SCIENTIFIC REPORTS

OPEN

Electrochemical removal of stains from paper cultural relics based on the electrode system of conductive composite hydrogel and PbO₂

Xingtang Liang^{1,2}, Lizhen Zheng¹, Shirong Li¹, Xiaoyu Fan¹, Shukun Shen¹ & Daodao Hu¹

Constructing methods for cleaning stains on paper artworks that meet the requirements of preservation of cultural relics are still challenging. In response to this problem, a novel electrochemical cleaning method and the preparation of corresponding electrodes were proposed. For this purpose, the conductive graphene (rGO)/polyacrylamide (PAM)/montmorillonite (MMT) composite hydrogel as cathode and PbO₂-based material as anode were prepared and characterized. The electrochemical cleaning efficiencies of real sample and mimicking paper artifacts were evaluated, and the effects of the electrochemical cleaning on paper itself were detected. Based on the above experiments, the following results were obtained. The composite hydrogel with attractive mechanical properties is mainly based on the hydrogen bond interactions between PAM chains and MMT. The results of cleaning efficiency revealed that the black mildew stains together with the yellowish foxing stains were almost completely eliminated within 6 min at 8 mA/cm², and various stains formed by tideline, foxing, organic dyes and drinks could be thoroughly removed at 4 mA/cm² within 5 min. In addition, the proposed cleaning method has advantages in local selectivity, easy control of cleaning course, and reusability, which represents a potential utility of this approach.

Paper-based artifacts are one kind of popular and important historical cultural relics. As one of the primary carriers for culture and art, the paper plays a vital role in the dissemination and inheritance of information. However, paper of any kind is prone to degrade and so is inherently vulnerable, which makes ensuring the survival of paper-based artifacts difficult. Preserving paper-based artifacts is still a challenge, even for professionals¹. Among of issues involved in the protection of paper-based artifacts, cleaning is of great significance because various contaminants can damage paper-based artifacts. For example, stains can severely damage artifacts not only in value but also in corrosion; mold growth not only deteriorates the structure of the paper itself but also permanently detracts from the visual appearance of an artifact^{1,2}. Therefore, cleaning of paper-based artifacts is necessary to decrease the further damage of contamination and improve the aesthetics of works. Additionally, cleaning of paper artifacts represents one of the most delicate operations of restoration because it is potentially invasive for the original materials as well as completely irreversible^{3,4}. One of the most important issues in cleaning process is the removal of foreign matters without affecting the original one. Namely, a controlled and selective cleaning action is advisable.

In order to clean paper-based artifacts, various approaches have been reported. Indubitably, it is the most popular that undesirable contaminants are removed by solvent dissolution. However, the cleaning of paper achieved by means of solvents (organic or water) presents several problems, such as the extensive diffusion of dissolved substances into deeper and broader areas of the artifact, the dramatic decay of the mechanical properties of paper due to swelling⁵, and adverse health effects probably caused by organic solvents. To confront these issues, thickeners such as cellulose ethers and polyacrylic acids were used to enhance the control of solvents over the cleaning process. In addition, solvent gels, mainly consist of organic solvent, water, surfactant and polymer (Carbopol), were also applied to decrease the diffusion of solvents. However, both the thickener and the solvent gel could

¹Engineering Research Center of Historical and Cultural Heritage Protection, Ministry of Education, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, 710062, China. ²School of Petroleum and Chemical Engineering, Qinzhou University, Qinzhou, 535000, China. Correspondence and requests for materials should be addressed to D.H. (email: daodaohu@snnu.edu.cn)

Figure 1. Schematic illustration of the HPEC method.

cause intractable residuals remaining on the artwork after the cleaning⁶. To solve this problem, the cleaning based on hydrogels such as rheoreversible hydrogels⁷, nanomagnetic hydrogels⁸, rigid hydrogels^{4,9,10}, and other peeled hydrogels^{11,12}, has been especially concerned in the past decade. During these cleaning processes, contaminants could be controllably dissolved in the hydrogel containing different detergents, and then they would be simultaneously removed when the hydrogel was peeled off from the paper in one piece^{13,14}. Owing to the high retention power and viscosity of hydrogels, the penetration of aqueous solution into the paper was significantly reduced, therefore minimizing damages^{4,6,15}. For example, acrylamide-based nanomagnetic hydrogel and acrylamide/bisacrylamide hydrogel were loaded with microemulsions for removing synthetic adhesives^{8,11}; rigid gellan based hydrogel loaded with α -amylase and proteinase has been used for selectively cleaning starch paste and animal glue^{6,9}, respectively.

Here, we design a new scheme for efficiently removing stains including tideline, foxing, organic dyes and fungi from paper artworks by incorporating electrochemical reactions into the hydrogel-based cleaning process. Generally, electrochemical reactions have significant advantages over traditional chemical reactions. For instance, the catalyst/electrode is immobilized, thus reducing the requirement to separate the catalyst from the reaction mixture; the variable parameters in current and potential are readily controlled, hence easily controlling the desired reaction; the main reagent is the hydroxyl radical, which can efficiently degrade the organic stains but without a hazardous product. Meanwhile, the desired cleaning area can be regulated by using the miniaturized hydrogel electrode. Inspired by the following ideas, the electrode system, being composed of the PbO_2 electrode as anode and reduced graphene oxide/polyacrylamide/montmorillonite conductive composite hydrogel pen (rGPM) as cathode, was employed for the cleaning of paper-based artifacts. (1) PbO_2 is the most extensively used anode material for electrochemical oxidation of organic pollutants, because of its favorable electrical conductivity and high electro-catalytic activity in the formation of hydroxyl radical¹⁶. (2) The rGPM possesses excellent mechanical strength and conductivity. It has been reported that the incorporation of exfoliated sodium montmorillonite in polyacrylamide hydrogels could evidently enhance the strength of hydrogels as the strong hydrogen bonding between them¹⁷, and the introduction of reduced graphene oxide into the hydrogel could promote its electrical conductivity^{18–20}. For hydrogels used in the electrochemical cleaning of paper artworks, both excellent mechanical strength and electrical conductivity are needed to avoid hydrogel residues on the paper and to transfer electrons on the electrode for electrochemical reactions.

