Graphene Nanoreactors: Photoreduction of Prussian Blue in Aqueous Solution

Silvia Nappini,* Alessia Matruglio,† Denys Naumenko,‡ Simone Dal Zilio,† Marco Lazzarino,† Frank M. F. De Groot,§ Coskun Kocabas,|| Osman Balci,¶ and Elena Magnano,†§

† IOM-CNR, Laboratorio TASC, S.S. 14 km 163.5, 34149 Basovizza, Trieste, Italy
‡ University of Trieste, Graduate School of Nanotechnology, Piazzale Europa 1, 34127 Trieste, Italy
§ Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, Utrecht, Netherlands
|| Department of Physics, Bilkent University, 06800 Ankara, Turkey
¶ Department of Physics, University of Johannesburg, P.O. Box 524, Auckland Park, 2006 Johannesburg, South Africa

Supporting Information

ABSTRACT: Prussian dyes are characterized by interesting photomagnetic properties due to the photoinduced electron transfer involved in the Fe oxidation and spin state changes. Ferromagnetic Prussian blue (PB) in contact with titanium dioxide (TiO2) can be reduced to paramagnetic Prussian white (PW) upon UV band gap excitation of TiO2. This process is promoted by the presence of a hole scavenger, such as water, fundamental to ensure the overall charge balance and the continuity of the process. In order to clarify the photoinduced reduction mechanism and the role of water, an innovative system of graphene nanobubbles (GNBs) filled with a PB aqueous solution was developed, enabling the application of electron spectroscopies to the liquid phase, up to now limited by the vacuum required to overcome the short electron inelastic mean free path in dense medium. In this work GNBs formed on the photocatalytic substrate are able to act as “nanoreactors”, and they can control and take part in the reaction. The evolution of Fe L2,3 edge X-ray absorption spectra measured in total electron yield through the graphene membrane revealed the electron reduction from PB (FeIII−FeII) to PW (FeII−CN−FeII) upon UV irradiation, shedding light on the photoinduced electron transfer mechanism in liquid phase. The results, confirmed also by Raman spectroscopy, unequivocally demonstrate that the reaction occurs preferentially in aqueous solution, where water acts as hole scavenger.

INTRODUCTION

Prussian blue (PB) and its analogues (ferrocyanides) are characterized by interesting photomagnetic, electrocatalytic, and optical properties that can be mainly attributed to intervalence charge transfer between low-spin FeII (LS-FeII−C) and high-spin FeIII (HS-FeIII−N) centers. Discoloration of the soluble ferromagnetic PB ionic species [FeIII(FeII(CN)6)]3− under intense illumination is due to the reduction of FeIII−N to FeII−N centers which leads to the formation of the paramagnetic colorless organometallic ion, well-known as Prussian white (PW) with formula [FeII(FeII(CN)6)]2+. Understanding the reduction mechanism of PB is important because it is the basic working principle of different biosensor and ion detection systems based on PB film electrodes.6,8,9,13−15 The photoinduced electron transfer is also responsible for the changes in the spin state of the metal centers of ferrocyanide compounds, leading to interesting photomagnetic properties which are widely used for several applications in the field of photomagnetism.2,16 For example, in Co−Fe Prussian blue, the electron excitation results in trapping the metastable high-spin state,16 showing that the efficiency of...
the photoinduced magnetization depends on a compromise between the number of excitable diamagnetic pairs and the amount of \([\text{Fe(CN)}_6]^-\) vacancies.27

Taguchi et al.18 have studied the photomagnetic effect in a composite system of semiconductive CdS and PB nanoparticles, evidencing the reduction of ferromagnetic PB to paramagnetic PW upon selective band gap excitation of CdS. Similarly, Yamamoto et al.1 have studied the photoinduced reduction of PB on titanium dioxide (TiO$_2$) nanosheets upon UV band gap excitation of TiO$_2$ by FT-IR measurements, exploiting the TiO$_2$ capability to reduce heavy metals and degrade organic compounds.20,21 It was observed that the electron transfer is promoted by the presence of water which acts as a scavenger of holes in the TiO$_2$ valence band, enabling the reduction of Fe$^{III}$ to Fe$^{II}$.

