

Strong, Conductive, Foldable Graphene Sheets by Sequential Ionic and π Bridging

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The goal of this work is to develop an inexpensive low-temperature process that provides polymer-free, high-strength, high-toughness, electrically conducting sheets of reduced graphene oxide (rGO). To develop this process, we have evaluated the mechanical and electrical properties resulting from the application of an ionic bonding agent (Cr^{3+}), a π - π bonding agent comprising pyrene end groups, and their combinations for enhancing the performance of rGO sheets. When only one bonding agent was used, the π - π bonding agent is much more effective than the ionic bonding agent for improving both the mechanical and electrical properties of rGO sheets. However, the successive application of ionic bonding and π - π bonding agents maximizes tensile strength, toughness, long-term electrical stability in various corrosive solutions, and resistance to mechanical abuse and ultrasonic dissolution. Using a combination of ionic bonding and π - π bonding agents, high tensile strength (821 MPa), high toughness (20 MJ m⁻³), and electrical conductivity (416 S cm⁻¹) were obtained, as well as remarkable retention of mechanical and electrical properties during ultrasonication and mechanical cycling by both sheet stretch and sheet folding, suggesting high potential for applications in aerospace and flexible electronics.

Interest in transferring the extraordinary properties of graphene nanosheets,^[1] such as high tensile strength^[2] and conductivity,^[3] from the molecular level to macroscopic materials has recently grown due to promising applications in the fields of aerospace and flexible electronic devices.^[4–9] Strategies for enhancing the properties of paper-like graphene sheets include optimizing the quality of the graphene in these sheets

and improving intersheet connectivity.^[10] The former strategies are important since graphene is typically derived from the more easily processed graphene oxide (GO). These include utilizing large-sized GO nanosheets,^[11–18] high-temperature annealing,^[15,19–22] and modulating the intrinsic GO chemical structure.^[23,24] For example, Lin et al.^[11] demonstrated that the tensile strength and electrical conductivity of GO sheets can be simultaneously enhanced by increasing the size of GO nanosheets. However, the GO sheets made from ultralarge GO nanosheets (average area of 272.2 μm^2) show a tensile strength of below 100 MPa. To maximize the electrical conductivity of resulting graphene sheets, Peng et al.^[15] thermally annealed GO sheets composed of giant GO nanosheets (average lateral size of 108 μm) at temperatures up to 3000 °C. Although the resultant rGO sheets were highly flexible and highly conductive, their tensile strength was only about 60 MPa.

Instead of using high-temperature annealing, Zhang et al.^[23] thermally annealed a GO nanosheets dispersion at 70 °C to form a gel, which was converted into a GO sheet having a strength of 614 MPa. Their explanation for this moderately high strength is that this low-temperature annealing enabled the useful segregation of oxidized and nonoxidized nanosheet domains.

On the other hand, interfacial cross-linking can enable highly efficient load transfer between graphene interlayers, resulting in high mechanical properties.^[5,6,10,25] Moreover, various different interfacial interactions can be integrated into the graphene sheets, including hydrogen,^[26–37] ionic,^[36,38–41] π - π ,^[42–46] and covalent bonding.^[47–53] However, the resulting graphene sheets generally show low electrical conductivities due to disruption of electron transport between graphene nanosheets by the cross-linking agents.^[5,6] Thus, it remains a challenge to integrate high mechanical and electrical properties into graphene sheets.

Herein, we describe a new strategy for sequential bridging, wherein the GO nanosheets are first bridged by ionic bonding. Thereafter, the graphene oxide is reduced to produce reduced GO (rGO), which is then further bridged by π - π bonding. The trivalent chromic ion (Cr^{3+}) is selected to provide ionic bonding since Cr^{3+} provides stronger bonding with oxygen groups than do other ions, like alkaline-earth metal ions.^[54] The π - π bonding interactions are provided by a molecule that has pyrene groups

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at opposite ends,^[55] which can bond between graphene sheets. The resulting sequentially bridged rGO (SBG) sheets provide high tensile strength (821.2 MPa) and toughness (20.2 MJ m⁻³) and electrical conductivity (415.8 S cm⁻¹), which are 4.0, 7.5, and 1.9 times higher, respectively, than for rGO sheets. Moreover, the SBG sheets retain ≈92% of their electrical conductivity during fatigue testing for 1 × 10⁵ cycles between 60 and 120 MPa. Also, ≈91% of the initial strength and ≈89% of the initial electrical conductivity were retained during 100 cycles of 360° folding. Additionally, the electromagnetic interference (EMI) shielding effectiveness of the SBG sheets is about 20 dB in the frequency range between 0.3 and 12 GHz, which is higher than for previously reported rGO sheets having similar thickness.^[17,20,44] Furthermore, the SBG sheets exhibit outstanding stability in harsh environments, including ultrasonication and long-term immersion in various corrosive solutions.

