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Original article

Characterization of Chinese ink in size and surface

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Abstract

Chinese ink, a mixture of soot and animal glue, has been used in East Asia for centuries as the sole black paint of choice. The combination of animal glue and soot particles create a distinctive dispersion system giving Chinese ink its unique properties among paints and inks. Photon correlation spectroscopy (PCS) size measurements and scanning electron microscopy (SEM) imaging revealed subtle differences in particle size and aggregation among inks of different soot origin. Surface chemistry of the particles was examined using laser Doppler electrophoresis (LDE) for determination of the isoelectric point (IEP). The IEPs of different inks were not distinct, but reflected the presence of the collagen-based glue on the particles' surface. The IEP and size dropped significantly when inks were treated with collagenase and when soot and carbon blacks alone were measured, pointing to the important role of animal glue in this dispersion system.

Keywords: Soot; Animal glue; Sol; Electrophoresis; Scanning electron microscopy (SEM); Photon correlation spectroscopy (PCS); Laser Doppler electrophoresis (LDE); Isoelectric point (IEP)

1. Introduction

Chinese ink, known as *mo* in China and *sumi* in Japan, refers to the black paint used almost ubiquitously in East Asian painting and calligraphy. Lampblack or soot, as a black pigment, with animal glue as a vehicle, has provided a robust, permanent, and versatile paint for two millennia. The endurance of such a material is owed to its traditional manufacture as well as its physical and chemical uniqueness among artists' materials. The present research uses state-of-the-art instrumentation to examine and illustrate the exceptional properties of Chinese ink through chemical and physical characterization, and to shed light on how raw materials affect the quality of the ink.

Physically, Chinese ink is distinct from that of traditional Western colored paints in that it is formed into solid inksticks from which the ink is dispersed into water as needed via mechanical action, i.e., rubbing the stick against an inkstone in water. For many centuries the carbon used has been soot either made by burning wood (usually pinewood) or lampblack made by burning oil at a wick. The animal glue binder is manufactured mostly from the hides of mammals to yield a strong collagen-based glue, also generally used as the medium in other East Asian paints. The final product has evolved to a small, handheld black stick, usually adorned with impressed designs or inscriptions and often gilded or painted. Many inksticks are regarded as works of art in their own right.

Chemically, Chinese ink is set apart from other types of dyes and pigments in that its primary particle size and surface play a unique role in its effectiveness and longevity as an artists' material. Typical artists' colorants are either dyes which form a true solution or may be precipitated onto an inorganic phase to form a lake, or large-sized pigments mixed with a vehicle to create paint. In contrast, the nano-sized carbon primary components of Chinese ink, 10–150 nm carbon soot particles, make it a colloidal dispersion or sol (aqueous dispersion). In addition, surface properties of sol particles become of utmost importance: a 10 nm particle has a specific surface area of about 300 m^2g^{-1}. Sols maintain dispersion stability by electrostatic forces (due to electric charges on the surface from surface ionization or adsorption of ionized surfactants), steric forces (entropic/enthalpic interactions induced by adsorbed polymers), or electrosteric forces (a combination of both effects).

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The two most important qualities of a typical dispersion system are the particles' size and surface chemistry: these will dictate the behavior of the dispersion and in this study can indicate characteristics of Chinese ink such as age, origin, or quality. Therefore, the morphology must be known in order for results from size and surface chemistry measurements to have meaning. Soot is composed of spherical primary carbon particles ranging in size from about 10 nm to 150 nm. These primary particles fuse during combustion to form small stable clusters (100–300 nm), which represent the characteristic physical unit of soot [1]. Subsequent annealing of the soot or soot-glue composite material leads to further formation of aggregate structure (up to 1 μm) producing a more even material consisting of smaller, more compact units. In general, primary carbon particles are amphoteric substances in aqueous solutions, consisting typically of sp^2 hybridized carbon atoms in planes of fused aromatic rings with weak van der Waals forces holding the layers together. For the most part, carbon particle surfaces produced from combustion of natural fuels contain heterogeneously distributed surface groups [2].

The model of Chinese ink particles in this study is clusters of nanosized spherical carbon particles (typically produced in sooting flames) with a surface layer of animal glue protein derived from collagen. This study attempts to examine the size of clusters as the characteristic unit of Chinese ink to indicate possible origin and its effect on the ink dispersion. Likewise, comparison of the surface chemistry of different Chinese inks will indicate how the glue layer impacts this material. The combination of these qualities may help in shaping methods to find the quality of Chinese ink.

1.1. Brief history of inksticks

Samples of Chinese ink have been excavated from as early as the third century B.C., though it is clear that a black ink, almost certainly based on carbon, was in use much earlier than this [3,4] Chinese ink in the form of inkcakes was being produced in the Han period (206 B.C.–A.D. 220); this evolved into sticks closer to the modern form by the Tang period (618–907). A timeline of major points in Chinese ink history is given in Table 1. Black inks based on carbon are known in other cultures, some of them predating the Chinese case. The use of such material in Egypt, for example, has been suggested for as far back as the fourth millennium B.C. [5]. A similar soot-and-gum-based ink is described in the ancient Jewish literature [6]. The Chinese, however, developed it into an unusually sophisticated product from such simple starting materials, and the approximately contemporary development of paper led to its increasing use in East Asia from the third century on. It is generally considered that this technology was soon transferred to the rest of East Asia,

Table 1
A brief timeline of Chinese ink history

Period	
Early Zhou (1030–722 B.C.) through "Spring and Autumn" (722–480 B.C.) periods	No evidence of ink cakes or sticks Type of carbon undetermined Documents written on wooden tablets
Warring States (480–221 B.C.); Qin period (221–207 B.C.)	Earliest text reference to *mo* Documents written on silk and wooden tablets Possible first archaeological sample?
Han period (206 B.C.–A.D. 220); three kingdoms through Northern and Southern Dynasties (221–581)	First historical description of ink making (sixth century). Some kind of soot specified First writings on painting technique Calligraphy now a major art form Wei Tan (179–253) traditionally credited with the "invention" of ink in third century; probably used pine soot Excavated samples of ink from graves Development of paper and use for writing from early second century; silk continues to be used; wood and bamboo peters out
Sui through Tang periods (581–907)	First evidence of inksticks molded by compression Wood soot evidently used as carbon; pinewood appears to have been favored
Song (960–1279) and Yuan (1260–1368) periods	Lampblack in use for ink by 11th century Numerous contemporary descriptions of ink making
Ming period (1368–1644)	Detailed recipe for pine soot ink in the *Tian gong kai wu* (17th century) Same source states that 90% of all ink made from pine soot and 10% from lampblack
Qing period (1644–1911)	Inksticks become a minor art form, distinguished from their use to make ink
Republic/modern 1911–	Use of secondary constituents has dropped off over time, usually by now just dyes and perfumes

notably to Japan and Korea. The ink that was developed, being carbon-based, is not prone to fading or other chemical change, and in most cases adheres well to the underlying support.