To our best knowledge, although the cleaning of water-sensitive cultural heritage artifacts by hydrogels^{2–5} and the degradation of contaminants by electrochemical reaction have been reported²¹, the hydrogel pen for electrochemical cleaning (HPEC) has never been presented. As illustrated in Fig. 1 for the HPEC, the PbO_2 electrode was placed under the paper to be processed, and the rGPM was attached on the area expected to be cleaned. Namely, the paper with stains was sandwiched between the two electrodes. During cleaning, a consistent DC current was charged to the pair of electrodes to generate a given current density for the electrochemical cleaning. After a given time, the cleaning was finished and the rGPM electrode could be readily removed from the paper. To investigate the feasibility and adaptability of HPEC, we used the model materials such as new and artificially aged Chinese rice paper with stains including organic dyes, commercial drinks, tideline and mildew for the cleaning test. For reasons of security in cleaning of paper-based artifact, the effect of HPEC on the morphology and the chemical structure of the paper cellulose was assessed. Moreover, the reusability of HPEC was also evaluated. Based on the above investigations, HPEC was used to clean an actual paper-based artwork with stains including foxing, tideline and mildew, confirming the effectiveness of HPEC. The results showed that HPEC had an outstanding capacity for cleaning local stains formed by organic contaminants without an obvious influence on the cellulose and original mineral pigments. Additionally, the prepared PbO_2 anode and rGPM cathode could be reused multiple times without loss of its efficiency. This work provides an alternative method for efficiently cleaning paper artworks.

Figure 2. Schematic illustration of the preparation of rGPM_n hydrogels (a); Raman spectra of PAM, graphite, GO, GPM_{5.0} and rGPM_{5.0} (b); FT-IR spectra of PAM and rGPM with different content of MMT (c); C 1s XPS spectra of PAM, GPM_{5.0} and rGPM_{5.0} (d).

Results and Discussion

Components and interactions in the reduced graphene oxide/polyacrylamide/montmorillonite composite hydrogel (rGPM). According to the process as illustrated in Fig. 2a for the fabrication of rGPM, the brown graphene oxide/polyacrylamide/montmorillonite composite hydrogel (GPM) was firstly synthesized by free radical polymerization of acrylamide (AM) and *N,N'*-methylenebisacrylamide (BIS) in the dispersion of graphene oxide (GO) and sodium montmorillonite (MMT). The prepared GPM possesses both chemical cross-linking and physical cross-linking. The chemical cross-linking created by BIS supports the stable hydrogel, and the physical cross-linking mainly based on the hydrogen bond interactions between polyacrylamide (PAM) chains and nanosheets of MMT and GO improves the mechanical strength of the hydrogel¹⁷. Then, the GO in GPM was reduced by L-ascorbic acid (VC) to form a black rGPM with enhanced electroconductivity¹⁸.

The graphene oxide (GO) was prepared according to the modified Hummers' method²². The spectra of FT-IR (Supplementary Figure S1) and XPS (Supplementary Figure S2) indicated that the prepared GO has abundant oxygen-containing functional groups (such as (-COC-), (-OH) and (-COOH)) compared with the graphite. Furthermore, XRD patterns (Supplementary Figure S3) revealed an outstanding peak at 26.3° attributed to d-spacing of 0.34 nm for graphite and an evident peak at 9.8° assigned to d-spacing of 0.90 nm for GO, also indicating the presence of oxygen-containing functional groups on the GO nanosheets³³. All these results suggest that GO has been successfully prepared.

It has been proven that MMT nanoplatelets enhance the mechanical strength of PAM hydrogels because of strong hydrogen bonds between amide side groups on PAM and units such as Si-OH and Si-O-Si on MMT¹⁷. Indeed, these interactions were also evidenced in the prepared GPM and rGPM. The diffraction peak at 7.2°

Figure 3. SEM images of PAM (a1,a2), rGPM₀ (b1,b2), rGPM_{2.5} (c1,c2) and rGPM_{5.0} (d1,d2); the photos of PAM (top) and rGPM_{5.0} (bottom) placed on the paper for 6 min (e).

ascribed to the basal spacing (d_{001} , 1.2 nm) of MMT was shown in Supplementary Figure S3. However, any diffraction peak from 3 to 12° was not observed for GPM and rGPM, indicating that the lamellar structure of MMT was destroyed and dispersed uniformly in the composite hydrogels owing to the interactions between PAM chains and MMT¹⁷. Actually, these interactions were also confirmed by FT-IR spectra as shown in Fig. 2c. Peaks at 3336, 3190, 1649 and 1602 cm^{-1} , severally attributed to the asymmetrical N-H stretching, symmetrical N-H stretching, amide-I (C=O stretching), and amide-II (N-H bending) of PAM^{30,31}, gradually shifted to 3322, 3174, 1634 and 1593 cm^{-1} with the increase of MMT in rGPM. In contrast, the band at 991 cm^{-1} originated from the Si-O-Si stretching of MMT³² (Supplementary Figure S1) was replaced by the peak at 1025 cm^{-1} in rGPM. These results from FT-IR spectra are in good agreement with the previous works^{17,33}, suggesting the strong interactions of hydrogen bonding between PAM and MMT. C 1s XPS spectra of PAM, GPM_{5.0} and rGPM_{5.0} are given in Fig. 2d. For GPM_{5.0}, the deconvolution of C 1s peak presented four peaks at 284.8, 286.1, 287.9, and 289.2 eV, attributed to $\text{C}-\text{C}/\text{C}=\text{C}$, $\text{C}-\text{O}/\text{C}-\text{N}$, $\text{C}=\text{O}/\text{O}-\text{C}-\text{O}$, and $\text{O}-\text{C}=\text{O}$, respectively³⁴. The relative amount of the bound carbons with oxygen increased from 32.9% for PAM to 44.5% for GPM_{5.0} due to the introduction of the rich oxygen-containing GO and MMT, decreased from 44.5% for GPM_{5.0} to 38.2% for rGPM_{5.0} owing to the reduction of GO¹⁹. Additionally, the peak at 289.2 eV attributed to $\text{O}-\text{C}=\text{O}$ appeared for GPM_{5.0} and disappeared for rGPM_{5.0}. These observations suggest that the reduction of GO in the hydrogel was proceeded by removing the oxygen-containing groups on GO.