The process for fabricating SBG sheets is shown in **Figure 1a**. First, a chromium trichloride (CrCl₃) solution was added dropwise into the GO (Figure S1, Supporting Information) suspension during continuous stirring. The resulting homogeneous dispersion was then vacuum filtered and subsequently rinsed with deionized water (DIW) to obtain a freestanding ionically bridged GO (IBGO) sheet. Afterward, hydroiodic (HI) acid was used to chemically reduce the IBGO sheet into an ionically bridged rGO (IBG) sheet. Finally, the IBG sheet was soaked successively in 1-pyrenebutyric acid *N*-hydroxysuccinimide ester (PSE) and 1-aminopyrene (AP) solutions, thereby providing an SBG sheet in which the PSE and AP molecules have bonded with adjacent rGO nanosheets through π interactions and covalently reacted to provide PSE–AP amide linkages.^[55] **Figure 1b** schematically illustrates the structural model of the resulting silver-gray SBG sheet (**Figure 1c**). In order to optimize the ratio of ionic bonding and π – π bonding, we fabricated four kinds of SBG sheets: from SBG-I to SBG-IV, with increasing Cr³⁺ content. For comparison, a π – π bridged rGO sheet (designated π BG) was obtained by eliminating the addition of Cr³⁺. The content of PSE–AP and Cr³⁺ in these bridged rGO sheets was obtained by thermogravimetric analysis (TGA) (**Figure S2**, Supporting Information) and are tabulated in Table S1 (Supporting Information). The cross-section of a SBG-III sheet (containing 0.78 wt% Cr³⁺ and 5.46 wt% PSE–AP; **Figure 1d,e**) has a nacre-like layered structure, which is similar to that for all the rGO, IBG, and π BG sheets (**Figure S3**, Supporting Information). Energy dispersive X-ray spectroscopy (EDS, **Figure 1f**) of the fracture surface of a SBG-III sheet shows that the Cr³⁺ has uniformly penetrated into the volume of the sheet. The Cr³⁺ content (Table S2, Supporting Information) derived from the EDS spectrum (**Figure 1g**) is consistent with TGA results.

Compared with the rGO sheet, the bridged rGO sheets have a longer interlayer diffraction spacing (Table S3, Supporting Information) and a narrower full width at half-maximum (FWHM, Table S4, Supporting Information) for the 002 peak in X-ray diffraction (XRD) curves, as shown in **Figure 2a**. This longer interlayer spacing might be a consequence of stress produced between neighboring rGO nanosheets that are interconnected by the bonding agents. Importantly, the XRD results of Table S3 (Supporting Information) show that the interplanar spacing within platelets for the ionically bridged, π -bridged,

and successively bridged samples does not exceed 3.68, 3.72, and 3.76 Å, respectively, which are not much longer than the interplanar spacing for the rGO (3.62 Å). This demonstrates that neither the ionic-bridging agent nor the π -bridging agent significantly intercalates between the layers within rGO platelets. Hence, the improved mechanical properties must result from interplatelet bridges. Since π -bridging agents with pyrene end groups interact with the sp²-conjugated network of rGO nanosheets, π -bridging likely predominately occurs by connecting the basal planes of neighboring platelets. Ionic interplatelet bridging can possibly occur between platelet edges, platelet faces, and platelet faces and edges. Interestingly, the FWHM of IBG-III (2.65°), π BG (1.98°), and SBG-III (1.94°) are narrower than that of rGO (2.72°), indicating that interlayer bridging can effectively improve the alignment of graphene nanosheets compared with previously studied biomimetic composites.^[56] Moreover, π – π bonding is more effective for improving alignment than ionic bonding, and the highest degree of alignment was achieved for the SBG sheets.

