Role of Cellulose Oxidation in the Yellowing of Ancient Paper

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The yellowing of paper on aging causes major aesthetic damages of cultural heritage. It is due to cellulose oxidation, a complex process with many possible products still to be clarified. By comparing ultraviolet-visible reflectance spectra of ancient and artificially aged modern papers with *ab initio* time-dependent density functional theory calculations, we identify and estimate the abundance of oxidized functional groups acting as chromophores and responsible of paper yellowing. This knowledge can be used to set up strategies and selective chemical treatments preventing paper yellowing.

Paper has been the most widely used writing support since the first centuries A.D. in China, Mesoamerica and the Far East, and since the Middle Ages in the Western World, with the result that for centuries a growing number of books, graphic works and ancient documents have been accumulating in archives, libraries and museums all over the world [1]. The preservation of these cultural properties must be based on an advanced knowledge of the microscopical characteristics of paper materials and their degradation processes.

Paper is a complex multicomponent material. Depending on the production period and technology employed, the paper composition varies. The ancient cotton or linen based papers contain mainly cellulose ($>90\%$ in weight) with the addition of animal glue as sizing compound, while modern soft or hardwood ones may also include lignin ($<30\%$ in weight) and additives such as alum, resin or chalk [2].

Cellulose is a biopolymer, representing 40% of the annual production of biomass on Earth [3], made of repeating units of β-(1,4)-D-glucopyranose [Fig. 1(a)]. Cellulose polymers form interchain secondary valence hydrogen bonds and organize themselves in a multilevel supramolecular hierarchical structure up to form fibers whose diameter ranges from ~ 1 to ~ 10 μm [4]. Microfibrils, the basic elements of the supermolecular structure, are composed of an assembly of highly ordered (crystalline) domains, and of disordered (amorphouslike) regions.

On macroscopic scale, paper degradation occurs by the weakening of mechanical properties of the sheets and by yellowing, as main consequences of hydrolysis and oxidation, the latter developing chromophores, in cellulose polymers [5]. While the mechanism of acidic hydrolysis is rather known and well-settled in the literature [6,7], cellulose oxidation running through the radical mechanism initiated by active oxygen species is a complex process with many possible reactions still to be clarified [7–9].

Pure cellulose shows no absorption bands in the ultraviolet-visible (UV-Vis) wavelength range up to around 6 eV (200 nm) [7]. Degraded cellulose, instead, shows an absorption spectrum with a broad peak around 4.8 eV (260 nm), and a long absorption tail towards lower energies. This feature has been attributed to carbonyl groups since Bos [10]. Only recently, however, detailed spectroscopic and chemical studies have been carried out, in an attempt to clarify the configuration within the glucopyranose ring of the carbonyls responsible for the observed absorption [8,11,12].

By comparing the infrared and UV-Vis spectra of degraded cellulose, conjugated ketonic groups were indicated to be the main chromophores responsible for paper yellowing [8,12]. However, because of the important role of the local chemical environment around the oxidized groups, this procedure prevents a full band assignment and does not allow us to distinguish, for example, between ketones and
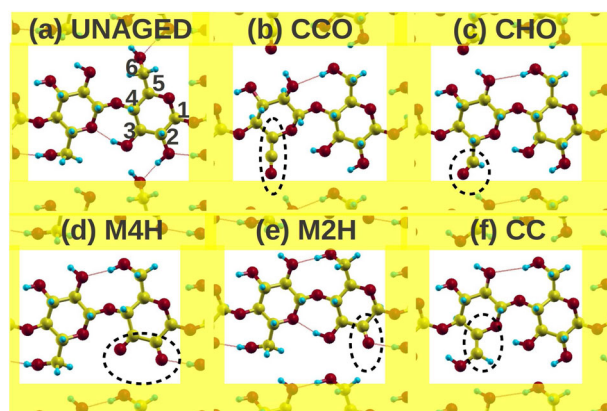

FIG. 1 (color online).   Chemical structure of: (a) unaged cellulose (with the carbon atom numbering); (b)–(f) of the oxidized groups studied in this work. (Light gray (yellow), dark gray (red), and small (blue) spheres represent, respectively, carbon, oxygen, and hydrogen atoms).

other enolic groups in the oxidized cellulose. To solve this problem, in this Letter, we have measured the UV-V is spectra of degraded cellulose in modern and ancient samples, and interpreted them with the aid of time-dependent Density functional theory (TDDFT) calculations [13]. To our knowledge, no theoretical investigations of the optical properties of cellulose have been performed up to now.