The earliest written account of ink making in China is found in a sixth century encyclopedia, the *Qi min yao shu* by Jia Sixie (the relevant passage is translated into English in [3], p. 243). This account specifies "fine and pure soot", which has been assumed to be some version of wood soot. Various later accounts describe pinewood soot as the carbon used, and this has generally been taken as one of the two main types. The wood was burned in a restricted supply of air and the soot allowed to drift either into connecting chambers or down a long tunnel: soot collected farther from the flame, with smaller particles, was prized as the best quality and used for scholar's inksticks, while that collected close to the flame was used for inferior inks, such as printing [3]. At some point, probably by the Song period though the dating is uncertain, lampblack made by burning oil at a wick came into use and is described in an 11th century account. It appears that both versions of carbon continued to be used in China. The 17th century *Tian gong kai wu* [7] gives detailed descriptions of making both pinewood soot, and lampblack from oil or lard. This source suggests that nine-tenths of all ink was from wood soot and one-tenth from lampblack. Modern ink manufacture seems to rely primarily on lampblack, the production of which is easier and more readily controlled than for wood soot, though industrial carbon blacks are frequently purchased and used. In Japan, the rather sparse historical evidence available seems to indicate that lampblack has been generally employed.

Animal glue manufacture has been a tradition in all of East Asia, producing a general purpose manufacturing adhesive, a binder for paints and so forth, and a size for paper and textiles [8,9]. Animal hides are depilated up to a month with lime, followed by washing and acidification. The hides are rinsed and the glue produced by extracting several times with hot water, allowing the solution to cool and gel, then cutting and drying the product. A solution of glue with the carbon forms a dough-like mixture that is subjected to laborious and extended mixing processes. Kneading, steaming, rewetting are all used but historical accounts tend to stress the importance of pounding the mixture repeatedly—thousands of times often being specified. Chinese ink is, therefore, assumed to be a thorough and intimate mixture of carbon and glue. In addition to animal glue and soot, a host of secondary additives have been used over the centuries, one account suggesting that up to 1100 have been mentioned in the historical literature [10]. The most common are perfumes (e.g., camphor, cinnamon) to conceal the smell of animal glue and to promote sales, and colorants (e.g., indigo) to accent the ink's hue. Other additives may have helped in ink dispersion or to avoid cracking of the inkstick. On the whole, earlier historical accounts describe a greater number and variety of secondary constituents than later ones.

1.2. Previous scientific work

Aspects of carbon particle science relating to Chinese ink (apart from color) are those concerned with size and surface chemistry. These two properties determine the ability of the particles to disperse and interact with solvents (dispersion), to function as artists' media (paints), and to be useful conductive additives (rubber and plastics). More importantly, these properties directly impact color strength, gloss, and transparency of soot-based pigments [11].

The first scientific studies on Chinese ink date back to the 1930s [12–15]. These studies focused on the qualitative colloidal nature of Chinese ink particles in aqueous solution. One notable result is Terada's determination of particle size in the 100–150 nm range using an ultramicroscope, a value on the order of findings with modern instrumentation. The nanoscale particle size of soot-based inks, in combination with a very high absorption coefficient for visible light, seriously limits the use of optical microscopy for studying the physical aspects of these systems. Optical microscopy can, however, be used to distinguish carbons of larger particle size, such as chars or cokes, and to differentiate them from flame carbons, such as lampblack. Therefore, electron microscopy or laser-based scattering methods, for instance, must be implemented.

More extensive work on the correlation between soot origin and particle size was carried out by Winter using scanning electron microscopy (SEM) [16]. These studies used SEM to measure particle size through manual examination of images. The conclusions, based on statistical mean and mode of size distributions, point to trends but are not unique enough to yield a fingerprinting size-to-soot correlation. Recent studies with SEM and electron spin resonance (ESR) have examined the effect of pounding on ink quality [17], and reveal that extensive pounding (more than 5000 times) is required to fully saturate the carbon with glue. Elemental studies using proton induced X–ray emission (PIXE) and Rutherford backscattering (RBS) showed that a suite of 20th century inksticks had 10 times less trace element content compared to that found in samples of pre-20th century inksticks [18].

2. Materials and methods

2.1. Samples

Samples for this study (Table 2) included five modern inksticks, two industrial carbon blacks from Columbia Chemicals (Marietta, GA)[2], and two soots used for ink making, one pinewood the other lampblack. A dot system is used

[2] Certain trade names and company products are mentioned in the text or identified in illustrations in order to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology or the Smithsonian Institution, nor does it imply that the products are necessarily the best available for the purpose.

Table 2
Samples used in this study

Sample	Comments
3 Dot Japanese inkstick	Kobaien Ink Factory
Kobaien pine soot inkstick	Pine soot carbon; Kobaien Ink Factory
Kobaien lampblack inkstick	Lampblack soot carbon; Kobaien Ink Factory
Commercial inkstick	None
Chinese Shanghai inkstick	Pine soot carbon
Raven 410 Powder Furnace Carbon Black	Reported mean particle size 101 nm
Raven 1250 Powder Furnace Carbon Black	Reported mean particle size 20 nm
Shoen pinewood soot	From Japanese printmaker
Kobaien lampblack soot	Obtained from Kobaien Ink Factory

in Japan to rate inkstick quality, one being the lowest quality, five the highest. The 3 Dot Japanese inkstick and the Kobaien inksticks were purchased at the Kobaien Ink Factory in Nara, Japan in the 1970s. The Chinese Shanghai inkstick was chosen to examine a Chinese inkstick reportedly composed with pine soot. A commercial inkstick was purchased as part of a widely available Chinese calligraphy gift-set and used as an inferior reference.

To produce samples of ink from the five inksticks mentioned above, inksticks require rubbing with water on a textured surface, most commonly an inkstone. In order to avoid contamination, a glass plate, textured by sanding with a 120 grit abrasive paper was used to rub each inkstick. Unlike an inkstone, the plate could be properly cleaned in between samples. The ink was not rubbed to the concentration used for writing or painting, as the sample would then need to be further diluted for analysis.

2.2. Scanning electron microscopy

It has been postulated that the size of soot particles could point to soot origin and certain primary properties of Chinese ink, such as its "color" [19,20]. However, reports of particle size data are often measurement dependent; a size from one technique is often not comparable to a size from another technique. Past studies have used electron microscopy—both scanning and transmission—to image ink particles and visually determine the size [16,21]. Although SEM is much less accurate than TEM in the sizing of nanoscale features, previous studies using the two techniques agree that on average soot from pinewood is larger in size and wider in size distribution, compared with lampblack. SEM imaging of ink deposited from aqueous dispersions, in the present work, provided information about primary particle, cluster, and aggregate size as well as follow-up on past work. For SEM imaging, each dispersed sample was deposited onto a 13 mm diameter glass microscope slide and coated with less than a nanometer of sputtered gold/palladium. This slide was adhered to an aluminum stub with carbon paint around its edges. A Philips XL30 Scanning Electron Microscope equipped with a tungsten filament was used for imaging, and an EDAX Microanalysis system for elemental analysis.