Fourier transform infrared (FTIR) spectra (**Figure 2b**) show that the sheets of IBG-III and SBG-III have a weaker carboxyl C=O peak (1731.8 cm⁻¹) and stronger hydroxyl C–O peak (1041.4 cm⁻¹) than does the rGO sheet. This indicates the coordination of Cr³⁺ with carboxyl groups and epoxide ring opening by the Cr³⁺.^[38] These peak changes were also observed for the IBGO-III sheet (**Figure S4a**, Supporting Information). Thus, the ionic bonds in the SBG-III sheet have two modes of interaction^[38] (**Figure 1b**): I) bridging the edges of rGO nanosheets by coordination between Cr³⁺ and carboxylic acid groups and II) interconnecting rGO layers by alkoxide or dative bonds from carbonyl and hydroxyl groups. Additionally, the FTIR results for π BG and SBG-III sheets show new peaks at 3247.7 and 1650.8 cm⁻¹, which are assigned to the stretching vibration of N–H and C=O in amide groups of PSE–AP (**Figure S4b**, Supporting Information), respectively. These peaks further confirm the formation of amide linkages via covalent reaction between PSE and AP molecules.^[55]

The X-ray photoelectron spectroscopy (XPS) spectrum of an SBG-III sheet (**Figure 2c**) has new main peaks, which are due to Cr_{2p1/2} (586.7 eV) and Cr_{2p3/2} (577.1 eV).^[57] These peaks are also observed for IBGO-III and IBG-III sheets (**Figure S5a,b**, Supporting Information). These XPS results demonstrate that the reduction of graphene oxide and the addition of π bonding agents do not eliminate the ionic bonding. Furthermore, the EDS results (Table S5, Supporting Information) show that the atomic ratio of Cr to carbon in IBG-III sheets is nearly equal to that in IBGO-III sheets, which indicates that most of the ionic bonds were retained after HI reduction and washing. Additionally, as shown in **Figure 2c** and **Figure S5c–g** (Supporting Information), the C(O)O peak is slightly downshifted from 289.5 eV for GO, rGO, and π BG sheets to 289.2 eV for IBGO-III, IBG-III, and SBG-III sheets, which is due to the coordination between Cr³⁺ and carboxylic acid groups on the GO nanosheets.^[38] By contrast, the C–C peak of sp² carbon is slightly upshifted from 284.6 eV for GO, rGO, IBGO-III, and IBG-III sheets to 284.9 eV for π BG and SBG-III sheets, which might result from π – π interactions between PSE–AP and rGO nanosheets.^[58] Moreover, the π BG and SBG-III sheets contain C–N peak at 286.1 eV, stemming from the amide

