD) using a diffraction grating 1800/500, which provides a spectral resolution of 1 cm^{-1}. So, there are quite clear Raman peaks on the Figure 2, fully corresponding to the sulfur. Other components do not show clear peaks, which may indicate their metallic nature. The peaks at 95 and 190 cm^{-1} maybe, relates to Ag-Ag lattice vibrations, while the bands at 240 and 400 cm^{-1} are caused by the Ag-Cl bond stretching and compression mode [12]. According to [13] Ag_2S correspond to two intense peaks between 90 and 109 cm^{-1} and there should be a weak band at 245 cm^{-1}. Silver chloride appears at 233 cm^{-1}, and there should be two small peaks in the area from 324 to 470 cm^{-1}.Thus, it can be seen from the spectrum (Fig. 3), our results echoes in some means with literature data.

The structural morphology of prepared samples and elemental composition were examined by SEM and EDAX, using scanning electron microscope Quanta 200i 3D. Figure 4*a* showed the SEM images of the S@AgCl-Ag_2S nanocomposite which revealed homogeneous structure of the sample. Closer examination of the sample shows that the majority of particles is represented by oval and sphere form with smooth surface (Fig. 4*b*). Figure 4*c* revealed that investigated material has both micro- and nano-sized particles. It can be seen that the powder is mainly represented by light particles. But at the same time, on closer examination, there can be seen the gray areas (particles) in the sample. The EDAX analysis (see Table) shows there is the highest percentage (At%) of such elements like Ag (24.05), Cl (16.46) and S (8.63 %). It should be noted that Ag and Cl are presented by pronounced peaks and wave shoulders (Fig. 5). Thus, based on the obtained data, it can be assumed that the light areas are silver chloride and sulfur (smaller particles), and the gray areas is silver sulfide. Also in the composition of nanocomposite present a small amount of Na, O, C, Si, P.