In order to clarify the role of water and the mechanism of the photoinduced reduction of PB in an aqueous solution in contact with a TiO$_2$ catalyst, we investigated by soft X-ray core-level spectroscopies the electronic evolution of Fe core levels.

X-ray photoelectron spectroscopy (XPS) and X-ray absorption (XAS) are suitable techniques to study processes based on the transfer of electrons from a solid substrate to a solution or vice versa. The emitted photons and electrons with characteristic energies resulting from the direct excitation or relaxation of the core holes can be detected and analyzed to obtain information regarding the chemical environment, oxidation state, ligand field strength, and charge transfer effects of the investigated system. Unfortunately, soft X-ray propagation and photoelectron detection require the ultra-high-vacuum (UHV) conditions, which hinder the application of soft X-ray techniques to the liquid−solid interfaces.

In the past decade substantial efforts have been devoted to the application of soft X-ray core-level spectroscopies to experiments under working conditions, such as ambient pressure photoelectron spectroscopy (AP-XPS)22–26 or the use of microfabricated liquid cells.27–34

Recently, we have presented a novel, simple, and robust method to apply conventional electron spectroscopies to investigate the evolution of electrochemical or chemical reactions directly in their liquid environment.35 Graphene nanobubbles (GNBs) filled with the desired solution between a titanium dioxide (TiO$_2$) (100) rutile single crystal and a monolayer of graphene (Gr) were used to follow the electronic evolution during the thermal-induced reduction of an aqueous solution of FeCl$_3$ encased inside the GNBs.

The small thickness (only one atomic layer) and the high elasticity, mechanical strength, and impermeability of Gr provide the transparency to both photons and electrons required for the electronic characterization of the system placed under the Gr membrane.27,36,37

Here we did a step forward by using the GNB system for two purposes: it is a “sample holder” for electron spectroscopy from the liquid phase and a “reactor” that can control the process and take part in the reaction exploiting the photocatalytic properties of TiO$_2$.20,38–40

A complete in situ spectroscopic study of the photoreduction mechanism of PB (soluble form, KFe[Fe$^{III}$\text{[Fe$^{II}$\text{(CN)}$_6$]]}) in aqueous solution encased in GNBs formed on a TiO$_2$ catalyst is presented. The photoreduction was induced by using a laser at 395 nm of wavelength, corresponding to the band gap of rutile (3.03 eV),41 and the process was monitored after different UV exposure time. The reaction was followed in situ by core-level electron spectroscopy on the BACH beamline at Elettra synchrotron facility: the presence of the aqueous solution inside the GNBs was proved by measuring O 1s spectra by XPS, while the photoinduced electron transfer was examined by XAS at the Fe L$_{3.3}$ edge measured in total electron yield (TEY) through the Gr membrane. The photoinduced reduction of Fe centers was clearly evidenced by XAS changes upon UV irradiation, and the partial evolution of PB (Fe$^{III}$−CN−Fe$^{III}$) to PW (Fe$^{II}$−CN−Fe$^{II}$) was observed and confirmed by ligand field multiplet calculation. The results have definitely demonstrated that the reduction process induced by the electron transfer from the valence band to the conduction band of TiO$_2$, and finally to PB molecules, requires the presence of water as hole scavenger. Raman spectroscopy in liquid phase was also performed to confirm the X-ray electron spectroscopy results.