2.3. Photon correlation spectroscopy

In addition to SEM sizing, an ensemble sizing technique applicable to liquid dispersed systems and statistically superior was employed. The technique, photon correlation spectroscopy (PCS), is ideal for sizing in the colloidal range (~1–1000 nm), based on the diffusion properties of particles undergoing Brownian motion [22]. The diffusive motion of particles is monitored in PCS by measuring the temporal fluctuations in scattered laser light intensity over very small time increments (of order microseconds). Larger particles move slower than smaller ones, therefore, positional correlations persist over longer times, giving rise to slower fluctuations in scattered light. By counting individual photon events, PCS determines the photon autocorrelation function of scattered light as a function of the delay time between increments. The decay constant (or line width) derived from the decaying autocorrelation function is related to the diffusion coefficient of the particles, D, from which we calculate an effective spherical diameter, d, using the Stokes–Einstein relationship ($D = kT/3\pi\eta d$), where k is the Boltzmann constant, T is the temperature in Kelvin, and η is the viscosity of the medium (water in our case). Our experiments employed a Malvern Instruments Zetasizer 3000HS at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD for all PCS measurements. The instrument uses a photon counter fixed at a scattering angle of 90° and a laser with incident wavelength of 632.8 nm. The polydispersity index, a measure of the size spread, was reported with a range from 0.05 (nearly monodisperse) to 0.7 (very wide distribution of sizes in the sample). The method of cumulants was used to determine the z–average particle size [22], which is the uncorrected intensity-weighted average representing a higher moment compared to mass, volume, or number averaging. Polydispersity values above 0.2 could warrant the use of more detailed analysis procedures, such as CONTIN or non-negatively constrained least squares. However, very few values exceeded 0.2, and the simpler cumulants analysis provided average size values comparable to CONTIN for samples tested.

2.4. Laser Doppler microelectrophoresis

Experiments using electrophoresis to examine surface properties of sol particles have been reported since the late 19th century [23,24]. By definition, electrophoresis is the movement of charged particles in an electric field. The charge, and to some extent the size, of the colloidal particles will govern its mobility when an electric field is applied across the dispersion. Adsorbed ions and charged sites on the particle surface coexist in the so-called Stern layer. This charged interface is balanced by a diffuse cloud of counter ions of opposite charge in the adjacent solution, creating an electrical double-layer. The boundary between the Stern and diffuse layers lies some short distance from the particle surface, in close proximity to a hydrodynamic shear plane between the bulk solution and the particle. When suspended

particles move in response to an applied field, it is the shear plane potential or zeta potential that is responsible, not the surface potential. Electrolytes in solution will contribute to the system's overall ionic strength and affect the zeta potential through a process called electrostatic screening; high ionic strength (I= 1/2 Σcz^2 where c= ion concentration and z= ion valence) leads to a lower zeta potential. In addition, the pH will affect the surface charge by chemically interacting through proton exchange with hydrolysable surface sites. Therefore, when reporting zeta potentials for any system, the ionic strength and pH of the solution must be defined.

To determine zeta potential, we begin by measuring the particle's motion in an electric field. The resulting mobility (velocity in relation to the applied field strength in units of μm cm $s^{-1}V^{-1}$), is then converted to zeta potential using an equation that relates mobility to various suspension properties, including the viscosity and dielectric constant of the liquid phase. The conversion may include a correction factor that takes into consideration the particle size and electrolyte concentration (e.g., the Henry equation, see [25]). Although mobility can be measured simply by viewing the motion of particles under an ultramicroscope, this process is tedious, unreliable, and yielded poor statistics, particularly important when a wide distribution of mobilities exists. The state-of-the-art method is based on laser Doppler electrophoresis (LDE), also known as electrophoretic light scattering. There are various implementations of LDE, but they all use the frequency shift of light scattered by particles moving through a laser beam under the influence of an applied field to determine mobility.

We used the Malvern Zetasizer 3000HS for all LDE measurements. In this instrument, two beams of light (632.8 nm), created by splitting the output of a low power laser, are focused at a crossing point within a rectangular quartz capillary cell, creating a pattern of interference fringes. One of these beams is reflected off a mirror attached to a vibrating piezoelectric oscillator, thereby causing the fringes to move at a known and constant frequency. As the particles move through the sensing zone and scatter light, the fringe frequency is shifted up or down due to the Doppler effect and depending on the direction of movement of the particles. The photon detector signal is sent to a digital correlator, and the resulting autocorrelation function is analyzed to produce the frequency spectrum (LDE is therefore a special application of PCS). This spectrum contains information on the distribution of particle velocities. Using this method, thousands of particles can be sampled in a single measurement and in a short experimental time frame (about 30 s), making LDE a convenient and statistically reliable technique.

2.5. Zeta potential measurement procedure

The Zetasizer 3000HS instrument uses a disposable syringe to deliver sample to the electrophoresis cell, with two valves positioned to seal the cell-electrode assembly during measurements. In our procedure, the cell was first conditioned by injecting 12 ml of suspension. A second 12 ml injection was then made, followed by a 1 min period for equilibration before beginning measurements. Each run consisted of three consecutive measurements with three runs performed for each pH, totaling nine zeta potential values. In order to measure the zeta potential at different pH values, the pH was adjusted first by adding 0.1 M NaOH to bring the solution to a pH around 9, then titrated stepwise down to a pH of about 2 with 0.1 M or 1 M HNO_3. Following titrant addition, the sample was stirred and the pH monitored until it became stable (±0.02 units) or for a period of time comparable to the experimental time frame (several minutes). If the relative standard deviation for any single measurement exceeded 2%, the measurement was discarded. A vendor-supplied latex standard in pH 9.2 buffer, traceable to NIST Standard Reference Material 1980 [26]was measured at the beginning and end of each day of operation to validate instrument efficacy.

2.6. Sample preparation

It is well known that carbon black and soots will aggregate, both upon formation and subsequently in ink development [27]. Due to this, reporting carbon particle size from different types of instrumentation has been a point of debate. It is advantageous to reduce the carbon to a uniform size (i.e., separate the large and loosely bound aggregates to obtain the smallest common cluster size) in order to produce reliable size measurements and uniform mobility when calculating zeta potential. To do this a Branson S–450A Sonifier was employed to disperse each ink sample. The sonifier uses a titanium horn immersed directly in the dispersion fluid. The efficiency of this instrument makes sample disruption incredibly fast when compared to a bath-type sonicator. The horn operates nominally at 20 kHz and causes microcavities to form and collapse, disrupting the suspension components. The immersion horn converts electrical energy to mechanical and directly transfers this energy to the solution, whereas a bath sonicator transfers the energy through the bath liquid and is dampened by the sample vessel. A test was performed to determine how much sonication was required to produce a consistent size measurement. Ink created from 3 Dot Japanese and Kobaien lampblack inksticks were sonicated in consecutive intervals and analyzed between each sonication until the size leveled off (for an example of the 3 Dot experiment, see Fig. 1). The appearance of a plateau with sonication time indicates that the materials are not being milled by the treatment; that is, once the physically aggregated soot is broken up, the energy level is insufficient to cause further size reduction of the primary (fused) clusters.

Solutions of NaCl with millimolar ionic strengths of 1, 10, and 100 were tested in size and zeta potential measurements to determine the most suitable concentration for analysis. A plot of the ionic strength vs. zeta potential for the inkstick is shown on a semi-log plot in Fig. 2 (note the reversal in y–axis direction to indicate increasing negative potential). This is an expected trend for zeta potential with increasing ionic strength: counter-ion screening reduces mobility. This effect

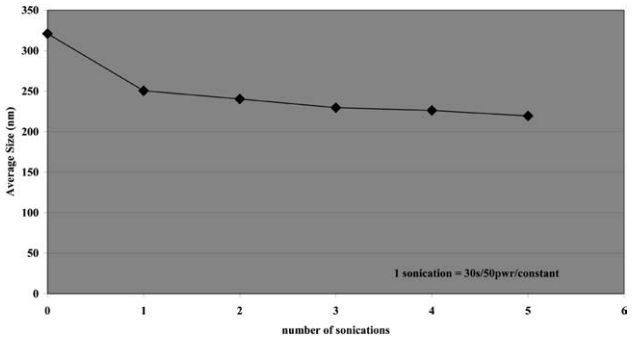

Fig. 1. 3 Dot Japanese Ink *z*–average PCS size measurement in between sonications, 1 mM NaCl solution.