For this study, we used ancient samples produced during the 15th century in European countries, consisting of 3 specimens, bearing no print, sized with gelatine, named A1 (made in Perpignan, France, in 1413), A2 and A3 (both made in Milan, Italy, in 1430), presenting increasing levels of yellowing [14,15].

One of the main problems in studying the degradation of ancient artifacts is that the environmental conditions to which the samples were subjected throughout their history are unknown. On the other hand, an artificial high-temperature degradation process allows a constant monitoring of environmental conditions, even though it cannot perfectly mimic a slow natural degradation process [7]. To understand the role of the different aging factors we used, therefore, model paper samples artificially aged.

Model samples, obtained from Netherlands Organization for Applied Scientific Research (TNO), are made of unbleached cotton linters, containing very low inorganic ingredients (ash content $<0.005\%$ in weight) and no additives or lignin, with high mean degree of polymerization. Following [8,16], we name these samples P2. P2 samples were artificially aged up to 48 days in three different reactors with different environmental conditions as reported in Table I.

Aging conditions were designed as a compromise in order to get measurable changes in the UV-Vis spectra of model paper samples within a reasonable period of time. At the chosen temperature of 90° a moderate oxidation of the cellulose functional groups towards the carbonylic groups of various degrees of freedom and chemical environment is expected [12,16].

Sample diffuse reflectance $R(\lambda)$ spectra were measured in a wavelength range $240 < \lambda < 800$ nm (from 1.5 eV to 5.17 eV) at room temperature and at 50% of relative humidity (RH) conditions by using a JASCO V-570 spectrophotometer equipped with a $BaSO_4$ coated integrating sphere and PbS detector. Spectra were normalized to a Spectralon diffuse reflectance reference standard (factory

calibrated). The spectra resolution was set to 2 nm. The Kubelka-Munk (KM) model was used to convert the reflectance $R(\lambda)$ spectra into pseudoabsorbance spectra $A_{KM}(\lambda) = \frac{(1-R(\lambda))^2}{2R(\lambda)}$ for comparison with simulations [17].

In Fig. 2(a) we report A_{KM} for P2 samples artificially aged for 48 days in D, C and V conditions (Table I). Unaged samples do not present any absorption below 5.1 eV; therefore, their spectra are not reported in the figure. Spectra of the samples artificially aged for shorter time show similar shapes but, overall, their absorbance is less intense. All A_{KM} spectra consist of a broad band around 4.8 eV (260 nm) already attributed to carbonyl groups within the cellulose rings [10]. For samples aged in C and V conditions it is possible to distinguish an additional peak at 4.2 eV (295 nm) and a smooth and long tail reaching the visible energies below 2 eV (620 nm).

For all ancient samples, the absorbance has a maximum value at the high energy side of the measured spectra, shows a plateau between 4.6 and 5 eV, and smoothly decreases with a tail extending up the beginning of the visible energy region between 2.5 and 3 eV [Fig. 2(b)]. Overall, the complexity of the absorbance spectra suggests the presence of several chromophores of different nature.

In order to obtain a quantitative interpretation of A_{KM} using a TDDFT-based method [13], we have considered several possible oxidized forms of cellulose polymers which have been supposed to give absorption effects in the visible range [8,12]. These are shown in Figs. 1(b)–1(f) and are named as follows: CCO—a complete oxidation of C(6) with carbonylic group and a double bond C(5) = C(6); CHO—the oxidation of C(6) with the formation of an aldehydic group; M4H—the conjugated diketones on C(2) and C(3); M2H—the oxidation to a single keton on C(2); CC—the formation of a double bond C(5) = C(6).

As a structural model for the simulation of optical properties we have chosen a three-dimensional (3D) infinite crystal of cellulose polymers as an approximation of cellulose crystalline domains. Cell parameters of the cellulose crystal were obtained by x-ray diffraction data [3] and refer to the monoclinic crystallographic phase called cellulose-I_β, which is the most common polymorph for higher-plant cellulose [3,4]. The unitary cell contains 42 atoms. The atom positions inside the cell were relaxed by DFT [18] calculations performed by a plane-wave pseudopotential code [19], using a BLYP functional for the exchange-correlation energy, an energy cutoff of 40 Ry

TABLE I. Environmental conditions used in the aging tests of modern samples (P2). RH indicates the relative humidity.