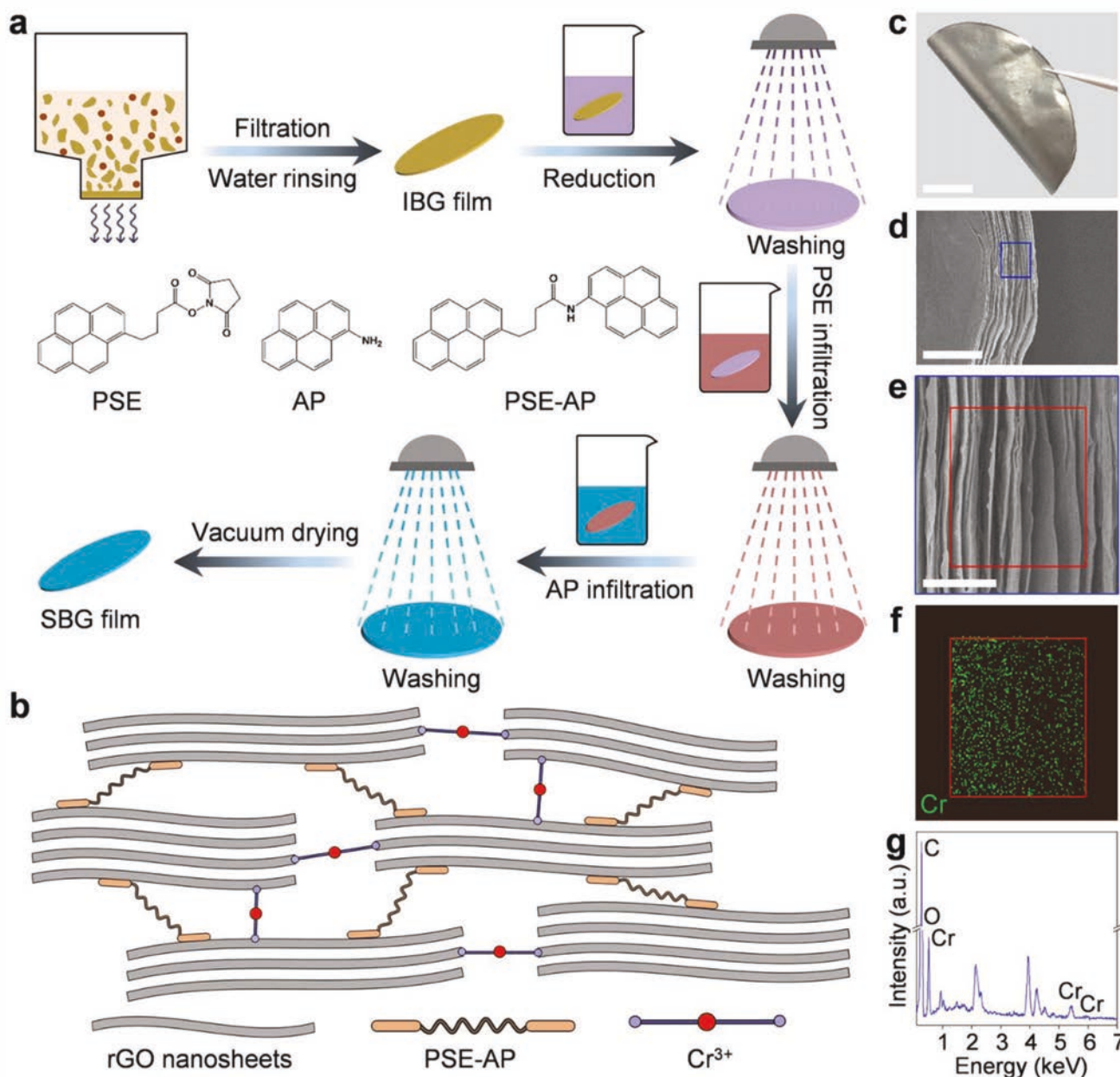


Figure 1. Preparation and structural characterization of SBG sheets. a) A homogeneous dispersion of GO and Cr^{3+} was first assembled into an IBGO sheet. Then, the IBGO sheet was reduced to make an IBG sheet using HI. Finally, PSE and AP were successively infiltrated into the sheet and reacted to form PSE-AP molecules, which could π -bond on rGO nanosheets. b) A schematic illustration of the structure of the resultant SBG sheet, where rGO platelets are bridged together by ionic and π - π bonding. c) Photograph of an SBG sheet, exhibiting its flexibility. Scale bar: 1 cm. d) A low-resolution scanning electron microscope (SEM) image of the cross-section of the SBG-III sheet. Scale bar: 5 μm . e) A high-resolution SEM image of the area outlined in (d). Scale bar: 1 μm . f) EDS mapping of Cr^{3+} and g) EDS spectrum of the area outlined in (e).

groups, which verifies the reaction between PSE and AP. The XPS results also show that the $\text{O}_{1s}/\text{C}_{1s}$ ratio decreases from 0.41 and 0.42 for GO and IBGO-III sheets to between 0.15 and 0.17 for rGO, IBG-III, π BG, and SBG-III sheets (Table S6, Supporting Information), suggesting the considerable elimination of oxygen-containing groups of GO nanosheets during reduction by HI.^[59–61]

Raman spectra (Figure 2d; Figure S6a,b, Supporting Information) show that the π BG and SBG-III sheets have a slightly

downshifted G band frequency (1578 cm^{-1}) and a slightly upshifted 2D band frequency (2690 cm^{-1}) compared with the rGO and IBG-III sheets (1581 and 2684 cm^{-1}). These Raman shifts are consistent with the electronic effects of the π - π interactions between PSE-AP and rGO nanosheets.^[62] Moreover, the D/G Raman intensity ratio (Table S7, Supporting Information) of the π BG sheet is similar to that for the rGO sheet, which indicates that π - π bridging has little effect on the sp^2 -conjugated structure of graphene nanosheets.^[55] However, the D/G