Raman spectra for the involved materials are displayed in Fig. 2b. The presentation of both G and D band in the graphene-based samples indicates that graphene-based unit has been successful incorporated into the PAM matrix. Additionally, the ratio ($I_{\text{D}(1358\text{ cm}^{-1})}/I_{\text{G}(1600\text{ cm}^{-1})}$) was 0.896 for GPM_{5.0} and 1.304 for rGPM_{5.0}, suggesting that the GO in GPM_{5.0} was partially reduced to the graphene in rGPM_{5.0}³⁵. The results shown in Supplementary Tables S1 and S2 indicated that the conductivity of rGPM_{5.0} was greater than that of GPM_{5.0}, further confirming the conversion of GPM_{5.0} into rGPM_{5.0}.

SEM images of the freeze-dried hydrogels are shown in Fig. 3. For the PAM hydrogel (Fig. 3a1), a typical porous structure with smooth pore wall was found. As shown in Fig. 3b1, the porous density of rGPM₀ obviously decreased in comparison to PAM, and some flakes immersed in the pore wall, implying that graphene flakes were well-dispersed in the PAM hydrogel. As the addition of MMT into the hydrogel (Fig. 3c1–d1), the pore density of the hydrogel further decreased, and flakes on the pore wall became denser (Fig. 3c2–d2). These results suggest that the covalently crosslinked PAM chains are intertwined with MMT and graphene, which leads to a stiff gel to prevent the growth of ice crystals during the freezing step. Compared to PAM, rGPM_{5.0} with less and smaller interconnected pores to trap water showed a better water retention as it was attached on the paper (Fig. 3e).

Mechanical performances of rGPM_n. For the hydrogel-based cleaning, the hydrogel with excellent mechanical property is necessary so that it can be readily peeled off from the paper without residues⁴. To show the excellent mechanical performance, Fig. 4a offered the photos of rGPM_{5.0} exhibiting recovery after compressing to 85% strain. In addition, rGPM_{5.0} could be peeled from a Chinese rice paper without any visible residuals after it was pressed at a stress of ~20 kPa on the paper for 10 min (Fig. 4b). In contrast, the PAM hydrogel was destroyed to leave some fragments on the paper. These observations indicate that rGPM_{5.0} possesses a highly resilient mechanical property. To confirm the mechanical performances of rGPM_n, compressive stress-strain curves, dynamic stress sweeps and dynamic frequency sweeps were carried out. These results are shown in Fig. 4c and Supplementary Figure S4. The corresponding values of compressive modulus (E , kPa), compressive stress (σ , MPa), strain (ε , %), fracture energy density (U , kJ/m³) and equilibrium swelling degree (ESD, g/g) for rGPM_n and GPM_n are listed in Supplementary Tables S1 and S2. The critical stresses (τ_c , Pa), plateau moduli (G , Pa), and effective network chain density (N_e , mol/m³) for the hydrogels of PAM and rGPM_n were obtained by the calculation according to the literature³⁶ and summarized in Supplementary Table S3. Based on these results, the following conclusions can be drawn. (1) MMT enhances the mechanical properties of the composite hydrogel when its amount is less than 5.0%. This conclusion is based on the changes of parameters (σ , ε , τ_c , E and U) with the amount of MMT, and the corresponding explanations are given as follows. The N_e increases with the content

Figure 4. Photographs showing the rGPM_{5.0} hydrogel before and after compressing at $\varepsilon = 85\%$ (a). Photos demonstrating the residues of rGPM_{5.0} and PAM hydrogel after placed on a paper under a stress about 20 kPa for 10 min (b). Typical compressive stress–strain curves of PAM and rGPM (c). Stress–strain curves of rGPM_{5.0} hydrogel under consecutively repeated loading at $\varepsilon = 80\%$ (d).

of MMT, indicating that MMT as physical cross-linkers directly binds to the polymer network, and the multi-site interactions are confirmed by the fact that the determined elastic modulus (E) is markedly larger than that of the calculated modulus by Guth-Gold model (Supplementary Figure S5)^{36,37}. Evidently, a higher cross-link density originated from excessive MMT in the composite hydrogel leads to higher rigidity and lower toughness²⁶. Therefore, a suitable amounts of MMT is inevitable to balance both rigidity and toughness of the composite hydrogel. (2) The increase of MMT results in the decrease of ESD, which is corresponding to the enhancement of crosslinking degree of hydrogel network^{18,26}.

Because of the removal of oxygen-containing groups from GO surface, the hydrogen bonding between PAM chains and rGO nanoplates could be decreased, which resulted in a smaller value of ε , σ , and U for rGPM_n in comparison to GPM_n (Supplementary Tables S1 and S2). In spite of this, as shown in Fig. 4d, the consecutive cyclic loading–unloading curves of rGPM_{5.0} at the strain range of 0–80% still demonstrate the excellent fatigue resistance and perfect reversibility, implying that rGPM_{5.0} can be repeatedly used as a hydrogel electrode without loss of its mechanical strength. Additionally, rGPM_{5.0} possesses an obvious conductivity (about 1.9 mS/cm), as shown in Supplementary Table S1, which is comparable with that of both pure graphene hydrogel (4.9×10^{-3} S/cm)²² and reduced GO–poly(N-isopropylacrylamide)–clay hydrogel (2.6–4.8 mS/cm)^{18,20}, indicating that rGPM_{5.0} can be used as electrode materials.

Stain-removing performance of HPEC. Results of the safranin T-contaminated papers cleaned by HPEC at 4 mA/cm² are shown in Fig. 5a. Figure 5a1,a2 and a3 are the photos of the undyed sample (a1), the surface contacted with rGPM_{5.0} electrode (a2) and the surface attached to the PbO₂ electrode (a3) after cleaning treatment for different time, respectively. Obviously, the cleaning was only performed in the area contacted with the electrode, and synchronously occurred on both sides of the paper with the almost same effect. The UV-vis reflectance spectra of the corresponding areas as shown in Fig. 5a2 are presented in Fig. 5a4. These spectra of the treated area gradually tend to that of the control as the increase of cleaning duration. Using the control as reference, the colour difference (ΔE^*) of the contaminated areas before and after cleaning are listed in Supplementary Table S4 together with the corresponding colorimetric data. The ΔE^* of the cleaning area gradually decreased with the treatment time of HPEC. Generally, a ΔE^* of 3.3 is the upper limit for human eyes to detect colour differences³⁸. After a treatment of 6 min, the ΔE^* of the area contacted with rGPM_{5.0} electrode was reduced from 54.03 (untreated area) to 3.56, suggesting that the color of the cleaning area is comparable to the control. As shown in Supplementary Figure S6, the excellent cleaning effect was also confirmed by the cleaning of the paper dyed with blue ink. However, as shown in Fig. 5a2(G) and a3(G), after a treatment with the PAM hydrogel for 2 h on the same dyed paper, the corresponding ΔE^* values for the both sides of the paper were 27.41 and 33.65, respectively, and the safranin T diffused through water beyond the contacted area of PAM hydrogel.