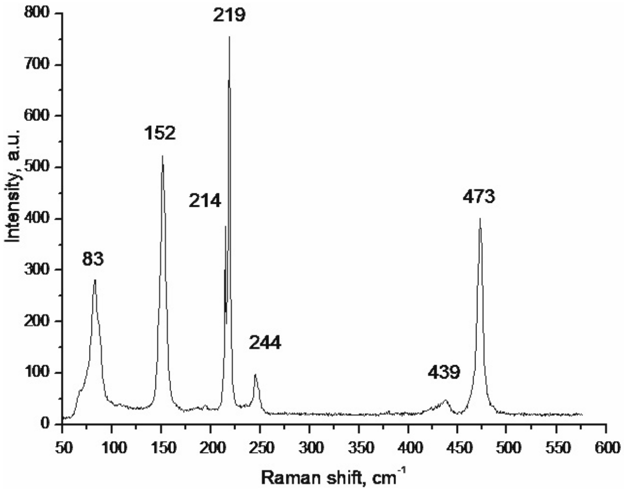


Figure 2. Raman spectra of elemental sulfur

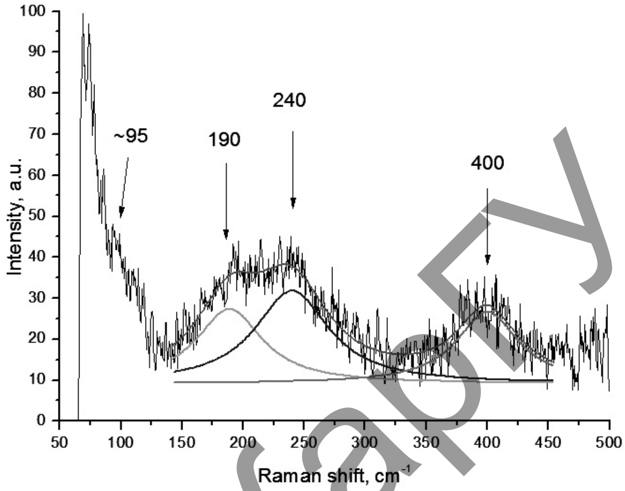
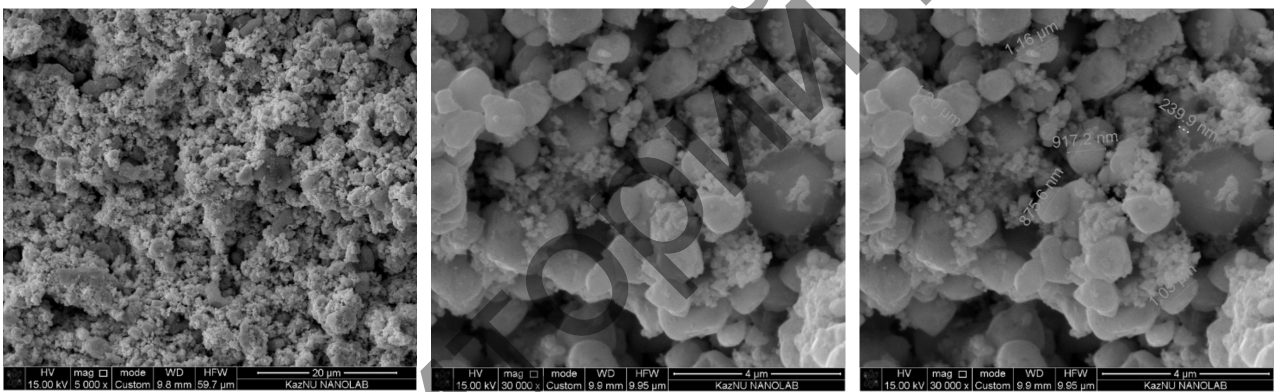


Figure 3. Raman spectra corresponding to AgCl and Ag_2S



a *b* *c*

Figure 4. SEM images of S@AgCl-Ag_2S nanocomposite

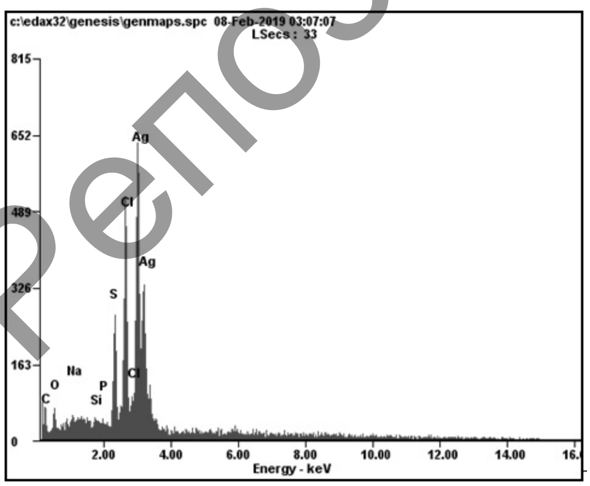


Figure 5. EDAX analysis of the S@AgCl-Ag_2S

Table

Elemental composition of S@AgCl−Ag_2S nanocomposite

Element	Wt.%	At.%
C	10.22	35.40
O	4.62	13.02
Na	1.11	2.01
Si	0.58	0.86
P	0.42	0.57
S	6.66	8.63
Cl	14.03	16.46
Ag	62.35	24.05

Conclusions

In summary S@AgCl-Ag_2S nanocomposite has been synthesized in aqua medium by two stages. The results of XRD analysis revealed that samples represented by silver chloride and silver sulfide. The Raman spectroscopy showed the presence of sulfur in composition of nanocomposite, also illustrated some areas, which can indicate the silver chloride and silver sulfide. EDAX analysis demonstrated the presence of elements like Ag (24.05 At%), Cl (16.46 At%) and S (8.63 At%). SEM analysis proved that S@AgCl-Ag_2S nanocomposite has micro- and nano-sized particles with oval and sphere form, and smooth surface.