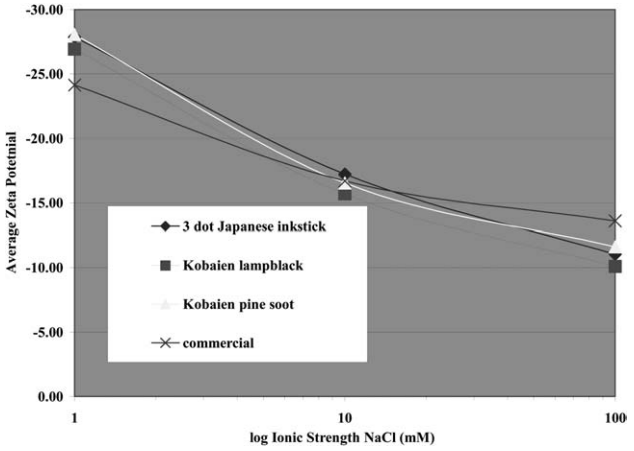

Fig. 2. Average zeta potential vs. ionic strength for four inksticks, log scale.

has been reported previously for protein-coated particles [28]. The lowest ionic strength, 1 mM, gave the most consistent results in both size and zeta potential measurements for all samples tested.

From these results each sample was prepared for sizing, SEM imaging, and microelectrophoresis using the following procedure:

(1) Each sample was rubbed in de-ionized water on a textured glass plate to produce about 3 ml of concentrated, opaque ink.
(2) A small amount of ink sample (100–600 μl) was diluted in about 75 ml of 1 mM NaCl solution until an optimum concentration was obtained based upon the obscuration level; this amount of ink varied for each material depending on its quality.
(3) The diluted dispersion was sonicated using a pulsed mode 50% duty cycle for 2 min intervals at the maximum output power level. This treatment was repeated three times. The duty cycle and off-time between treatments was needed to prevent the sample from overheating.
(4) Immediately before analysis, the sonicated sample was filtered through a sterile, 1.2 μm filter to remove oversize abnormalities (e.g., dust).

In order to simulate analysis of actual ink samples from an artifact, small pieces of inkstick were dispersed directly by ultrasonic treatment to create the ink, instead of rubbing on a textured surface. Pieces of the inkstick were placed in a glass vial and sonicated in about 3 ml of de-ionized water with a 2 mm diameter microtip titanium horn. A shorter duty cycle of 30% was used to avoid heating effects and five sonications were needed to yield a consistent size. After the ink was prepared from the inkstick sample, the same sample preparation procedure described above was implemented. It was found that around 1 mg or less of the inkstick was needed to produce an ink comparable to that produced from rubbing, resulting in a sample suspension with about 8–16 mg l^{-1}solid content.

2.7. Collagenase treatment

In order to investigate the effect of the glue layer on the ink particles, the inks were treated with collagenase enzyme to preferentially remove all collagen. The reaction was carried out in a 0.05 M TES/0.36 mM $CaCl_2$buffer solution, adjusted to pH 7.5. A Type IA collagenase (Sigma Aldrich) solution was made up the same day it was used at 1 mg of enzyme to 1 ml of buffer. The inksticks were rubbed up in the buffer instead of de-ionized water and about 0.8 ml of this ink was placed in a glass concentrator vial. The vials were heated to 37 °C for 20 min then 0.1–0.2 ml of the collagenase solution was added to each vial. These solutions remained at 37 °C for 5 h, after which they were removed and a few drops of dilute acetic acid were added to cease the reaction. Three samples of collagen (Sigma Aldrich, Type I from calf skin) in increasing amounts were also digested in this manner. Buffer solutions with and without collagenase enzyme were digested as controls. To remove digestion byproducts (e.g., salts, residual enzyme, etc.), the digested ink suspension was processed by centrifugation followed by washing of the particle sediment with hot de-ionized water three times.

The supernatant was tested using the well-known reaction with ninhydrin to ensure that the glue was in fact removed from the ink. This reagent gives a violet product with most amino acids, and measurement of the absorption intensity at 540 or 570 nm is used to obtain the concentration. The imino acids proline and hydroxyproline yield a yellow product for which the intensity is measured at 440 nm. A few drops of a 0.2 g ninhydrin in 50 ml de-ionized water solution was added to the supernatant following the first centrifugation of the sample (and before the first precipitate washing). The mixtures were placed in a boiling water bath for 30 s. After the solutions cooled to room temperature, they were analyzed for absorption using a Cary 50 UV/VIS spectrometer. All three wavelengths were measured, along with the collagen samples for comparison, and all showed absorption well above a blank at all three wavelengths, while the control (buffer alone) remained below detection limits. The known collagen samples were fit to a linear curve with a high degree of correlation ($r^2 > 0.99$ for all three wavelengths).

The entire collagenase treatment was repeated a second time on the treated samples to ensure all gelatin was digested. A second ninhydrin test was performed and all readings were

Table 3
Size analyses results

Sample	SEM average size (nm)after sonication and filtration	±S.D. [a]	PCS *z*–average size (nm)	±S.D. [a]	PCS *z*–average size after collagenase treatment (nm)	±S.D. [a]	Apparent collagen adlayer thickness (nm)
3 Dot Japanese inkstick	172	31	215	6	155	7	30
Kobaien pine soot inkstick	215	42	212	4	151	17	30
Kobaien lampblack inkstick	163	27	182	2	140	8	21
Commercial inkstick	199	58	220	10	175	4	23
Chinese Shanghai inkstick	241	35	232	6	221	4	6

[a]Standard uncertainty calculated from replicate measurements.

below detection limits, ensuring that all surface glue had been removed from the ink.

3. Size studies

In this study, SEM was used to evaluate cluster and primary particle size, while PCS was used to provide a robust value for cluster size and to approximate the number of primary particles per cluster. The results are summarized in Table 3.

3.1. Scanning electron microscopy

Previous work with SEM was used as a point of departure for these size studies; past studies show a lampblack size distribution narrower and smaller in average size than pine soot, but with both in the range 100–150 nm [16]. Most primary particles were roughly spherical in shape. Imaging the ink dispersions revealed both large aggregates and the individual primary particles. Samples were imaged in each stage of preparation: without treatment (Fig. 3), post sonication, and post sonication plus filtering (Fig. 4). It is clear from SEM images that sonication made a large difference in the average cluster size confirming the sonication experiment with PCS to achieve uniform size (see Fig. 1). In order to compare the SEM data with PCS measurements, the cluster size was measured using a manual sizing application on the microscope software. The application allows a user to select two ends of a particle, then using the microscope magnification the length between the two points is calculated and stored in a worksheet. The longest distance across an irregular cluster was selected for each measurement. Two different samples for each ink were imaged and up to 50 measurements were averaged.