**RESULTS AND DISCUSSION**

An array of GNBs filled with an aqueous solution of PB (10 mM) was obtained by transferring a CVD grown Gr layer onto a TiO$_2$ single crystal using a thermoplastic polymer as sacrificial layer (see Methods). The formation of GNBs was described in detail in our previous work35 and proved by several techniques, such as atomic force microscopy (AFM), Raman spectroscopy, XPS, and XAS. As previously described, the wettability of the bare TiO$_2$ substrate, and thus the number of GNBs, was modulated by oxygen plasma and thermal treatments up to 700 $^\circ$C.42–44

Surface defects and adsorption of OH$^-$ groups on the crystal surface contribute to the formation of GNBs filled with an aqueous solution during the transfer protocol.

The presence of the aqueous solution inside GNBs was proved by measuring XPS O 1s spectra before the UV irradiation and after 45 min of irradiation with a laser tuned at 395 nm of wavelength and 15 mW of power (Figure 1 a).

As previously reported for the GNBs filled with an aqueous solution,35 the O 1s peaks can be deconvoluted in four components at 531.2 eV is related to oxygen dehydroxylation and to bridging hydroxyls on the surface vacancies,99 of bulk TiO$_2$; this latter component is very low due to the dense media interposed between the TiO$_2$ substrate and the Gr layer. XPS spectra of C 1s before and after 45 min of irradiation were also measured to check the Gr condition after the UV treatment. The obtained spectra are shown in Figure 1 b, evidencing that the UV irradiation does not change Gr components. Before and after irradiation, C 1s spectra present a pronounced sp$^2$ component at 284.6 eV associated with high-quality Gr, a sp$^3$ component at 285.3 eV associated with defects in the lattice and grain boundaries, and weak C−OH and O−C−C=O components at 286.5 and 288.6 eV due to atmospheric contamination and polymer residuals. The irradiation does not introduce additional defects or damage into the Gr layer; indeed, a little decrease of the O−C−O components is visible, indicating a cleaning effect of the UV laser in the presence of TiO$_2$ substrate.50,51

XPS spectra of Fe 2p are not reported in the paper because the oxidation state of iron can be analyzed with a higher
accuracy by XAS measurements. Indeed, Prussian blue photoreduction was examined by XAS at the Fe L\textsubscript{2,3} edge measured in total electron yield (TEY) exploiting the high electrical conductivity of the Gr/liquid interface which enabled the measurement of spectra with unprecedented high signal/noise ratio. Fe L\textsubscript{2,3} edge XAS corresponds to 2p \rightarrow 3d transition and provides a direct and sensitive measure of the fraction of Fe 3d orbitals hybridized with ligand 2p as a function of the metal valence and spin state. The sensitivity of the XAS line shape of Fe in a particular ligand field allows a quantitative analysis of the valences of Fe atoms.

Indeed, XAS spectra can be accurately modeled by ligand field multiplet calculation enabling a direct assignment of each spectroscopic feature to a specific oxidation and spin state of Fe atoms in PB. In Figure 2a XAS spectra measured at different intervals of UV exposure time are reported: before the irradiation (black line), after 20 min (green line), after 40 min (blue line), and after 70 min (red line) of irradiation. Before irradiation the Fe L\textsubscript{2,3}-edge XAS spectrum has the typical line shape expected for a mixed iron complex system such as PB, where Fe\textsuperscript{III}−CN Fe\textsuperscript{II}−CN, which is a mixture of low-spin Fe\textsuperscript{II} centers (LS-Fe\textsuperscript{II}−C) and high-spin Fe\textsuperscript{III} centers (HS-Fe\textsuperscript{III}−N). Fe L-edge XAS spectra clearly show the progressive formation of reduced Fe species as a function of the UV exposure time: Fe\textsuperscript{III}−CN−Fe\textsuperscript{II}−CN−Fe\textsuperscript{II}−CN, as shown by the intensity increase of the peaks at 707.15 and 720.3 eV as indicated in Figure 2a. In order to prove the reduction of HS-Fe\textsuperscript{III}−N to HS-Fe\textsuperscript{II}−N centers, XAS spectra were simulated by linear combination of the calculated spectral components present in PB molecules before and after UV exposure. The simulated curves of each spectroscopic feature (LS-Fe\textsuperscript{II}−C, HS-Fe\textsuperscript{II}−N, and HS-Fe\textsuperscript{II}−N) were calculated with the ligand field multiplet approach (see Methods), and their linear combination was optimized to reproduce the experimental line shape of PB spectra reported in Figure 2b.