The experimental results also indicated that the rGPM_{5.0} electrode could be repeatedly used for six times without any loss of efficacy (Supplementary Figure S7a) and the rGPM_{5.0} electrode could be prepared in different sizes to regulate the cleaning area (Supplementary Figure S7b). Additionally, it is worth noting that HPEC could only eliminate organic dye on the paper but without a visible effect on the mineral pigments (Supplementary

Figure 5. Performance of HPEC for cleaning safranin T from paper at 4 mA/cm² (a). The control (a1). Face (a2) and back (a3) of the paper treated using HPEC for different time: A. 1 min, B. 2 min, C. 3 min, D. 4 min, E. 5 min, F. 6 min; G. treated for 2.0 h using the only PAM hydrogel. (a4) Normalized UV-vis reflectance spectra obtained from the areas corresponding to (a2). The efficiency of HPEC for cleaning stains of various drinks at 4 mA/cm² within 5 min (b). The efficiency of HPEC for eliminating tideline (c). (c1) Before, (c2) face and (c3) back of the paper with tideline after treatment by using HPEC at 3.0 mA/cm² for 3 min. The efficiency of HPEC for eliminating mildew (d).

Figure 6. Performance of HPEC for eliminating various stains (mildew, foxing and tideline) on a real artwork. (a) A Chinese painting created by Xu Shi (Qing Dynasty, ~1850); (b) an original piece with mildew stains collected from the painting (red box region); (b1) the piece with mildew stains after treatment by using HPEC at 8.0 mA/cm² within 6 min; (c) an original piece with foxing stains collected from the painting (red box region); (c1) the piece with foxing stains after treatment by using HPEC at 3.0 mA/cm² within 3 min.

Figure S7c). Generally, the colors used in traditional Chinese painting are mineral pigments. It can be deduced from these case studies that HPEC does not noticeably impact the traditional Chinese painting itself.

To evaluate the performance of HPEC for various stains, different stains eliminated by HPEC were conducted, and the results are also shown in Fig. 5. As shown in Fig. 5b, various drink stains on the paper could be erased by HPEC at 4 mA/cm² within 5 min. The tideline stains originated from the cellulose degradation products not only detract the aesthetics of paper artworks but also accelerate the degradation of cellulose²⁴. The excellent performance of HPEC in cleaning of tideline stains was also found (Fig. 5c). Evidently, the tideline stains on the both sides of paper are completely eliminated by using HPEC at 3.0 mA/cm² within 3 min. However, although the PAM hydrogel attached on the paper for 3.0 h could slightly remove tideline stains, fulvous contaminants were diffused beyond the contacted area to generate new tideline stains (Supplementary Figure S8).

Molds and mildews not only deteriorate the aesthetics of paper artworks but also further decompose the paper cellulose³⁹. To remove molds and mildews, various protocols including mechanical cleaning⁴⁰, freeze-drying⁴¹, laser⁴², UV irradiation⁴³ and biocleaning⁴⁴, have been developed. However, these methods still have certain issues such as low cleaning efficiency and impacting on the paper itself. Interestingly, the mildew stains on both sides of the paper could be distinctly not only eliminated (Fig. 5d) but also inactivated (Supplementary Figure S9) by using HPEC at 8 mA/cm² within 6 min.

The excellent efficiency of the new method was also confirmed in practical applications. As a real example, results for cleaning various stains (mildew, tideline, foxing) on a Chinese painting (created by Xu Shi, Qing Dynasty, ~1850) by using HPEC are shown in Fig. 6. Obviously, the black mildew stains together with the yellowish foxing stains were almost completely eliminated at 8 mA/cm² for 6 min (Fig. 6b1), and the tideline stains could be thoroughly removed at 3 mA/cm² within 3 min (Fig. 6c1).

All above results indicate that HPEC is well adaptive and efficient to locally clean various stains on the paper artworks under mild conditions.

Stain-removing mechanism of HPEC. Employing the prepared PbO₂-based electrode as working electrode, rGPM_{5.0} as counter electrode and Ag/AgCl as reference electrode, the cyclic voltammetry curves recording for the papers with and without contamination of safranin T are shown in Fig. 7a. Similar to the cyclic voltammetry curves of PbO₂-based electrode used in the degradation of organic pollutants⁴⁵, any new anodic current peak was not found in the curve for the dye-contaminated paper in comparison to the uncontaminated one, indicating that safranin T is not oxidized directly on the surface of PbO₂ anode but decomposed by hydroxyl radicals generated through the anodic discharge of water on the surface of PbO₂ electrode⁴⁵. The formation of hydroxyl radicals in this case was verified by the sodium terephthalate (ST) fluorescence probe method. As illustrated in Supplementary Figure S10, an obvious emission peak at 426 nm derived from ST oxidized by hydroxyl radicals was found⁴⁶, indicating the formations of hydroxyl radicals during HPEC procedure.

Actually, hydroxyl radical is a powerful oxidant to degrade various organic compounds. During this process, organic compounds are broken down through a series of reactions including hydroxylation, decarboxylation, dehydration, demethylation and ring-opening reaction and even mineralization⁴⁷. Based on our investigation and the conclusions in literatures^{45,47}, a stain-removing mechanism of HPEC as shown in Fig. 7b was proposed. The hydroxyl radicals generated on the surface of PbO₂ anode diffuse into the soiled paper between the two electrodes and react with contaminants (S) to form some colorless products. For the local release of water from rGPM_{5.0} electrode, the degradation reactions occur only in the electrode attached area. It is worth noting that the pigments used for Chinese painting are usually derived from minerals. Mineral pigments are hardly oxidized in the high standard electrode potential of HO[•]/H₂O (2.80 V)⁴⁸ and, therefore, HPEC can not change the mineral pigments.