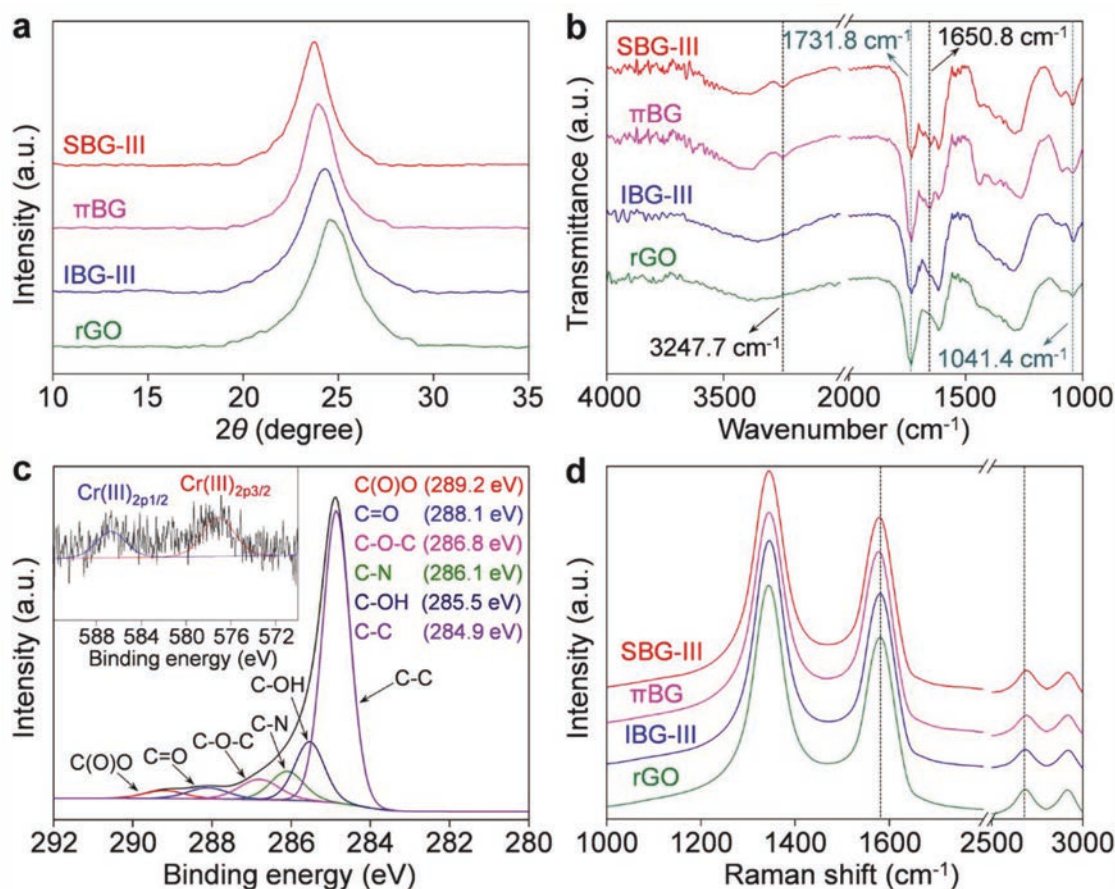


Figure 2. Interlayer chemical bridging in SBG sheets. a) Cu K α XRD patterns for sheets of rGO, IBG-III, π BG, and SBG-III. The bridged graphene sheets have a larger interlayer spacing and a narrower FWHM. b) FTIR spectra for sheets of rGO, IBG-III, π BG, and SBG-III. The peaks around 3247.7 and 1650.8 cm⁻¹ indicate reaction between PSE and AP to form an amide linkage, while the weaker peak at 1731.8 cm⁻¹ and stronger peak at 1041.4 cm⁻¹ demonstrate ionic bonding with rGO nanosheets.^[38] c) XPS spectra for C_{1s} and Cr_{2p} (inset) of an SBG-III sheet. The peaks around 586.7 and 577.1 eV demonstrate the presence of Cr³⁺.^[57] d) Raman spectra for sheets of rGO, IBG-III, π BG, and SBG-III.

ratio for the IBG-III sheet is higher than for the rGO sheet, which is likely due to ionic bridging with rGO nanosheets.^[63]