The hopping parameters and back-bonding configuration energies were adjusted to reproduce the spectral components found in the literature and to model as best as possible the energy splittings of our experimental XAS spectra. The parameters optimized for the calculations are reported in Table 1 in the Methods section. As expected, a linear combination of 50% LS-Fe\textsuperscript{II}−C and 50% HS-Fe\textsuperscript{II}−N reproduces quite well the line shape of the XAS spectrum of fresh PB. The best simulation of the XAS spectrum of PB irradiated 70 min with UV light was achieved by a linear combination of 30% HS-Fe\textsuperscript{II}−N and 70% LS-Fe\textsuperscript{II}−C. Indeed, the calculation provides a direct verification that about 30% of Fe\textsuperscript{III}−N atoms were reduced to Fe\textsuperscript{II}−N species upon 70 min of UV irradiation. Despite the good

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**Figure 1.** (a) XPS O 1s spectra of GNBs obtained before the UV irradiation (black curve) and after 45 min of irradiation (red curve) indicating the presence of water during the time scale of the experiment. (b) C 1s XPS spectra of GNBs before (black curve) and after 45 min of UV irradiation at 395 eV (red curve) show no additional defects in the Gr layer induced by UV exposure.

**Figure 2.** (a) Experimental XAS spectra at Fe L\textsubscript{2,3} edge measured before (black line) and after 20 min (green line), 40 min (blue line), and 70 min of UV irradiation (red line) of an aqueous solution of PB. (b) From top to bottom: experimental Fe L\textsubscript{2,3} edge XAS spectra of PB before (black solid line) and after 70 min of UV irradiation (red solid line); calculated spectra of PB before (black dashed line) and after laser exposure (red dashed line); simulated spectroscopic components of Fe\textsuperscript{II}−C (yellow line), Fe\textsuperscript{II}−N (green line), and Fe\textsuperscript{II}−N (blue line) atoms coordinated to cyano groups. The linear combination of the simulated spectral features (PB calculated spectra) indicates that 30% of Fe\textsuperscript{III}−N atoms are reduced to Fe\textsuperscript{II}−N species after 70 min of UV irradiation.
agreement, the calculated XAS are not perfectly superimposed to the experimental ones. The difference between theoretical and experimental curves may be related to the presence of negligible amount of $K_2[Fe(CN)]_6$ and FeCl$_2$ residuals from the PB preparation, which were not accounted for in the simulation. For sake of clarity, the calculated spectroscopic components Fe$^{III}$–C and Fe$^{II}$–Cl ascribed to the two PB precursors are reported in Figure S-3 in the Supporting Information.

In order to be sure that the Fe reduction is due exclusively to the UV irradiation in our experimental conditions, but not to the possible damage induced by the X-rays,$^{4,53}$ the synchrotron light contribution was evaluated as well. A second fresh sample of GNBs filled with a 10 mM solution of PB was used as reference and exposed only to the synchrotron light for 45 min adopting the same experimental conditions used for XAS measurements (photon energy and beam flux) without laser irradiation. Figure 3 a reports the comparison between the spectrum measured before irradiation and the spectra collected after exposure to the UV laser for 45 min (bottom spectra) and to X-rays for 45 min (top spectra).

As visible in Figure 3 a, upon UV irradiation the intensity of peaks at 707.15 and 720.3 eV increases, and the spectrum line shape approaches the one reported for reduced Fe$^{III}$–CN–Fe$^{II}$ species typical of PW (as described before).$^{6,52}$ In the case of the sole X-ray irradiation, no evident change in the Fe L$_{2,3}$ edge is visible after 45 min of exposure, confirming that the main factor responsible for the Fe reduction is the UV light exposure, whose energy corresponds to the band gap of TiO$_2$.