Figure 7. The typical cyclic voltammograms of HPEC process (a) and a proposed mechanism of the elimination of stains during HPEC process (b). A the safranin T undyed and dyed paper were respectively inserted between rGPM_{5.0} cathode and the PbO₂ anode, and the scan rate was 50 mV/s.

Effect of HPEC on the paper fibres. To assess the possible damage of the paper caused by cleaning processes, the effect of HPEC on the paper fibers was investigated.

Figure 8a displays the representative SEM images of the papers treated by HPEC at 4 mA/cm² for different time. Clearly, for the papers treated with various time, the boundary of fiber bundle is almost perfect and coherent, which is closely similar to that of the untreated one. Additionally, the determining results shown in Supplementary Figure S11 indicated that HPEC scarcely alters the degree of polymerization (DP) of the paper cellulose.

FT-IR spectra for the papers with different treatments are presented in Fig. 8b. Compared with the FT-IR spectrum of the control, no new peaks appeared in FT-IR spectra of the papers treated with different durations, demonstrating that no new detectable functional groups generated during HPEC. The Total Crystallinity Indices (TCI, I_{1372}/I_{2903})⁴⁹ for all paper samples were calculated based on the ratio of intensity at 1372 cm⁻¹ and at 2903 cm⁻¹ and listed in Supplementary Table S5. TCI levels for the treated papers were approximately equal to that of the control, suggesting that HPEC does not affect the crystallinity of the paper cellulose. This conclusion was further confirmed by XRD experiments. As shown in Fig. 8c, for all treated papers, the typical diffraction patterns of native cellulose (or cellulose I) were found, and the peak at about 16.0° assigned to the (110) lattice plane in the triclinic structure as well as the peak at about 22.0° ascribed to the (200) lattice plane in the monoclinic structure appeared⁴⁹, which are similar to that of the untreated paper. According to the methodology described in the literatures^{50,51}, Crystallinity Indices (CrI) and Crystallite Sizes (L_{002}) for all samples were calculated and listed in Supplementary Table S5. Compared with the control, the CrI and L_{002} of the treated papers were almost unchanged. These results also support the conclusion that the fibers are hardly affected by the given HPEC process. The high-resolution C 1s XPS spectra of the papers treated with different durations are given in Fig. 8d. For all papers, three peaks at about 284.8, 286.3 and 287.8 eV respectively attributed to ($\text{C}-\text{C}$), ($\text{C}-\text{O}$) and ($\text{O}-\text{C}-\text{O}$) were found⁵², and these peaks were almost the same as that of the control, revealing that the proposed PHEC treatment does not cause a significant oxidation of the paper fibres.

In fact, hydroxyl radicals can degrade paper through autocatalytic reaction on the long time scale (years)¹⁰. In the current work, however, the treatment is very mild, and the treated duration is a few minutes. Based on our experimental results and reports in literature⁴⁸, it is reasonable to believe that the influence of HPEC on the paper cellulose is slight.

Effect of HPEC on the mechanical performance of paper. The stress-strain curves as well as the corresponding values of ultimate tensile strength (σ_t), and breaking strain (ε_t) for the papers with different treatment are shown in Supplementary Figure S12 and Supplementary Table S6, respectively. The σ_t of the HPEC treated paper mildly decreased with the increase of treatment time, but the corresponding ε_t increased slightly, indicating that PHEC treatment does not cause a significant decay in the mechanical performance of the paper. Meanwhile, both stress-strain curves of the papers treated for 6 min by HPEC and by the only rGPM_{5.0} were almost overlapped, suggesting the same effect of the two procedures on the mechanical strength of the paper. However, the paper showed a significant decrease for σ_t and an evident increase for ε_t in comparison to the control one when it was dipped in water for 6 min. In fact, here the slight change of the mechanical performance for the paper treated by HPEC may be attributed to the difference in drying history. It has been reported that a wetting-drying cycle, more or less, makes fibers overlap less and bent, resulting in a dramatic decay in σ_t and a significant increase in ε_t ^{1,5}. In the current work, the released water (i. e. the weight increment of the paper sheet after the treatment, Δw) from the rGPM_{5.0} electrode slightly increased with the increase of HPEC treatment time (Supplementary Table S6), resulting in a mild increase in change of the fiber texture. This morphology change could be found in Fig. 8a. In any case, the effect of HPEC treatment on the mechanical performance is weak, and this effect mainly originates from water rather than the electrochemical process itself.

Figure 8. SEM images (a), FT-IR spectra (b), XRD patterns (c) and C 1s XPS spectra (d) for the control paper and the paper treated by HPEC with different time.

Conclusion

In summary, by using the graphene based composite hydrogel and PbO₂-based material as electrode, we develop a simple and efficient system for electrochemically cleaning paper-based artworks. The proposed method has significant advantages over traditional methods. (1) The variables in current and potential are readily controlled, hence easily controlling the desired reaction for treating different stains. (2) The main reagent is hydroxyl radical, which degrades the organic stains, even the intractable mildew stains, within several minutes. For a short-term treatment, the influence of HPEC on the paper cellulose is very slight. (3) The miniaturized hydrogel electrode can tailor the electrochemical reaction not only in the desired area but also the expected reaction. (4) Owing to the special cleaning mode and the outstanding mechanical performances, the composite hydrogel electrode can be easily peeled off from the surface of paper without any residues after cleaning, and can be repeatedly used for several times without loss of efficiency. From aforementioned points of view, we constructed a electrochemistry method with peculiar characteristics for cleaning paper-based artifacts. This process can remove the stains including organic dyes, drinks, tideline, foxing and mildews from paper-based artworks in a controllable area. However, for safety, we suggest that this method should be first applied in a mimic to evaluate the influence of HPEC on the artwork itself before application.

Methods

Materials. Acrylamide, and *N,N'*-methylenebisacrylamide were purchased from Sigma-Aldrich and used as received. Graphite powder (100 meshes, 99.99%), ammonium persulfate (APS), *N,N,N',N'*-tetramethylethylenediamine (TEMED), L-ascorbic acid (VC), and other reagents were of analytical grade and used as received from Sinopharm Chemical Reagent Co. Ltd. Sodium montmorillonite (MMT) was supplied by Zhejiang SAND Technology Co. Ltd. and used after washing and freeze-drying. Ultrapure water (18.2 MΩ at 25 °C) was used throughout the experiments. 316 stainless steel plates with a size of 150 × 35 × 2 mm were obtained commercially. Chinese rice papers (Xuanzhi in Chinese), widely used in Chinese traditional painting and calligraphy, were purchased from Chongxing Xuanzhi Factory and used as model paper samples. The used Xuanzhi with a density of 45.3 g/m² was made of sandalwood pulp (>75%) with trace amount of Chinese alpine rush.