Sequential bridging results in a tensile strength of 821.2 ± 17.7 MPa and a toughness of 20.2 ± 0.6 MJ m⁻³ for the SBG-III sheet (Table S8, Supporting Information), which are 1.3 and 1.9 times higher than for the π BG sheet, 2.4 and 2.6 times higher than for the IBG-III sheet, and 4.0 and 7.5 times higher than for the rGO sheet, respectively, as shown in Figure 3a,b and Figure S7 (Supporting Information). Moreover, the Young's moduli for the SBG-III (9.3 ± 0.6 GPa) and SBG-IV (12.2 ± 0.3 GPa) sheets are significantly higher than for the π BG (6.2 ± 0.4 GPa), IBG-III (4.7 ± 0.4 GPa), and rGO (2.7 ± 0.2 GPa) sheets. Note that SEM images of fracture surface show curling of nanosheet edges for the bridged rGO sheets, but not for the rGO sheet (Figures S8 and S9, Supporting Information). This curling indicates strong interlayer bonding in the SBG sheets.

As a result of π -bridging-induced improvement in graphene nanosheet alignment^[64] and the conductance between graphene nanosheets,^[55] the electrical conductivity and gravimetric electrical conductivity of the π BG sheet (425.6 ± 24.2 S cm⁻¹ and 206.6 ± 11.7 S cm² g⁻¹, Figure 3c; Table S9, Supporting

Information) are much higher than for the rGO sheet (216.3 ± 18.5 S cm⁻¹ and 107.1 ± 9.2 S cm² g⁻¹), whereas those of the IBG-III sheet (204.9 ± 16.1 S cm⁻¹ and 99.0 ± 7.8 S cm² g⁻¹) are slightly lower than for the rGO sheet. This is likely mainly due to ionic bridging-induced obstruction to electron transportation between graphene nanosheets. Moreover, the SBG-III sheet has a much higher electrical conductivity (415.8 ± 26.3 S cm⁻¹) and gravimetric electrical conductivity (198.0 ± 12.5 S cm² g⁻¹) than the rGO and IBG-III sheets.

Reflecting their higher electrical conductivities, the π BG (≈ 20.5 dB) and SBG-III sheets (≈ 20 dB) also have much higher EMI shielding effectiveness in the frequency range between 0.3 and 12 GHz than rGO (≈ 14.2 dB) and IBG-III (≈ 13.4 dB) sheets having similar thicknesses, as shown in Figure 3d. Note that the observed high EMI shielding capability for π BG and SBG-III sheets can be attributed to the combination of increased intrinsic electrical conductivity and improved alignment of graphene nanosheets, enabling more effective multiple internal reflections and absorption of electromagnetic (EM) radiation. Additionally, the EMI shielding capability of SBG-III sheet is higher than for previously reported rGO sheets having similar thicknesses.^[17,20,44]