The role of the aqueous environment was investigated as well to understand if the presence of water is necessary for the photo-reduction process. Fe L$_{2,3}$ edge XAS spectra of PB solution encased inside GNBs were compared with those acquired on a dry sample before and after laser exposure. The dry PB sample was prepared by drop-casting method on TiO$_2$ rutile single crystal. Both samples were irradiated with the same UV laser for 20 min, a sufficient time to see Fe reduction (as previously observed in Figure 2 a). The obtained results are shown in Figure 3 b.

As widely discussed above, the PB solution inside GNBs on TiO$_2$ shows the clear sign of Fe reduction upon UV irradiation. On the contrary, the dry PB sample drop casted on TiO$_2$ does not show any feature of reduced Fe. These results indicate that the water environment is a fundamental requirement for the photoinduced reduction of PB, and the GNB approach ensures this basic condition.

In light of the observed results, it is clear that the gradual photoinduced reduction of Fe$^{III}$–CN–Fe$^{II}$ species (PB) to Fe$^{III}$–CN–Fe$^{III}$ species (PW) occurs preferentially under the 395 nm laser excitation energy and in the presence of an aqueous environment. Indeed, upon UV band gap excitation of rutile ($E_g = 3.03$ eV), the electrons of the valence band are photoexcited to the conduction band of TiO$_2$, generating both holes and electrons in the valence and conduction bands, respectively.

Figure 3. (a) XAS Fe L$_{2,3}$ edge spectra of an aqueous solution of PB in GNBs exposed for 45 min to UV irradiation (red curve, bottom spectra) and for 45 min to X-rays irradiation (red curve, top spectra). (b) XAS Fe L$_{2,3}$ edge spectra measured after 20 min of UV exposure of the following: a PB aqueous solution in GNBs/TiO$_2$ (red curve, bottom spectra) and a PB dry film on TiO$_2$ (red curve, top spectra). The black spectra are measured before the irradiation. The photoreduction of Fe occurs only under UV light and in wet environment. No evident photoinduced effects are visible under X-rays exposure and in the absence of water.

The role of water is extremely important to allow the evolution of the reaction; in fact, water acts as a scavenger and reduces the generated holes in the valence band, preventing the electrons excited to the conduction band from being easily recombined with holes.$^{54}$

These conditions are required to ensure a continuous supply of photoexcited electrons to the conduction band of TiO$_2$, which can be injected into the electronic states of PB to reduce Fe$^{III}$–N to Fe$^{II}$–N atoms. The remaining holes in the valence band of TiO$_2$ oxidize water molecules to produce protons, which are used to ensure the charge balance of the partial reduced dye.$^7$ The proposed photoreduction mechanism is reported in Figure 4.

The process was further studied by Raman spectroscopy in liquid phase. Raman spectra of GNB samples (black and red lines in Figure 5 a, corresponding to fresh and UV irradiated samples, respectively) show the characteristic features of Gr at

<table>
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<th>Component</th>
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<th>$E_{p1}$</th>
<th>$E_{p2}$</th>
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<td>0.5</td>
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<td>1.0</td>
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<tr>
<td>Fe$^{II}$–N</td>
<td>1.7</td>
<td>$-$</td>
<td>$-$</td>
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Table 1. Ligand Field Multiplet Parameters Used for Simulations of Prussian Dye Components

1590 and 2695 cm$^{-1}$ which are ascribed to G and 2D peaks, respectively.$^{55,56}$

G and 2D bands are not affected by UV illumination, and no defects are introduced within the exposure time, as also evident in Figure S-4 in the Supporting Information. Other features at 443.4 cm$^{-1}$ ($E_g$ rutile mode) and 610.8 cm$^{-1}$ ($A_g$ rutile mode) are ascribed to TiO$_2$ substrate, while the small components between 200 and 700 cm$^{-1}$ can be assigned to Fe--C and Fe--N stretching and Fe--C--N and Fe--N--C bending modes$,^{11,57}$ typical of ferrocyanides, which are visible also on dry PB (blue line).