Synthesis of hydrogel-based electrode. Graphene oxide (GO) was firstly prepared from graphite powder according to the literature²², and then an aqueous dispersion of GO and exfoliated MMT was prepared by mixing 10.0 mL GO (8.0 mg/mL) and a certain amount of MMT under ultrasound for 2.0 h. Subsequently, 2.0 g AM and 4.0 mg BIS were added into the dispersion and stirred in ice-water bath for 3.0 h. After purging with nitrogen gas for

30 min, an aqueous solution of APS (100 μ L, 0.1 mol/L) and TEMED (10 μ L) were successively added into the dispersion. The resultant mixture was rapidly injected into a sealed plastic tube with different diameters, and the columnar GO-poly(acrylamide)-MMT nanocomposite hydrogel (GPM) was formed at 20 °C for 24 h.

GPM hydrogels were immersed in the aqueous solution of VC (20 mg/mL) at 40 °C for 3 days to form reduced GO-poly(acrylamide)-MMT nanocomposite hydrogels (rGPM)¹⁸, and then rGPM were washed with water to remove excessive VC. To explore the effect of MMT on the mechanical strength of rGPM, rGPM composite hydrogels with different MMT content were synthesized by the analogous procedure and they were designated as rGPM_n (here n refers to the weight percentage of MMT to AM). For comparison, poly(acrylamide) hydrogel (PAM) was also prepared in the absence of GO and MMT.

Fabrication of PbO₂ electrode. The PbO₂ electrode was prepared according to the literature procedure²³.

Preparation of papers with simulated stains. To assess the HPEC performance, Chinese rice papers with various simulated contaminants including organic dyes, commercial drinks (coffee, tea, cola, and red wine), tideline, and mildew were prepared using the following processes.

Simulated papers contaminated with different organic dyes were prepared by soaking Chinese rice papers in safranin T solution (1.0 wt%) or in blue ink for 1.0 h. After removing from the solution and drying in air, the desired papers were gained. Analogously, commercial drinks (coffee, tea, cola, and wine) were brushed on Chinese rice papers, and then the corresponding various stains on the papers were produced after the evaporation of water.

Molds were carefully collected from a book of our library and incubated by potato dextrose agar (PDA) at 28 °C for 10 days. The colonies were separated and dispersed in water to form a mold suspension. Papers after immersion in the suspension were pasted on the fresh PDA and cultivated for 8 days in a incubator with a relative humidity (RH) of 95% at 28 °C. Then, the papers contaminated with mildew were obtained after they were peeled from the surface of PDA and dried at room temperature.

Chinese rice papers were first treated by moist heat aging at 80 °C and 90% RH for 7 days. In this process, yellowish or brownish products of cellulose degradation in the papers were formed. A few drops of water were dropped onto the aged paper, and then the paper with tideline stains were obtained after drying at room temperature because of the diffusion of cellulose degradation products at the wet/dry interface²⁴.

Actual paper-based cultural relic with stains. A Chinese painting created by Xu Shi (Qing Dynasty, ~1850) exists various stains including mildew, foxing and tidelines. As a cleaning example of actual paper-based cultural relic, this painting was selected to evaluate the performance of HPEC.

Characterizations. The relevant properties of the composite hydrogels, the cleaning performance of HPEC and the effect of HPEC on the paper, were characterized.

The swelling behavior of composite hydrogels. The morphologies of freeze-dried hydrogels were observed by using a Hitachi SU-8020 field emission scanning electron microscopy. The equilibrium swelling degree (ESD, g/g) of the swollen hydrogel was calculated from the equation (1).

$$\text{ESD} = (W_e - W_d)/W_d, \quad (1)$$

where W_e and W_d represent the weights of the swollen hydrogel and the corresponding dried hydrogel, respectively.

The composition of composite hydrogels. Raman spectra of the involved materials were obtained by using a Renishaw inVia Reflex microspectrometer with an excitation wavelength of 532 nm. Fourier transform infrared (FT-IR) spectroscopy was recorded in the range from 500 to 4000 cm^{-1} using a Perkin Elmer FT-IR spectrophotometer with attenuated total reflectance (ATR) mode. X-ray photoelectron spectroscopy (XPS, Axis Ultra Kratos Analytical Ltd.) of the relevant composite hydrogels was performed using Al K α radiation (1486.6 eV) as the excitation source. X-ray diffraction (XRD) experiments were carried out on a Rigaku D/Max-2500 X-ray diffractometer with Cu K α X-ray beam at 40 kV and 30 mA.

The mechanical performances of composite hydrogels. Mechanical performances of the swollen hydrogels were measured with a universal mechanical testing apparatus (QT-1136, Dongguan Qualitest Instrument Co., Ltd.) in compression mode. A cylindrical sample (~15 mm in diameter and ~10 mm in height) was compressed at room temperature and a rate of 10 mm/min with a 1000 N load cell. The compressive modulus (E , kPa), compressive stress (σ , MPa), strain (ε , %) and fracture energy density (U , kJ/m³) were calculated from the stress-strain curves according to the literatures^{25,26}. The fatigue resistance of the swollen hydrogel was investigated by consecutive 6 cycles of compressive loading-unloading test at the strain range of 0–80%. Oscillatory shear measurements for the relevant hydrogels were performed on a TA Instruments AR-G2 rheometer equipped with parallel plate geometry (20 mm diameter) at 25 °C. Dynamic stress sweep experiments were carried out at the frequency of 1 Hz. Dynamic frequency sweep experiments were performed over the frequency range from 0.1 to 100 rad/s under a constant stress of 10 Pa.

The electrochemical behavior of HPEC. The electrical conductivity of the composite hydrogels was determined by using a four-probe technique on a SX1934 digital multimeter (Suzhou Telecommunication Factory, China). Cyclic voltammograms were recorded in a three-electrode system using a CHI 760D electrochemical workstation (CH Instruments) at room temperature and a scan rate of 50 mV/s. The PbO₂-based

electrode, rGPM_{5,0}, and Ag/AgCl were performed as working electrode, counter electrode, and reference electrode, respectively.