The computer-assisted sizing technique mentioned above was also used to determine the average agglomeration number (AAN), which is the average number of primary carbon particles in a cluster. At high magnification, the number of primary carbon particles was counted in each cluster. The AAN is an average of the number of primary carbon particles per cluster for at least 50 clusters per inkstick type. The lampblack ink yielded an AAN of 1.7 ± 0.3 while the pine soot inkstick gave a higher value of 2.6 ± 0.5. It should be noted that the dead space between particles and the possibility of particles beneath the viewable area (i.e., shadowed by other particles) are not accounted for in this treatment. In contrast the 3 Dot ink, most likely a student's inkstick of lampblack, yielded an AAN of 3.1 ± 1.1, showing both a higher degree of agglomeration and greater variation in cluster AAN for the lower quality ink.

3.2. Photo correlation spectroscopy

Averaged results from PCS measurements (see Table 3) yielded more robust numbers then SEM and with lower uncertainty. All averages showed less than 3% uncertainty

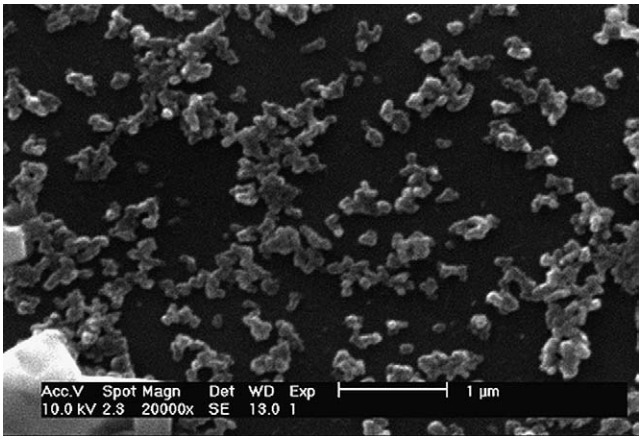

Fig. 3. SEM image of Kobaien pine soot ink without sample preparation.

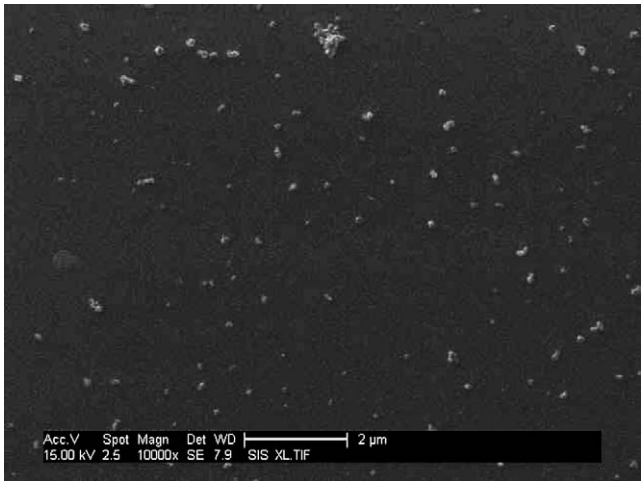

Fig. 4. SEM image of Kobaien lampblack ink after sonication and filtration. Note the sample has been reduced to clusters of about 1–3 primary particles each.

among repeat measurements, except the commercial inkstick with an uncertainty of 4.5%. The PCS method uses a size number particular to light scattering, namely the *z*–average mean, which includes the glue adlayer in ink samples. As stated before, sizing measurements are often relative to the method used. In PCS the sizes are comparable to SEM sizes if the system is monodisperse as indicated by the polydispersity value. Most inks were relatively monodisperse or had an average polydispersity less than 0.2. The only values that were higher than 0.2 were occasional measurements with the commercial inkstick and the Chinese Shanghai, exhibiting a significantly greater degree of uncertainty between measurements and a higher polydispersity on average (between 0.3 and 0.55). This is indicative of greater variability in size, and results probably from increased aggregation in solution or increased spread in the primary cluster size, or both. Sizes from SEM images calculated using imaging software were about 20% smaller but correlated well with the PCS values. The difference in size is attributed to the large uncertainty in image-based measurements and the addition of the glue layer, the latter being included in the PCS values but absent in the SEM sizes.

3.3. Collagenase treated samples

All five inksticks underwent the collagenase treatment as outlined in the previous section, the 3 Dot Japanese and Kobaien pine soot inksticks having duplicate samples. The dispersions were sized using PCS and all samples were found to have smaller sizes than their native (coated) state counterparts by about 20–28%, except the Chinese Shanghai inkstick (see Table 3). A large size and greater aggregation of this inkstick would correlate to a smaller specific surface area and hence a lower reduction due to glue removal. These results give evidence to the theory that each ink particle is coated in a layer of glue, composing up to one-fourth the overall size of the particle. SEM images of the collagenase treated inks showed little difference from their non-treated counterparts.

3.4. Soots and carbon blacks

Results of size analyses of the two soots and two industrial carbon black samples are given in Table 4. The smaller size for the lampblack soot agrees with previous research in ink sizing and with our sizing of inks in this study. The lampblack soot being much lower than the lampblack ink size may imply the same cluster size, but with a protein layer on the ink (40 nm difference, about 18%). But this is in contrast to the pinewood soot, which is not much different than the pine soot ink size measurements. The AAN is slightly larger for pine soot indicating the possibility that some of the larger PCS values are owed to large clusters, not large primary particles. This could account for the much lower size in the lampblack soot and the high PCS size for the 3 dot—the AAN for the 3 Dot indicates that it could still be lampblack but in a highly agglomerated state.

Company literature provided with the industrial carbon blacks indicate the size was determined by measuring the primary particles by SEM. The reported primary particle sizes are 101 nm and 20 nm, for Raven 410 and Raven 1250, respectively. Using these values, our PCS sizing results calculate an AAN of 2.4 for Raven 410 and 6.6 for Raven 1250.

Table 4
Soot and carbon black size results

Sample	PCS size (nm)	±S.D. [a]	Company particle size measured by SEM (nm)
Kobaien lampblack soot	140	17	N/A
Pinewood soot	210	19	N/A
Carbon black Raven 410	242	2	101
Carbon black Raven 1250	132	7	20

[a]Standard uncertainty calculated for replicate measurements.

Table 5
IEPs of Chinese ink related materials

Sample	IEP	Reference
Activated carbon, untreated	2.5	[28]
Activated carbon, KOH	3	[32]
Sub-bituminous coal	2–4.3	[33]
Gelatin	4.7	[30]
Fibrinogen	5.3	[29]
Bovine serum albumin on oil droplets	4.9	[27]
Human plasma albumin	4.5/4.3	[34]
Human plasma albumin on polystyrene	4.8	[34]

4. Laser Doppler microelectrophoresis

4.1. Isoelectric point determination

The charge residing on a suspended particle having e.g., hydroxyl surface sites will change with pH. In the absence of specific adsorption of ions, when the net surface charge at the particle shear plane is zero (i.e., positive and negative sites just cancel), the zeta potential will be zero and the particle will have no measurable mobility. This pH value, the isoelectric point (IEP), is a characteristic property for many types of colloids, some of which are listed for comparison in Table 5). In order to determine the IEP experimentally, a set of zeta potential values vs. pH is obtained and the *x*–intercept of the interpolated curve is taken as the IEP. Each point on each curve from this study represents an average of up to nine measurements taken with the Zetasizer, and three IEP curves were averaged for each ink dispersion (two examples are shown in Figs. 5 and 6. Each curve in this study resulted from a four-parameter sigmoidal fit of data with a high degree of correlation ($r^2 > 0.99$). The values in Table 6 reflect an average of these curves. The IEPs of the two soots tested in this study—lampblack and pine soot—were also evaluated, with little success. A wide range of IEPs from 1 to 4 was measured for these soots owed to the heterogeneous nature of