Finally, the characteristic C--N vibrational peak around 2162 cm$^{-1}$ is ascribed to the Fe$^{II}$--C--N--Fe$^{III}$ $A_g$ (symmetric) stretching mode of PB.$^{16,11}$

An expanded view of the C--N vibrational component is presented in Figure 5 b, and all the spectra have been normalized to this peak for a comparative analysis.

On dry PB sample on glass (blue line), this mode is observed at 2160 cm$^{-1}$, resulting downshifted by 2--3 cm$^{-1}$ with respect to PB solution in GNBS (red and black lines). This shift is most likely due to the presence of water or OH$^-$ ions, which can play an important role in the frequency shift of $A_g$ stretching mode. This finding proves again the presence of aqueous solution in GNBS. The weak peak around 2098 cm$^{-1}$ is attributed to the $E_g$ mode (asymmetric) of the Fe$^{II}$--C--N--Fe$^{III}$ stretching vibration,,$^7$ and its intensity remains unchanged upon UV illumination. Finally, the relative intensity of the shoulder at 2127 cm$^{-1}$, corresponding to Fe$^{III}$--C--N--Fe$^{II}$ stretching mode of CN group coordinated to two Fe$^{II}$ atoms, grows after 15 h of UV illumination (red line).

The higher intensity of this feature upon UV exposure proves the formation of partial photoreduction of PB to PW in aqueous solution on a TiO$_2$ substrate.

**METHODS**

**Prussian Blue Solution.** An aqueous solution of the soluble form of PB (100 mM) was prepared by mixing at room temperature equal volumes of 100 mM solutions of K$_3$[Fe(CN)$_6$] (potassium ferri-cyanide, Sigma-Aldrich) and FeCl$_2$·4H$_2$O (iron(II) chloride tetrahydrate, Sigma-Aldrich). The reaction is described by the chemical eq 1:

$$\text{Fe}^{II}\text{Cl}_2 + \text{K}_3[\text{Fe}(\text{CN})_6] \rightarrow \text{KFe}^{III}[\text{Fe}^{II}(\text{CN})_6] + 2\text{KCl}$$

The final PB solution was diluted 10 times to avoid the formation of aggregates, but the concentration of Fe was chosen high enough to have a good XAS signal. A picture of the starting and the final solutions of K$_3$[Fe(CN)$_6$] and KFe$^{III}$[Fe$^{II}$(CN)$_6$] is shown in Figure S-1 in the Supporting Information.

**Graphene Nanobubbles Fabrication.** The Gr layers were provided by the Department of Physics of Bilkent University in Ankara, Turkey. Graphene was synthesized on copper foils by chemical vapor deposition (CVD) according to the procedure described elsewhere.$^{58,59}$ The copper foils were placed in a quartz chamber and heated to 1000 °C under flow of hydrogen.
and argon gases. After the annealing process, methane gas with a flow rate of 15 sccm (standard cubic centimeters per minute) was sent to the chamber for 20 min. The chamber pressure was kept at 5 Torr during the growth. The growth was terminated by stopping the flow of methane gas, and then the chamber was cooled back to room temperature. The high quality of as-grown Gr was proved by SEM and Raman spectroscopy at IOM-CNR laboratory (see S-2 in the Supporting Information). For the samples preparation, the same procedure described in our previous work was adopted:35 a layer of 250 nm of mr-I 7020 (Micro Resist technology GmbH) was spin-coated on Gr, and then Cu foil was etched overnight in FeCl3 (1.6 M). After the rinse in deionized water, the mr-I/Gr/Cu membrane was put floating in the PB solution and directly fished with a TiO2(100) rutile single-crystal substrate, allowing the formation of GNBS. Dry samples were also prepared by drop-casting method in order to analyze the role of water.