The cleaning performance. The colorimetric coordinates (L^* , a^* , b^*) of the papers were obtained by using a spectrophotometer (VS450, X-Rite) in the range from 360 to 750 nm. The degree of cleaning was evaluated through the color difference (ΔE^*) that was calculated by the equation (2)³.

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (2)$$

where ΔL^* , Δa^* , and Δb^* are respectively differences between the measured Lab values of the non-soiled and the soiled or the cleaned sample.

The microstructure and composition of cleaned papers. To explore the effect of HPEC on the paper, the morphology, composition as well as mechanical performances of the papers before and after HPEC treatment were measured. The morphology was observed on a scanning electron microscope (Quanta 200, FEI), and the composition was characterized by a Rigaku D/Max-2500 X-ray diffractometer, a Perkin Elmer FT-IR spectrophotometer with ATR mode, and a Kratos Axis Ultra X-ray photoelectron spectrometer. The degree of polymerization of paper cellulose was estimated by the determination of intrinsic viscosity as described in the literature²⁷. Tensile tests were performed on a universal testing machine equipped with a 100 N load cell at a deformation rate of 20 mm/min. Before testing, all samples were dried in air for 24 h and then stored for at least 48 h in a desiccator with a RH of 58% to achieve a complete equilibrium. For comparison, the paper samples treated by the only rGPM_{5,0} hydrogel for 6 min and dipped in water for 6 min were also used for the tensile test.

Data availability. All data generated or analyzed during this study are included in this published article (and its Supplementary Information file).

References

1. Zervos, S. & Alexopoulou, I. Paper conservation methods: a literature review. *Cellulose* **22**, 2859–2897 (2015).
2. Mazzuca, C. *et al.* Gellan hydrogel as a powerful tool in paper cleaning process: A detailed study. *J. Colloid Interface Sci.* **416**, 205–211 (2014).
3. Domingues, J. A. *et al.* Innovative hydrogels based on semi-interpenetrating p (HEMA)/PVP networks for the cleaning of water-sensitive cultural heritage artifacts. *Langmuir* **29**, 2746–2755 (2013).
4. Mazzuca, C. *et al.* Cleaning of paper artworks: development of an efficient gel-based material able to remove starch paste. *ACS Appl. Mater. Interfaces* **6**, 16519–16528 (2014).
5. Isca, C., Fuster-López, L., Yusá-Marco, D. J. & Casoli, A. An evaluation of changes induced by wet cleaning treatments in the mechanical properties of paper artworks. *Cellulose* **22**, 3047–3062 (2015).
6. Stulik, D. Solvent gels for the cleaning of works of art: the residue question. 16–17 (Getty Publications, 2004).
7. Mazzuca, C. *et al.* Versatile hydrogels: an efficient way to clean paper artworks. *RSC Adv.* **3**, 22896–22899 (2013).
8. Bonini, M., Lenz, S., Giorgi, R. & Baglioni, P. Nanomagnetic sponges for the cleaning of works of art. *Langmuir* **23**, 8681–8685 (2007).
9. Mazzuca, C. *et al.* How to tune a paper cleaning process by means of modified gellan hydrogels. *Microchem. J.* **126**, 359–367 (2016).
10. De Filipo, G. *et al.* Gellan gum hybrid hydrogels for the cleaning of paper artworks contaminated with *Aspergillus versicolor*. *Cellulose* **23**, 3265–3279 (2016).
11. Pizzorusso, G. *et al.* Physicochemical characterization of acrylamide/bisacrylamide hydrogels and their application for the conservation of easel paintings. *Langmuir* **28**, 3952–3961 (2012).
12. Carretti, E. *et al.* Physicochemical characterization of partially hydrolyzed poly (vinyl acetate)–borate aqueous dispersions. *Soft matter* **10**, 4443–4450 (2014).
13. Carretti, E. *et al.* New frontiers in materials science for art conservation: responsive gels and beyond. *Acc. Chem. Res.* **43**, 751–760 (2010).
14. Baglioni, P. *et al.* Micelle, microemulsions, and gels for the conservation of cultural heritage. *Adv. Colloid Interface Sci.* **205**, 361–371 (2014).
15. Baglioni, P., Carretti, E. & Chelazzi, D. Nanomaterials in art conservation. *Nat. Nanotechnol.* **10**, 287–290 (2015).
16. Niu, J. *et al.* Electrochemical mineralization of perfluorocarboxylic acids (PFCAs) by Ce-doped modified porous nanocrystalline PbO₂ film electrode. *Environ. Sci. Technol.* **46**, 10191–10198 (2012).
17. Gao, G., Du, G., Sun, Y. & Fu, J. Self-healable, tough, and ultrastretchable nanocomposite hydrogels based on reversible polyacrylamide/montmorillonite adsorption. *ACS Appl. Mater. Interfaces* **7**, 5029–5037 (2015).
18. Zhang, E. *et al.* Robust and thermo-response graphene–PNIPAm hybrid hydrogels reinforced by hectorite clay. *Carbon* **62**, 117–126 (2013).
19. Wu, L. *et al.* Magnetically induced anisotropic orientation of graphene oxide locked by *in situ* hydrogelation. *ACS Nano* **8**, 4640–4649 (2014).
20. Teng, C. *et al.* Hierarchical Layered Heterogeneous Graphene-poly (N-isopropylacrylamide)-clay Hydrogels with Superior Modulus, Strength, and Toughness. *ACS Nano* **10**, 413–420 (2015).
21. Yeung, A. T. & Gu, Y. Y. A review on techniques to enhance electrochemical remediation of contaminated soils. *J. Hazard. Mater.* **195**, 11–29 (2011).
22. Xu, Y., Sheng, K., Li, C. & Shi, G. Self-assembled graphene hydrogel via a one-step hydrothermal process. *ACS Nano* **4**, 4324–4330 (2010).
23. Song, Y., Wei, G. & Xiong, R. Structure and properties of PbO₂-CeO₂ anodes on stainless steel. *Electrochim. Acta* **52**, 7022–7027 (2007).
24. Jeong, M. J., Dupont, A. L. & René de la Rie, E. Degradation of cellulose at the wet-dry interface: I-study of the depolymerization. *Cellulose* **19**, 1135–1147 (2012).
25. Stevens, L., Calvert, P. & Wallace, G. G. Ionic-covalent entanglement hydrogels from gellan gum, carrageenan and an epoxy-amine. *Soft Matter* **9**, 3009–3012 (2013).
26. Gao, G., Du, G., Cheng, Y. & Fu, J. Tough nanocomposite double network hydrogels reinforced with clay nanorods through covalent bonding and reversible chain adsorption. *J. Mater. Chem. B* **2**, 1539–1548 (2014).