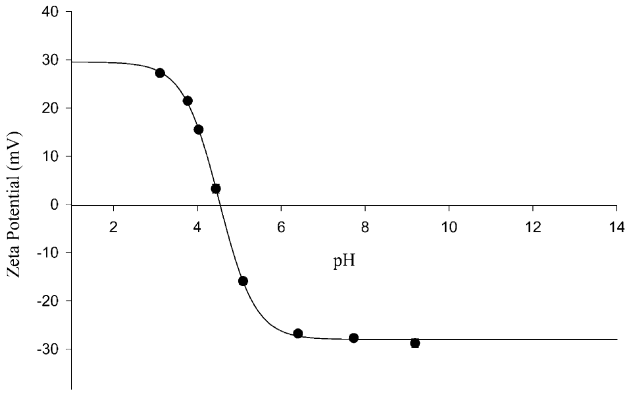

Fig. 5. 3 Kobaien pine soot inkstick ink IEP curve, H_2O dispersion, 1 mM NaCl ionic strength.

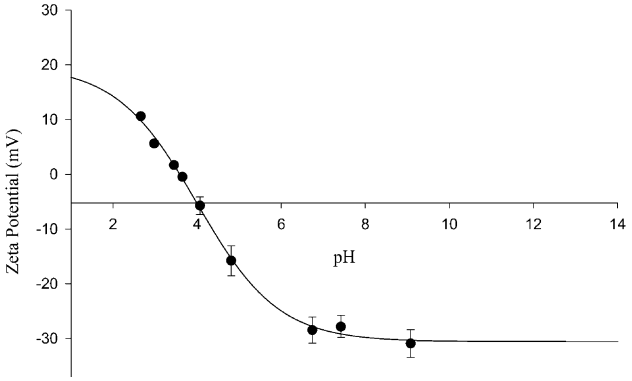

Fig. 6. Commercial inkstick ink IEP curve, H_2O dispersion, 1 mM NaCl ionic strength.

their surfaces. IEP values for the two soots were well below the IEP for the inksticks and within the IEP of most uncoated carbon materials (e.g., coal and pollution-type soots [29]).

The reason for investigating the IEP of ink particles was based on the expectation that it would be determined largely by a layer of protein glue adsorbed on the surface. According to the literature [30], the IEPs of gelatins and glues can vary according to the manufacturing method; acid-processed gelatins have in general a higher IEP than lime-processed gelatins. This suggested the possibility of "fingerprinting" inks, if the IEP varied in some way over different amples.

The IEP results for the traditionally produced inksticks agree well with the reported IEP values of gelatin at 4.5–4.7 [28,31,32], and exhibit a narrow spread. Measurements of the commercial inkstick were inconsistent, and as a result a reasonable average was unattainable. Based on the present results, it appears it may be difficult to fingerprint individual inksticks based on IEP alone. The fact that all samples, some manufactured in different countries and with different source materials and qualities, have similar IEPs indicates that the collagen-based glue coating is chiefly responsible for the surface chemistry of the ink particles and the dispersion properties of Chinese ink in general. This was reinforced by determining the IEPs of the same inks treated with collagenase (Table 6). All post-collagenase IEPs were lower than their native counterparts, but not by a consistent amount as seen in the sizing results. Furthermore, when these IEPs are compared to the soots and carbon IEPs found in the literature and the native IEPs determined in this study, they land between the raw and the coated carbon. This could suggest a partial, rather than complete, removal of the glue layer adsorbed directly on the carbon. But without knowledge of the IEPs of the raw soots and the fact that all IEPs of treated inks are varied, we can only conclude that at least some amount of glue is removed, up to and including complete removal.

Table 6
Native and collagenase treated IEP of inksticks and soots

Sample	Native IEP	±S.D. [a]	Collagenase treated IEP	±S.D. [a]
3 Dot Japanese	4.47	0.06	3.74	0.06
Kobaien pine soot	4.55	0.10	4.01	0.01
Kobaien lampblack	4.66	0.10	4.14	0.04
Commercial	4–4.46	N/A	3.91	0.06
Chinese Shanghai	4.72	0.08	4.15	0.04
Kobaien lampblack soot	1.6–3.6	N/A	N/A	N/A
Japanese pinewood soot	1.5–3.7	N/A	N/A	N/A

[a]Standard uncertainty calculated from replicate measurements.

An additional consideration is the impact of pH measurement errors. The accuracy and precision of reported IEP values depends to a large extent on the underlying pH measurement, since IEP is in fact a pH value. These determinations, therefore, are subject to variations in electrode response time, measuring conditions, and calibration. Under the best of circumstances, it is possible to obtain a precision of 0.01–0.02 pH units on a properly calibrated, good quality combination glass electrode as used in the present work. Improper calibration, uncontrolled temperature fluctuations, variations in hydrodynamics near the electrode surface, and slowly responding or improperly functioning electrodes can combine to produce rather significant pH errors, exceeding 0.1 pH unit. Thus, pH measurement error must be considered whenever interpretation of IEP values is an issue.

5. Discussion

Although subtle differences are evident, overall the results from zeta potential and size measurements do not point to a clear fingerprinting method in differentiating between Chinese inks by soot or country of origin. Comparison of three forms of ink samples—ink, collagenased ink, and soots—did reveal important properties about Chinese ink. The addition of glue to soot particles not only makes a suitable artists' material, but also provides a uniform surface chemistry on the soot particles. Both PCS and IEP results were similar when analyzing either rubbed-up ink or samples from inksticks, showing that these same methods should be valid if applied to artifact samples.

The soot particles found in Chinese ink are distinguishable from other types of carbon (i.e., chars, cokes, or graphite) through their morphology as visualized by SEM. Soots and flame carbons are also referred to as carbon black, and although their morphology is similar, a clear distinction

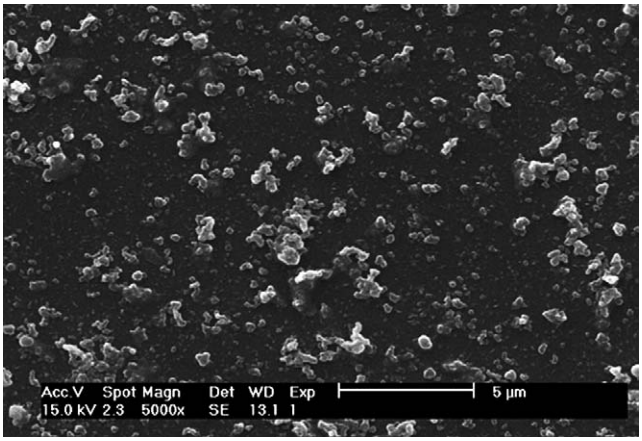

Fig. 7. SEM image of Chinese Shanghai pine soot ink.