**Electron Spectroscopies.** XPS and XAS measurements of the samples were carried out on the CNR BACH beamline at Eletra Sincrotrone in Trieste (Italy).60,61 XPS spectra of C 1s and O 1s core levels were recorded at 596 eV of photon energy. A VG-Scienta R3000 hemispherical analyzer,62 working with an overall energy resolution of 0.2 eV, was used. All spectra were fitted by a Gaussian function after the prior subtraction of a Shirley background to account for the inelastic photoelectrons. XAS spectra at the L2,3 edge of Fe before and after the UV laser (15 mW, 395 nm) exposure were measured in TEY collecting the current flowing through the Gr membrane.

The laser (PS-LBX, 395 nm, 15 mW, Oxxius) was placed on a laser board, and the light was impinged on the samples through an optical window mounted on the experimental chamber of BACH beamline at 22.5° from the sample surface normal.

**Raman Spectroscopy.** Raman measurements were performed in the reflection geometry on an inverted optical microscope (Axiovert 200, Zeiss) coupled with a 750 mm long spectrometer (Shamrock SR-750, Andor Technology plc). CW laser with the excitation wavelength of 532 nm (Cobolt Samba, 50 mW, bandwidth 1 MHz) was used as an excitation source. A laser beam was reflected by 45° orientated beamsplitter (532 nm RazorEdge Dichroic), directed to the inverted microscope and then focused on the mounted sample by 100x air objective (NA 0.8, EC Epiplan), resulting in a diameter of laser spot of around 0.35 μm. The laser power on the sample was controlled by variable neutral density filter (NDC-50C-4M, Thorlabs) and kept at 1 mW to avoid temperature-induced effects. The Raman scattered light was collected by the same objective and sent to the spectrometer by the same optical path, dispersed by a diffractive grating of 600 lines mm−1, and finally analyzed using TE-cooled EMCCD (Newton DU971-UVB, Andor Technology plc). The Rayleigh scattered light was blocked by the long-pass edge filter (532 nm RazorEdge) at the entrance of spectrometer. The acquisition time in all experiments was 60 s.

**Simulations.** Ligand field multiplet simulations were carried out exploiting the multiplet model implemented by Thole63 and Cowan48 and by using the CTRM4XAS 5.5 program developed by Stavitski and de Grooth65 which includes spin–orbit coupling, Coulomb interactions, and crystal field effects. Atomic Slater integrals were used, and all spectra were broadened by a Lorentzian with a half-width of 0.2(0.3) eV and by a Gaussian with a sigma value of 0.3 eV. Metal-to-ligand and ligand-to-metal charge transfer (MLCT and LMCT) were considered as a linear combination of three Fe 3d configurations: 3d^0 L, 3d^6, and 3d^51 H, where L is a ligand orbital and H is a hole in another ligand orbital. The configuration energies of different Fe ground states were defined by EG2 and EG3 parameters, which are the energy differences of all the averaged configuration energies of Fe with the nominal electron number (3d^5), without one electron transferred to cyano CN-group (3d^5N−1) and with an extra electron transferred from CN-group (3d^5N+1). The configuration energies of different Fe final states (core hole states), EG2 and EG3, were defined identically as the ground states EG2 and EG3.62 The effects of α- and π-donation from water to Fe ions were not accounted for in these simulations.

The parameters used to simulate FeII−C, FeIII−N, and FeII−N components expected in PB and PW species are reported in Table 1. The best simulation of high-spin state FeII−N was achieved using a single configuration (3d^6) and without the use of mixing parameters.

Since the presence of additional components due to PB precursors cannot be completely excluded, extra components of FeIII−C and FeVI−Cl ascribed to FeCl3 and K3[FeIII(CN)6] were simulated and reported in Figure S-3 together with the corresponding parameters in Table S-1 (Supporting Information).