27. Zhang, Y. *et al.* A green and efficient technology for the degradation of cellulosic materials: structure changes and enhanced enzymatic hydrolysis of natural cellulose pretreated by synergistic interaction of mechanical activation and metal salt. *Bioresour. Technol.* **177**, 176–181 (2015).
28. Shi, K. *et al.* Near-Infrared Light-Responsive Poly (N-isopropylacrylamide)/Graphene Oxide Nanocomposite Hydrogels with Ultrahigh Tensibility. *ACS Appl. Mater. Interfaces* **7**, 27289–27298 (2015).
29. Cong, H. P., Wang, P. & Yu, S. H. Highly elastic and superstretchable graphene oxide/polyacrylamide hydrogels. *Small* **10**, 448–453 (2014).
30. Byrne, P. *et al.* Metal-induced gelation in dipyrindyl ureas. *New J. Chem.* **34**, 2261–2274 (2010).
31. Hu, H., Xin, J. H. & Hu, H. PAM/graphene/Ag ternary hydrogel: synthesis, characterization and catalytic application. *J. Mater. Chem. A*, **2**, 11319–11333 (2014).
32. Skelton, S. *et al.* Biomimetic adhesive containing nanocomposite hydrogel with enhanced materials properties. *Soft Matter* **9**, 3825–3833 (2013).
33. Liu, R. *et al.* Tough and highly stretchable graphene oxide/polyacrylamide nanocomposite hydrogels. *J. Mater. Chem.* **22**, 14160–14167 (2012).
34. Chai, L. *et al.* A Cu-m-phenylenediamine complex induced route to fabricate poly (m-phenylenediamine)/reduced graphene oxide hydrogel and its adsorption application. *Carbon* **81**, 748–757 (2015).
35. Gupta, B. *et al.* Role of oxygen functional groups in reduced graphene oxide for lubrication. *Sci. Rep.* **7**, 45030, doi:10.1038/srep45030 (2017).
36. Das, S. *et al.* Rheology and morphology of pristine graphene/polyacrylamide gels. *ACS Appl. Mater. Interfaces* **5**, (8633–8640 (2013).
37. Guth, E. Theory of filler reinforcement. *J. Appl. Phys.* **16**, 20–25 (1945).
38. Ruyter, I. E., Nilner, K. & Möller, B. Color stability of dental composite resin materials for crown and bridge veneers. *Dent. Mater.* **3**, 246–251 (1987).
39. Sterflinger, K. & Pinzari, F. The revenge of time: fungal deterioration of cultural heritage with particular reference to books, paper and parchment. *Environ. Microbiol.* **14**, 559–566 (2012).
40. Cumming, L. & Colbourne, J. The conservation of Mrs. Marton, an eighteenth-century pastel and gouache portrait by Daniel Gardner. *Pap. Conserv.* **22**, 38–47 (1998).
41. Sequeira, S., Cabrita, E. J. & Macedo, M. F. Antifungals on paper conservation: An overview. *Int. Biodeterior. Biodegrad.* **74**, 67–86 (2012).
42. Pouli, P., Selimis, A., Georgiou, S. & Fotakis, C. Recent studies of laser science in paintings conservation and research. *Acc. Chem. Res.* **43**, 771–781 (2010).
43. De Filipo, G. *et al.* Gellan gum/titanium dioxide nanoparticle hybrid hydrogels for the cleaning and disinfection of parchment. *Int. Biodeterior. Biodegrad.* **103**, 51–58 (2015).
44. Bosch-Roig, P. & Ranalli, G. The safety of biocleaning technologies for cultural heritage. *Front. Microbiol.* **5**, 155 (2014).
45. Liu, Y., Liu, H. & Li, Y. Comparative study of the electrocatalytic oxidation and mechanism of nitrophenols at Bi-doped lead dioxide anodes. *Appl. Catal. B* **84**, 297–302 (2008).
46. Li, Y. *et al.* In situ fabrication of Mn₃O₄ decorated graphene oxide as a synergistic catalyst for degradation of methylene blue. *Appl. Catal. B* **162**, 268–274 (2015).
47. Figueredo-Sobrinho, F. *et al.* Insights into electrodegradation mechanism of tebuconazole pesticide on Bi-doped PbO₂ electrodes. *Electrochim. Acta* **154**, 278–286 (2015).
48. Meng, D., Li, G., Liu, Z. & Yang, F. Study of depolymerization of cotton cellulose by Pb/PbO₂ anode electrochemical catalysis in sulfuric acid solution. *Polym. Degrad. Stab.* **96**, 1173–1178 (2011).
49. Huang, Z. *et al.* Influence of mechanical activation on the graft copolymerization of sugarcane bagasse and acrylic acid. *Polym. Degrad. Stab.* **94**, 1737–1745 (2009).
50. Segal, L., Creely, J., Martin, J. & Conrad, C. M. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Text. Res. J.* **29**, 786–794 (1959).
51. Zheng, A. *et al.* Comparison of the effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs. *Bioresour. Technol.* **176**, 15–22 (2015).
52. Belgacem, M. N., Czeremuszkin, G., Sapieha, S. & Gandini, A. Surface characterization of cellulose fibres by XPS and inverse gas chromatography. *Cellulose* **2**, 145–157 (1995).

Acknowledgements

The authors gratefully acknowledge the financial support of the Natural Science Foundation of China (21173140 and 20973105), and the National Program on Key Basic Research Project of China (2012CB725302).

Author Contributions

X.L. conducted the experiments and wrote the manuscript; L.Z. analyzed the results; R.L. and X.F. prepared the figures and tables; K.S. designed the experiments and revised the manuscript; D.H. conceived and supervised the project. All authors reviewed the manuscript. X.L. and L.Z. are co-first authors.

Additional Information

Supplementary information accompanies this paper at doi:10.1038/s41598-017-08907-w

Competing Interests: The authors declare that they have no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2017