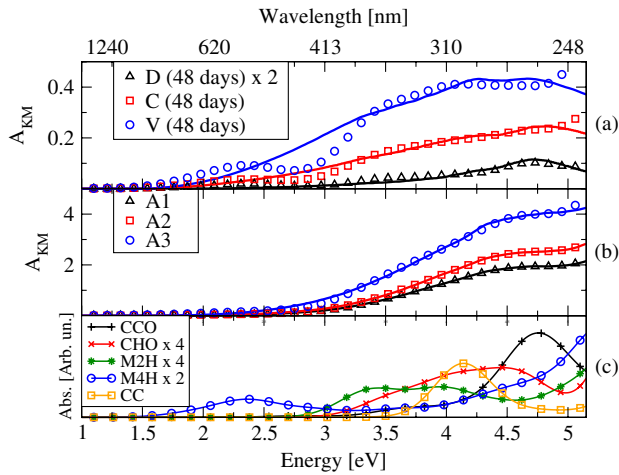| Aging process label	Reactor Type	Aging conditions	Expected impact factors
D	Open (drier)	Dry air, $T = 90\,°C$	Air
C	Open (climatic chamber)	Air, $RH = 59\%$, $T = 90\,°C$	Air and water vapor
V	Closed (vial)	Air, $RH = 59\%$, $T = 90\,°C$	Air, water vapor and gaseous by-products

FIG. 2 (color online).   (a) P2 samples: experimental pseudoab-sorbance A_{KM} (solid line) and corresponding theoretical absorption spectra (symbols). (b) Ancient samples: experimental pseudoabsorbance A_{KM} (solid line) and corresponding theoretical absorption spectra (symbols). (c) TDDFT-based theoretical absorption spectra for each single oxidized form.

for the wave functions, and 14 k points in the irreducible Brillouin zone. Optical properties were calculated by the Casida algorithm implemented in the [20] plane-wave code, by using 15 occupied and 15 unoccupied bands, and 4000 plane-waves for the kernel.

The calculated optical absorption spectra do not present absorption below 5.1 eV for unaged cellulose, in agreement with the experimental data. The oxidized groups, instead, are characterized by the appearance of maxima between 2 and 5 eV as shown in Fig. 2(c). The hole-electron charge distribution related to these peaks is mainly localized on the double bonds induced by the oxidation, and reveals a $\pi - \pi^*$ character of these transitions. Because of this strong localization, for a given oxidized form, the optical absorption spectrum below 5 eV can be considered as produced by several isolated not-interacting chromophores. Therefore, a change of the concentration of chromophores in the crystal does not involve a change of the shape of the spectrum, but only modifies its intensity. Indeed, a direct proportionality relation between the intensity of the absorption spectrum and the concentration of defects was checked by computational tests. Our results are in agreement with the experimental observation of the invariance of the spectral shape with aging time [8,12].

Our theoretical simulations showed that this proportionality does not hold above 5.1 eV since, above this energy threshold, also transitions from optical active oxidized groups to cellulose (and vice-versa) electronic states do contribute to the optical absorption spectra.

The lack of interactions between the chromophore groups inferred from the simulations allows us to consider the optical absorption spectrum of aged cellulose as a linear combination of the spectra calculated for every

single oxidized group in the cellulose backbone [Fig. 2(c)]. In Figs. 2(a) and 2(b), the symbols represent the linear combination that better reproduce the experimental spectrum obtained by a minimal-square based algorithm carried out in the energy range 1.5–5.1 eV. The best fit was achieved using Gaussian smearing of theoretical optical signals of 0.22 and 0.30 eV for, respectively, P2 and ancient samples. This smearing takes into account the finite number of k points used to sample the Brillouine zone, the disorder, and the finite temperature effect. A blueshift of 0.3 eV has been used in all theoretical spectra. This shift is due to the tendency of the local density approximations used in TDDFT to underestimate the optical gap in 3D systems [21]. In cellulose, the optical gap underestimation is small, as compared to that of other crystals [22], probably because of the strong localization of the excitonic charge distribution, typical of a molecular system, rather than of a crystal.

A good agreement between calculated and experimental spectra is obtained for P2 samples [Fig. 2(a)], and the congruence is excellent [Fig. 2(b)] for ancient samples. This could be explained by the consumption of the amorphous region caused by degradation, leaving, mainly, the crystalline regions of cellulose fibers [3,4,15], which are better represented in our model.