As a result the goal of this study was successfully achieved.

This research work was supported by scientific projects of the Ministry of Education and Science of the Republic of Kazakhstan AP05133115 and BR05234566 (program-target financing).

References

1 Уракаев Ф.Х. Механохимический синтез коллоидных частиц бромида серебра в системе NaBr−$AgNO_3$−$NaNO_3$ / Ф.Х. Уракаев, Б.Б. Татыкаев, М.М. Буркитбаев, А.М. Бахадур, Б.М. Уралбеков // Коллоидный журн. — 2016. — Т. 78, № 4. — С. 501–508.

2 Han C. (2014). Site-selected synthesis of novel Ag@AgCl nanoframes with efficient visible light induced photocatalytic activity/ C. Han, L. Ge, C. Chen, Y. Li, Z. Zhao, X. Xiao, Zh. Li, J. Zhang // Journal of Materials Chemistry A. — 2016. — Vol. 2(31). — P. 12594–12600.

3 Mohler J.S. Silver bullets: A new luster on an old antimicrobial agent / J.S. Mohler, W. Slim, M.A.T. Blaskovich, M.A. Cooper, Z.M. Ziora // Biotechnology advances. — 2016. — Vol. 36. — P. 1391–1411.

4 Su M. Synthesis of cube-like Ag@AgCl photocatalyst with enhanced photocatalytic activity / M. Su, H. Liu, J. Ma // Journal of material sciences. — 2016. — Vol. 27 — P. 10707–10711.

5 Ma B. Highly stable and efficient Ag/AgCl core shell sphere: controllable synthesis, characterization, and photocatalytic application. / B. Ma, J. Guo, W.-L. Dai, K. Fan // Applied Catalysis B: Environmental. — 2013. — Vol. 130–131. — P. 257–263.

6 Pan Sh. Preparation of Ag_2S-Graphene nanocomposite from a single source precursor and surface enhanced Raman scattering and photoluminescent activity / Sh. Pan, X. Liu, X Wang // Material characterization. — 2011. — Vol. 62. — P. 1094–1101.

7 Xue J. Recent progress in synthesis methods and applications in solar cells of Ag_2S quantum dots. / J. Xue, J. Liu, S. Mao, Y. Wang, W. Shen, W. Wang, L. Huang, H. Li, J. Tang // Materials research bulletin. — 2018. — Vol. 106. — P. 113–123.

8 Liu S. Effects of silver sulfide nanoparticles on the microbial community structure and biological activity of freshwater biofilms / S. Liu, C. Wang, J. Hou, P. Wang, L. Miao, T. Li // Environmental science: Nano. — 2018. — Vol. 5. — P. 2899–2908.

9 Griffith C.M. Environmental behavior and analysis of agricultural sulfur / C.M. Griffith, J.E. Woodrow, J.N. Seiber // Pest Management Science. — 2015. — Vol. 71. — P. 1486–1496.

10 Xiao P. Unexpected effect of electrode architecture on high-performance lithium-sulfur batteries / P. Xiao, L. Sun, D. Liao, O. Ph. Agboola, I. Shakir, Yu. Xu //Applied materials and interfaces. — 2018. — Vol. 10. — P. 33269–33275.

11 Натрия тиосульфат [Электронный ресурс]. — Режим доступа: http://www.pharmspravka.ru/neorganicheskie-lekarstvennyie-veschestva/6-gruppa-periodicheskoy-sistemyi/natriya-tios.html

12 Martina I. Micro-Raman Spectroscopy of Silver Corrosion Products / I. Martina, R. Wiesinger, J.-S. Dubravka, S. Manfred // e-Preservation science. — 2012. — Vol. 9. — P. 1–8.

13 Marucci G. Non invasive micro-Raman spectroscopy for investigation of historical silver salt gelatin photographs / G. Marucci, A. Monno, I. D. van der Werf // Microchemical journal. — 2014. — Vol. 117. — P. 220–224.