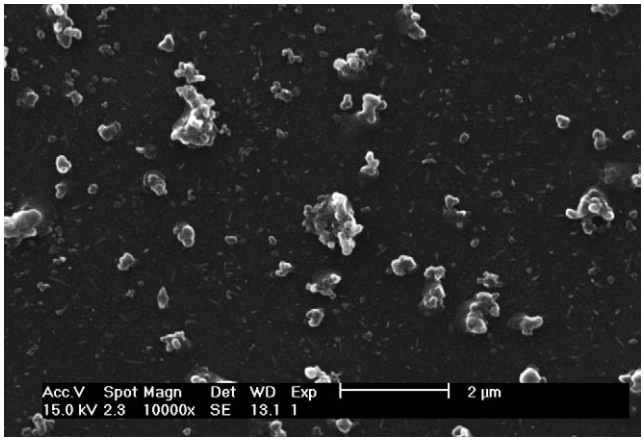

Fig. 8. SEM image of Chinese Shanghai pine soot ink.

should be made. Strictly speaking, carbon blacks are industrial particulates manufactured since about 1872 for a variety of purposes. Like soots, the carbon is formed in the gas phase and has spherical primary particles that can form clusters and aggregates. The difference is in composition: carbon black, made from a purer organic compound pyrolyzed in an inert atmosphere, is over 97% elemental carbon, while soots, made from complex materials such as oils and wood burned in air, may have an elemental carbon content as low as 60% with variable amount of organic carbon [33]. The compositional difference is probably represented by heteroatoms such as sulfur, phosphorus, and nitrogen, and hydrogenated compounds, from incomplete carbonization, with the possibility of inorganic ash in lower quality material.

Both SEM and PCS sizing produced results that agreed qualitatively with previous work: lampblack soots tend to be smaller and more uniform in size than the pine soot inks. The SEM images provided more information about aggregation of ink particles, whereas the PCS data yielded more robust numbers for comparison among samples, insight into the collagenated surface of the particles, and the fundamental cluster size. Comparing the SEM apparent sizes with the PCS measurements, we find that the PCS technique "sees" an average primary cluster size (which is a function of the dispersion state). The larger sizes in the Kobaien pine soot found by PCS are represented by correspondingly large clusters imaged by SEM, and not fully by larger single particles. However, the Chinese Shanghai inkstick produced an even larger PCS size, and both larger primary particles and larger aggregates were evident in the SEM images (Figs. 7 and 8). This combined with the high polydispersity for the Chinese inkstick accounts for the large uncertainty exhibited in the PCS and IEP measurements and may indicate the low quality of this particular inkstick.

Furthermore, the soot size measurements when compared to an inkstick of the same soot component do not correlate exactly—and herein lies an important point about attempts to fingerprint this material. When comparing the PCS soot sizes alone, it seems to agree with previous and our current size studies, that lampblack particles in fact have a smaller size and narrower distribution than their pine soot counterparts. But when this data is compared to the inkstick PCS size data, we notice a discrepancy: although the lampblack is again smaller in size and narrower in distribution than pine soot, the lampblack ink size is reasonably larger than the lampblack soot size (explained by the absence of a glue adlayer on these particles), while the pine soot ink is too similar to the uncoated pine soot particles to account for the presence of glue. The difference is most likely explained with the AAN of each type of soot and ink, indicating that PCS size alone cannot distinguish between different types of soot, but may point to quality. A good example of this is the large AAN for the 3 Dot inkstick when compared to the other inksticks. The 3 Dot inkstick is a student ink of lampblack, but the size is on order with pine soot because of the increase in agglomeration, not because of a larger primary particle size. In addition, higher variability in these measurements, and a correspondingly higher polydispersity, would lead to a lower quality ink because of size irregularity in the dispersion state. A lower-quality inkstick of higher structure would have less tinting strength (not as "black" or full color) than one characterized by smaller clusters (e.g., a highly dispersed lampblack), and this (in addition to availability) could be a significant reason for the switch from pine soot to lampblack over the centuries. This comparison demonstrates how imaging and PCS complement each other to reveal details concerning the structural hierarchy of carbon soot particles.

Their similarity in structure makes both types of carbon useful in dispersions, but their difference in composition may point to the advantages of soot over carbon black in Chinese ink. In addition, it has been found that carbon blacks contain more non-polar polynuclear aromatic hydrocarbons (PAHs) as opposed to soots, which contain a high amount of polar organic compounds. [33]. This latter point was exploited with a few additional experiments. When initially added and agitated in water, the two Columbia Chemical carbon blacks in this study did not disperse. They required a surfactant, like sodium dodecylsulfate, to achieve a stable colloidal suspension; this behavior can be attributed to their hydrophobic surfaces. By comparison, both the lampblack and pine soots

remained in suspension for 3 weeks, without agitation or chemical additives, and in this context can be considered self-dispersing. To further define the differences in behavior between soot and carbon black, both were mixed with small amounts of cow hide glue to create a quick ink dispersion, and were then left undisturbed at room temperature. All mixtures retained their dispersion qualities, that is the glue produced the necessary stabilization for a sol. But in less than a week the carbon black-glue inks indicated the appearance of mold, while the soot-glue mixtures were free of mold for over a month. These two experiments point to further differences in surface chemistry between soots and carbon blacks: the soot surface chemistry enables it to remain in suspension and resist microbiological attack, two important advantages for an artists' material. The appearance of mold may also indicate that less glue adhered to the particle surfaces on the carbon black than on the soots. This would support the idea that soots have richer surface chemistry than the carbon black and more readily support a glue adlayer.

In order to determine if other compositional factors may affect ink dispersion, each inkstick was examined by inductively coupled plasma–mass spectrometry (ICP–MS) for analysis of almost 30 elements. These results are used to interpret surface chemistry with caution, because ICP–MS is a bulk chemical technique, and is not surface-sensitive. The ICP–MS results did show a more diverse composition for the commercial inkstick compared to the others, possibly indicating a low quality soot source such as petroleum or oil mixtures, or even contamination from the manufacturing process. In particular the high phosphorus and sulfur levels found in the commercial inkstick could create a more acidic sol and might account for the inkstick's relatively low IEP (assuming these elements exist on the particle surface and can act through the collagen layer). Likewise, the addition of more surface units may reduce the ability of the glue layer to adhere to the surface, thereby modifying the typical uniform glue layer and ink quality. The Kobaien inksticks were similar only in the lack of trace elements present, the 3 Dot Japanese and Chinese Shanghai inksticks having a few trace amounts of various transition metals. The carbon blacks were also tested, and confirmed company literature that little else was above detection limits other than carbon. In comparison to previous elemental studies, the inksticks used in this study showed little difference to modern ones [18]. The only notable differences were elevated zinc and strontium levels for the commercial inkstick, again possibly explaining its difference in IEP and size from the other traditionally produced inksticks.

The removal of collagen glue from Chinese ink proved to alter the surface chemistry as seen in the PCS and IEP measurements. The reduced z–average size points to a surface alteration, although the smaller particle size after treatment is still too large to represent primary particles or smaller clusters. The reduction is roughly the same among all samples, indicating the size consistency of the glue bound layer. Therefore, the primary clusters are fused primary particles, and not separated by either aggressive sonication or by glue removal. It is also worth noting that these collagenased inks remained dispersed for long periods of time, much like their ink and soot counterparts, retaining a certain amount of useful surface chemistry to enable a dispersion to exist. The similar IEPs for the collagenased inks as well as the radical inconsistency of raw soot IEPs, illustrates how the animal glue is the dominant factor in creating a consistent surface chemistry on a substrate that is otherwise considered heterogeneous [2]. The wider range of IEPs for the collagenase treated inks also demonstrates the variation in soot chemistry in the absence of the homogenizing glue coating.