In particular, our calculations are able to identify the most significant structure observed in the experimental spectra around 4.8 eV, as principally due to CCO group. The band at 4.2 eV is mainly due to the CHO group, while the smaller contribution around 3.8 eV is due to both M2H and M4H oxidized groups. The long tail in the absorption spectra, reaching the visible energies below 2 eV, is mainly due to the M4H oxidized groups. M4H was previously expected to be the most significant oxidation causing paper yellowing [8,11,12] and to be the only one active in the UV-Vis wavelength range. Instead, we show that at least other two different oxidized groups in cellulose, namely, M2H and CHO, can be optically active, since, despite their absorption peaks are located in the UV region, their absorption tails affect the lower wavelength part of the visible region. The aldehydic CHO group is expected to be the transient product of the subsequent oxidation of the C(6) to carboxylic group (COOH) in the moderate cellulose oxidation [12]. Interestingly, simulations performed with COOH showed, instead, no absorption bands in the UV-Vis range up to 5.1 eV and therefore no contribution to paper yellowing.

By normalizing the linear combination coefficients, the relative concentrations of chromophores producing yellowing on the samples after aging can be estimated (Fig. 3). Very different results appear when comparing P2 samples aged in various environmental conditions. The CHO groups emerge as the most abundant species in the sample aged under pure oxidative conditions (D). The results of simulations also show possible contributions of CCO, M2H and
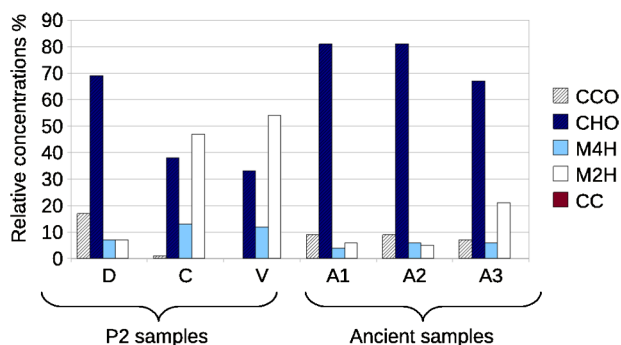
FIG. 3 (color online).   The relative concentration of the 5 oxidized groups acting as chromophores as calculated from simulations for modern P2 samples and ancient samples. The CC oxidized group is always absent in all samples.

M4H at pure oxidative atmosphere. Moisture present in *C* and *V* environments appears to favor the oxidation towards of M2H and also to a lesser extent M4H chromophores, inhibiting the CHO and causing almost complete disappearance of CCO groups. Apparently, water molecules provide additional oxygen radicals which facilitate the formation of ketones on glucopyranose rings [23].

In ancient samples, CHO has been found to be the most abundant oxidized group. Coming from A1 to A3 sample, the increasing yellowing can be accounted for by the increasing contribution of ketones M2H. It is worth pointing out that the CC oxidized group is always absent in all samples, regardless of their origin.

It can be noted that the relative concentrations of the oxidized groups of all ancient samples studied are close to those of the P2 sample aged in dry atmosphere (*D* conditions, Fig. 3). This is particulary true for the relative concentrations of conjugated diketones M4H, which are the main responsible of paper optical degradation in the visible range, and of M2H.

M4H and M2H relative concentrations are the highest in *C* and *V* sample. These observations suggest that even in a natural aging process water and degradation by-products trapped in paper when conserved in a closed environment can play an important role.

Additionally, M2H and M4H relative concentrations can be used as an indicator of the conservation history of a manuscript.

In conclusion, by combining UV-Vis spectroscopy with TDDFT-based calculations, it has been possible to identify and quantify the relative concentrations of chromophores responsible for ancient paper yellowing. In all samples studied the formation of carbonyls on aldehydic groups (CHO) and conjugated diketons (M4H) appears to be, respectively, responsible for paper optical degradation in the UV and visible range.

Such results are relevant, since we introduce an experimental-theoretical scheme that, contrary to ordinary investigation techniques, allow us to identify the chromo-phores responsible for cellulose optical degradation in a completely nondestructive way. Besides boosting the knowledge of the oxidative processes of cellulose itself, this scheme could be used as a powerful diagnostic method in the research of bleaching treatments of fragile and ancient piece of art on paper.

In addition, the information provided in this work about the local environment of the oxidized groups mainly involved in paper yellowing, and the dependence of their relative concentration from aging environment conditions, could be used for the generation of a new class of reducing agents to be employed in paper conservation and restoration techniques.

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