Н.В. Хан, М.М. Бүркітбаев, Ф.Х. Уракаев

Сулы ортадағы S@AgCl–Ag_2S нанокомпозитін синтездеудің технологиясын дайындау

Мақала құрамында күкірт, күміс хлориді және сульфиді бар нанокомпозиттерді синтездеудің техологиясын дайындауға арналған. Аталған нанокомпозиттің құрамына кіретін компоненттер оның ғылым мен техниканың әртүрлі салаларында қолдануға мүмкіндік береді: яғни, биомедицинадан бастап ауылшаруашылығына дейін. S@AgCl–Ag_2S нанокомпозиті сулы ортада екі сатымен синтезделді: 1) компоненттерді жеке-жеке синтездеу; 2) барлық жүйелерді (реакция өнімдері) араластыру арқылы. Бірінші саты күміс нитраты мен натрий хлориді ерітінділерінің және натрий тиосульфаты (артық мөлшерде) мен тұз қышқылының әрекеттесуіне негізделген. Одан бөлек, аталған реакциялар жеке дара да жүргізілді. Екінші сатыда бірінші сатының реакция өнімдерінің әрекеттесуінің нәтижесінде күміс сульфидінің және S@AgCl–Ag_2S нанокомпозитінің түзілуі жүзеге асады. Сынамалардың физика-химиялық қасиеттері рентгенофазалық талдау (РФТ), Раман спектроскопиясы, сканирлеуші электронды микроскопия (SEM) және энергодисперсионды ренгенді спектроскопия (SEM-EDAX) әдістерінің көмегімен анықталды. РФТ және Раман спектроскопиясы талдауларының нәтижелері нанокомпозиттің құрамында күкірт, күміс хлориді және сульфиді бар екенін анықтады. EDAX талдауы нанокомпозиттің құрамында күміс, хлор, күкірт және де т.б. элементтердің бар екенін дәлелдеді. Зерттелінген материалдың пішіні микроөлшемнен бастап наноөлшемге дейін таралғанын SEM талдауының нәтижелері көрсетті. Бөлшектердің морфологиясы негізінен сопақ және шар тәрізді, беттік қабаты тегіс екені анықталды.

Кілт сөздер: нанокомпозит, нанобөлшектер, күкірт, күміс галогенидтері, күміс хлориді, күміс сульфиді, сулы орта, сулы ерітінділер.

Н.В. Хан, М.М. Буркитбаев, Ф.Х. Уракаев

Разработка технологии синтеза нанокомпозита $S@AgCl–Ag_2S$ в водной среде

Статья посвящена разработке технологии синтеза нанокомпозита на основе серы, хлорида серебра и сульфида серебра. Компоненты, входящие в состав данного нанокомпозита, позволяют использовать его в различных отраслях науки и техники: от биомедицины до сельского хозяйства. Нанокомпозит $S@AgCl–Ag_2S$ был синтезирован в водной среде, в две стадии: 1) раздельное получение каждого из компонентов; 2) смешение всех систем (продуктов реакций). Первая стадия основана на взаимодействии водных растворов нитрата серебра с хлоридом натрия, а также тиосульфата натрия (в избытке) с соляной кислотой. Причем каждая из этих реакций проводилась отдельно друг от друга. На второй стадии происходит образование сульфида серебра и непосредственно самого нанокомпозита $S@AgCl–Ag_2S$, при взаимодействии всех продуктов реакций первой стадии. Физико-химические характеристики образцов были определены с помощью рентгенофазового анализа (РФА), рамановской спектроскопии, сканирующей электронной микроскопии и энергодисперсионной рентгеновской спектроскопии (SEM-EDAX). Результаты РФА-анализа и рамановской спектроскопии показали, что образцы представлены хлоридом серебра, сульфидом серебра и серой. EDAX-анализ установил присутствие в составе нанокомпозита серебра, хлора, серы и других элементов. В то время как SEM анализ показал, что исследуемый материал представлен частицами от микро- до наноразмеров. Морфология частиц представлена в основном овальными и сферическими формами, с гладкой и ровной поверхностью.