6. Conclusion

The use of modern instrumentation in the characterization of Chinese ink has provided much information on the chemical and physical properties of this unique artist's material. When the inkstick is rubbed-up in water, the product is a colloidal dispersion of nanosize carbon particles with an adlayer of collagen-based animal glue. Therefore, nanoscale sizing and electrokinetic analysis become the most useful means to characterize these materials.

Chinese ink particles viewed by SEM gave reliable dimensional data on primary particles and less easily definable information regarding clusters and larger-scale aggregates. A statistically more robust method, PCS, was employed to determine primary cluster size in suspension. By combining SEM and PCS analyses, we were able to calculate an AAN value roughly representative of the number of primary particles contained in an average size cluster. The results obtained here agree with previous reports that showed lampblack inks tend to be smaller in size and narrower in size distribution compared to pine soot inks. We suggest that because the primary cluster size is the fundamental unit of a Chinese ink dispersion, dispersion-based PCS measurements may be more suitable as an indicator of the ink quality. However, it was also revealed that conclusions based on a single sizing technique can be misleading—e.g., a larger PCS size may imply a larger AAN value and not necessarily a larger primary particle size. Finally, it is proposed that a second indicator of ink quality may manifest in the width of the cluster size distribution and the measurement precision (standard uncertainty) obtained by PCS, both of which appear to increase with decreasing ink quality.

The surface chemistry of a colloidal dispersion determines its ability to stabilize in an aqueous solution and is a function of the surface phase material composition. Doppler-based microelectrophoresis was used to measure zeta potential and to establish the IEP of the inksticks and soots. All inksticks yielded IEPs close to that of lime-processed gelatin, confirming that the collagen-based glue creates a uniform surface on an otherwise heterogeneous soot particle. Upon removal of the glue layer, the z–average cluster size was always reduced by about the same absolute quantity for all inksticks (50–60 nm, with the exception of the low quality

Shanghai inkstick) and the IEPs of collagenased inks were always lower than the untreated inks, but by varying amounts. The principal purpose of the glue is, therefore, twofold: as a dispersing agent to provide a stable liquid suspension of ink particles and as a binder to fix the ink during its application. The glue, when tightly bound to a soot particle, may also resist fungal growth, as suggested by experiments.

The methods developed during these investigations will be employed to investigate the effects of age on the size and chemistry of the glue layer, by sampling older inksticks and artifacts.

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References

[1] R.A. Dobbins, R.A. Fletcher, H.C. Chang, The evolution of soot precursor particles in a diffusion flame, Combustion and Flame 115 (1998) 285–298.
[2] P.A. Thrower, Chemistry and Physics of Carbon, Marcel Dekker Inc. New York, 1994.
[3] J. Needham, T.H. Tsien, Science and Civilisation in China, Vol. 5, Chemistry and Chemical Technology. Part 1, Paper and Printing, Cambridge University Press, Cambridge, 1985.
[4] R.H. v. Gulik, Chinese Pictorial Art as Viewed by the Connoisseur Roma Istituto Italiano per il Medico ed Estremo Oriente, 1958.
[5] A. Lucas, J.R. Harris, Ancient Egyptian Materials and Industries, Edward Arnold Ltd. London, 1962.
[6] M. Levey, Some black inks in early medieval Jewish literature, Chymia 9 (1964) 27–31.
[7] Y.-h. Sung, T'ien-kung K'ai-wu, Chinese Technology in the Seventeenth Century, The Pennsylvania State University Press, University Park and, London, 1966.
[8] T. Morita, 'Nikawa'—Traditional production of animal glue in Japan, International Institute for Conservation of Historic and Artistic Works, Paris, France, 2–8 September 1984, pp. 121–122.
[9] J. Winter, Natural adhesives in East Asian paintings, International Institute for Conservation of Historic and Artistic Works, Paris, France, 2–8 September 1984, pp. 117–120.
[10] H. Franke, Kultergeschichtliches uber die chinesische Tusche (Cultural History of Chinese Ink), Bayerische Akademie der Wissenschaften, Philosophisch-historisch Klasse, Abhandlungen 54 (1962) 1–157.
[11] G. Battersby, Dispersions of Pigments into Printing Inks, Marcel Dekker Inc. New York, 1994.
[12] T. Terada, R. Yamamoto, Experimental studies on colloid nature of Chinese black ink, Part I, Sci. Pap. Inst. Phys. Chem. Res. 23 (1934) 173–184.
[13] T. Terada, R. Yamamoto, Cataphoresis of Chinese ink on water containing deuterium oxide, Proceedings of the Imperial Academy 11 (1935) 214–215.
[14] T. Terada, R. Yamamoto, Experimental Studies on Colloid Nature of Chinese Black Ink, Part II, Sci. Pap. Inst. Phys. Chem. Res. 27 (1935) 75–92.
[15] S. Mitsukuri, Some colloidal chemistry studies on colloidal dispersions Nihon Gakujutsu Kyokai Hokoku 6 (1930) 147–150.
[16] J. Winter, Preliminary investigations on Chinese ink in far eastern paintings, Advances in Chemistry Series 138 (1975) 207–225.
[17] W. Zhang, H. Liu, S. Guo, A study of the manufacture and conservation of ancient ink-stick, Wenwu baohu yu kaogu kexue 7 (1995) 21–27.
[18] H. Cheng, W. He, H. Yao, J. Tang, F. Yang, C. Ma, G. Shan, Y. Zhong, W. Wang, A study on the elemental compositions of ancient and modern Chinese inks, Wenwu baohu yu kaogu kexue 9 (1997) 16–19.
[19] H. Oguchi, Research on ink, Kobunkazai no kagaku 20–251 (1977) 38–66.
[20] J. Winter, The characterization of pigments based on carbon, Studies in Conservation, 28, 1983, pp. 49–66.
[21] K. Miyasaka, Bokugei no Shiori, Unsodo, Tokyo, 1979.
[22] B.J. Berne, R. Pecora, Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics, Dover Publications, Minneola, NY, 2000.
[23] E.F. Burton, Phil. Mag. 6 (1906) 425.
[24] A. Tiselius, A new apparatus for electrophoretic analysis of colloidal mixtures, Trans Faraday Soc. 33 (1937) 524–531.
[25] R.J. Hunter, Zeta Potential in Colloid Science, Academic Press, London, 1981.
[26] V.A. Hackley, R.S. Premachandran, S.G. Malghan, S.B. Schiller, A standard reference material for the measurement of article mobility by electrophoretic light scattering, Colloids Surf. A 98 (1995) 209.
[27] The importance of pigment diversion in printing inks, Pigment and Resin Technology, 1983, pp. 15–16.
[28] D.J. Shaw, Electrophoresis, Academic Press, London and New York, 1969.
[29] J.A. Menendez, J. Philips, B. Xia, L.R. Radovic, On the modification and characterization of chemical surface properties of activated carbon: in the search of carbons with stable basic properties, Langmuir 12 (1996) 4404–4410.
[30] A.G. Ward, A. Courts, The Science and Technology of Gelatin, Academic Press, London, 1977.
[31] H.W. Douglas, D.J. Shaw, Electrophoretic Studies on Model Particles Trans. Faraday Soc., 1956, pp. 512–522.
[32] E.J.M. a, S. Gay, Collagen: An Overview, Meth. Enzymol. 82 (1982) 1–32.
[33] A.Y.P.A.V. Watson, Carbon black and soot: two different substances, AIHAJ 62 (2001) 218–228.