## CONCLUSION

This work sheds light on the photoinduced reduction mechanism of a PB dye in aqueous solution in the presence of TiO2 catalyst. The role of the solvent was analyzed, and the photochemical reaction was monitored for the first time by using conventional electron spectroscopy methods in UHV conditions. GNBS were employed to follow in situ and in operando the evolution of the electronic properties of the sample in liquid environment. Thanks to the possibility of filling “quasi” transparent to photons and electrons GNBS with liquids, the well-known UV-induced reduction of an aqueous solution of PB catalyzed by band gap excitation of TiO2 was followed by XAS measurements.

XAS spectra at the L2,3 edge of Fe showed the gradual evolution from PB (FeIII−CN−FeII) to PW (FeII−CN−FeIII), confirmed also by ligand field multiplet calculation, and O 1s XPS measurements proved the presence of water inside GNBS before and after UV irradiation.

Our data suggest that photoexcited electrons promoted to the conduction band of TiO2 are used by PB to reduce HS−FeIII−N to HS−FeII−N species. The results clearly demonstrate that this process requires the presence of water as scavenger to reduce the generated holes in the valence band of rutile; otherwise, the excited electrons could be easily recombined with holes, stopping the reduction of Fe species. The results were further confirmed by Raman measurements of PB solution in GNBS, evidencing changes of the C≡N vibrational stretching modes as a function of the Fe oxidation state.

In conclusion, thanks to the GNBS approach, the mechanism of photocatalytic reduction of PB in aqueous solution was finally investigated by electron spectroscopy. This paper proves again the robustness and reliability of GNBS as a valuable method to study the evolution of a large variety of physical–chemical processes in liquid phase, with a particular attention to liquid/solid electron transfer in catalysis, energy conversion processes, photocatalysis, water splitting, and so on.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07898.

Preparation of PB (pictures of the starting solution K$_2$[Fe(CN)$_6$] and the final solution KFe$^{III}$[Fe$^{II}$(CN)$_6$]); Raman and SEM of “as-grown” Gr on Cu foil; LFM calculation of PB precursors (FeCl$_3$ and K$_2$[Fe(CN)$_6$]) and PB components; Raman spectra of G and 2D peaks of GNBs and a dry film of PB (PDF).

AUTHOR INFORMATION

Corresponding Authors
*E-mail: nappini@iom.cnr.it.
*E-mail: magnano@iom.cnr.it.

ORCID
Silvia Nappini: 0000-0002-4944-5487
Marco Lazzarino: 0000-0003-1077-6569
Frank M. F. De Groot: 0000-0002-1340-2186
Coskun Kocabas: 0000-0003-0831-5552

Present Addresses
‡CERIC-ERIC (Central European Research Infrastructure Consortium), S.S. Fourteen Km 163.5, 34149 Basovizza, Trieste, Italy.
□Elettra-Sincrotrone Trieste S.c.p.A, S.S. Fourteen Km 163.5, 34149 Basovizza, Trieste, Italy.

Author Contributions
S.N. and E.M. planned and executed electron spectroscopy experiments and evaluated the data. S.N. drafted the manuscript. E.M. actively participated in planning the manuscript. S.N. and A.M. prepared PB solutions. A.M. prepared GNBs filled with liquid and helped with data acquisition. F.D.G. actively helped in ligand characterization and analysis. M.L. and S.D.Z. gave general advisory and actively participated in planning the experiments. C.K. and O.B. provided the Gr layers grown on Cu foils. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
Gr, graphene; GNB, graphene nanobubble; PB, Prussian blue; PW, Prussian white; XPS, X-ray photoemission spectroscopy; XAS, X-ray absorption spectroscopy; AFM, atomic force microscopy; SEM, scanning electron microscopy; UHV, ultrahigh vacuum; BE, binding energy; TEF, total electron yield; CVD, chemical vapor deposition

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