Ключевые слова: нанокомпозит, наночастицы, сера, галогениды серебра, хлорид серебра, сульфид серебра, водная среда, водные растворы.

References

1 Urakaev, F.Kh., Tatykaev, B.B., Burkitbayev, M.M., Bakhadur, A.M., & Uralbekov, B.M. (2016). Mekhanokhimicheskii sintez kolloidnykh chastits bromida serebra v sisteme $NaBr-AgNO_3-NaNO_3$ [Mechanochemical synthesis of colloidal silver bromide particles in the $NaBr-AgNO_3-NaNO_3$ system]. *Kolloidnyi zhurnal — Colloid Journal*, *78*, *4*, 525–532 [in Russian].

2 Han, C., Ge, L., Chen, C., Li, Y., Zhao, Z., & Xiao, X., et al. (2014). Site-selected synthesis of novel Ag@AgCl nanoframes with efficient visible light induced photocatalytic activity. *Journal of Materials Chemistry A, 2(31),* 12594–12600.

3 Mohler, J.S., Slim, W., Blaskovich, M.A.T., Cooper, M.A., & Ziora, Z.M. (2018). Silver bullets: A new luster on an old antimicrobial agent. *Biotechnology advances, 36*, 1391–1411.

4 Su, M., Liu, H., & Ma, J. (2016). Synthesis of cube-like Ag@AgCl photocatalyst with enhanced photocatalytic activity. *Journal of material sciences, 27*, 10707–10711.

5 Ma, B., Guo, J., Dai, W.-L., & Fan, K. (2013). Highly stable and efficient Ag/AgCl core shell sphere: controllable synthesis, characterization, and photocatalytic application. *Applied Catalysis B: Environmental, 130–131*, 257–263.

6 Pan, Sh., Liu, X., & Wang, X. (2011). Preparation of Ag_2S-Graphene nanocomposite from a single source precursor and surface enhanced Raman scattering and photoluminescent activity. *Material characterization, 62*, 1094–1101.

7 Xue, J., Liu, J., Mao, S., Wang, Y., Shen, W., & Wang, W., et al. (2018). Recent progress in synthesis methods and applications in solar cells of Ag_2S quantum dots. *Materials research bulletin, 106*, 113–123.

8 Liu, S., Wang, C., Hou, J., Wang, P., Miao, L., & Li, T. (2018). Effects of silver sulfide nanoparticles on the microbial community structure and biological activity of freshwater biofilms. *Environmental science: Nano, 5,* 2899–2908.

9 Griffith, C.M., Woodrow, J.E., & Seiber, J.N. (2015). Environmental behavior and analysis of agricultural sulfur. *Pest Management Science*, *71,* 1486–1496.

10 Xiao, P., Sun, L., Liao, D., Agboola, O. Ph., Shakir, I., & Xu, Yu. (2018). Unexpected effect of electrode architecture on high-performance lithium-sulfur batteries. *Applied materials and interfaces, 10*, 33269–33275.

11 Natriia tiosulfat [Sodium thiosulfate]. *pharmspravka.ru*. Retrieved from http://www.pharmspravka.ru/neorganicheskie-lekarstvennyie-veschestva/6-gruppa-periodicheskoy-sistemyi/natriya-tios.html [in Russian].

12 Martina, I., Wiesinger, R., Dubravka, J.-S., & Manfred, S. (2012). Micro-Raman Spectroscopy of Silver Corrosion Products. *e-Preservation science, 9*, 1–8.

13 Marucci, G., Monno, A., &van der Werf, I.D. (2014). Non invasive micro-Raman spectroscopy for investigation of historical silver salt gelatin photographs. *Microchemical journal, 117*, 220–224.