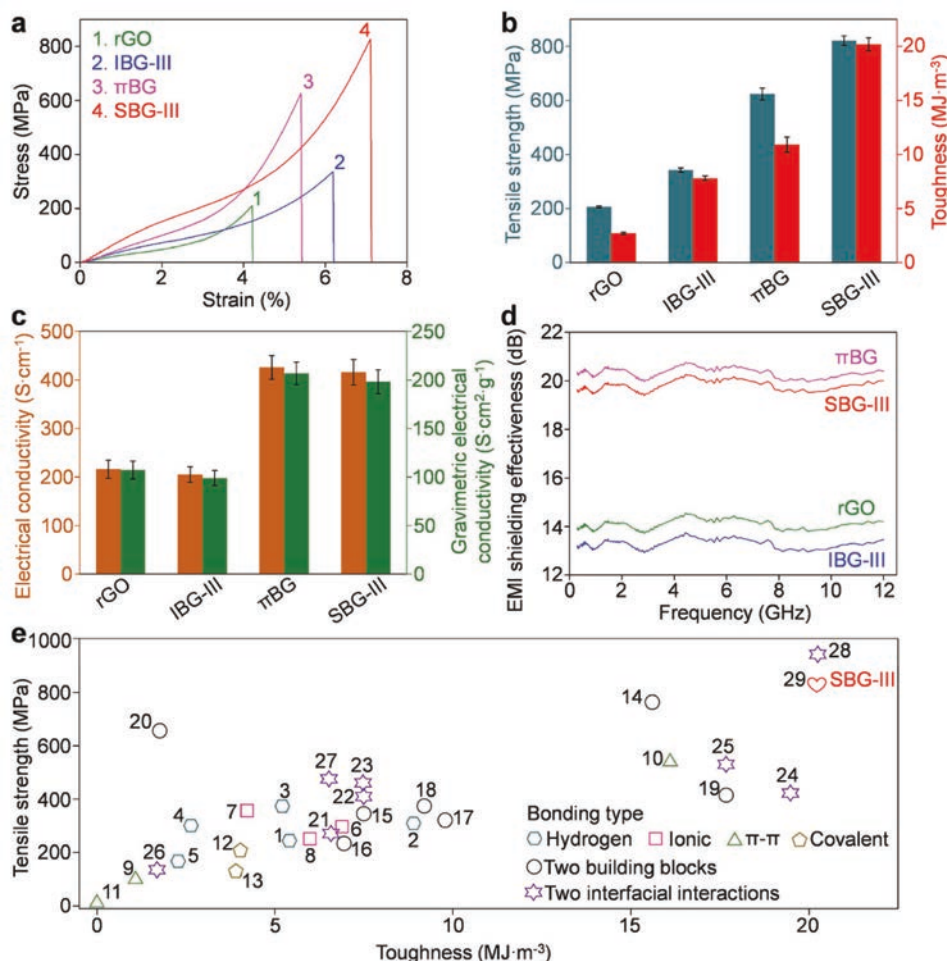


Figure 3. Properties of SBG sheets. a) Typical stress–strain curves for sheets of 1) rGO, 2) IBG-III, 3) π BG, and 4) SBG-III. b) Comparison of the tensile strength (cyan) and toughness (red) for sheets of rGO, IBG-III, π BG, and SBG-III. c) Comparison of absolute electrical conductivities (brown) and gravimetric electrical conductivities (green) for sheets of rGO, IBG-III, π BG, and SBG-III. d) EMI shielding effectiveness as a function of frequency for rGO, IBG-III, π BG, and SBG-III sheets having thicknesses between 3.2 and 3.8 μm . e) Comparison of the tensile strength and toughness of the SBG-III sheet (red heart) with the tensile strength and toughness of previously reported rGO sheets bridged through hydrogen bonding (cyan hexagons), ionic bonding (pink squares), π - π bonding (green triangles), covalent bonding (brown pentagons), two building blocks (black circles), and two interfacial interactions (purple hexagrams). The numbers associated with these symbols correspond to those for the material types and associated literature references tabulated in Table S10 (Supporting Information).

While methods^[15] that use high-temperature thermal annealing of graphene oxide sheets can result in much higher electrical conductivities than realized for the present low-temperature process, these methods have so far resulted in lower strength and toughness than for SBG-III sheets. Regarding low-temperature-processed graphene oxide, recently reported rGO-cellulose nanocrystal (CNC) sheets^[65] have about 2.7 times higher electrical conductivity than SBG-III sheets, but a lower strength (765.0 MPa) and toughness (15.6 MJ m^{-3}) than do SBG-III sheets (821.2 $\pm$ 17.7 MPa and 20.2 $\pm$ 0.6 MJ m^{-3}). Similarly, rGO sheets made at low temperature by modulating GO chemical structure^[23] have 1.9 times higher electrical conductivity than do SBG-III sheets, but a lower strength (614 MPa) and toughness (14.9 MJ m^{-3}). Moreover, as shown in Figure 3e, the tensile strength and toughness for the SBG-III sheet are higher than for previously reported rGO sheets bridged through various bonding types,^[29,32,34–36,39,40,42,44,46,47,52,65–73]

except for our very recently reported rGO sheets that are sequentially bridged by π - π bonding and covalent bonding agents.^[25] The detailed mechanical properties of these rGO sheets are tabulated in Table S10 (Supporting Information). To further enhance the properties of SBG sheets, GO nanosheets with larger flakes (provided by GaoxiTech Co., Ltd.) were assembled into graphene sheets using the sequentially bridging process (Figure S10, Supporting Information). The resultant SBG sheets comprising these larger GO nanosheets (denoted as L-SBG) show much higher mechanical properties and electrical conductivity than the described SBG-III sheets comprising relatively small GO flakes, as shown in Figure S11 (Supporting Information) and tabulated in Tables S8 and S9 (Supporting Information). The average lateral dimensions of the precursor GO nanosheets were 4.4 and 25.1 μm for SBG-III and L-SBG, respectively, resulting in improvement of mechanical strength from 821.2 to 924.8 MPa, toughness from 20.2 to 31.4 MJ m^{-3} ,

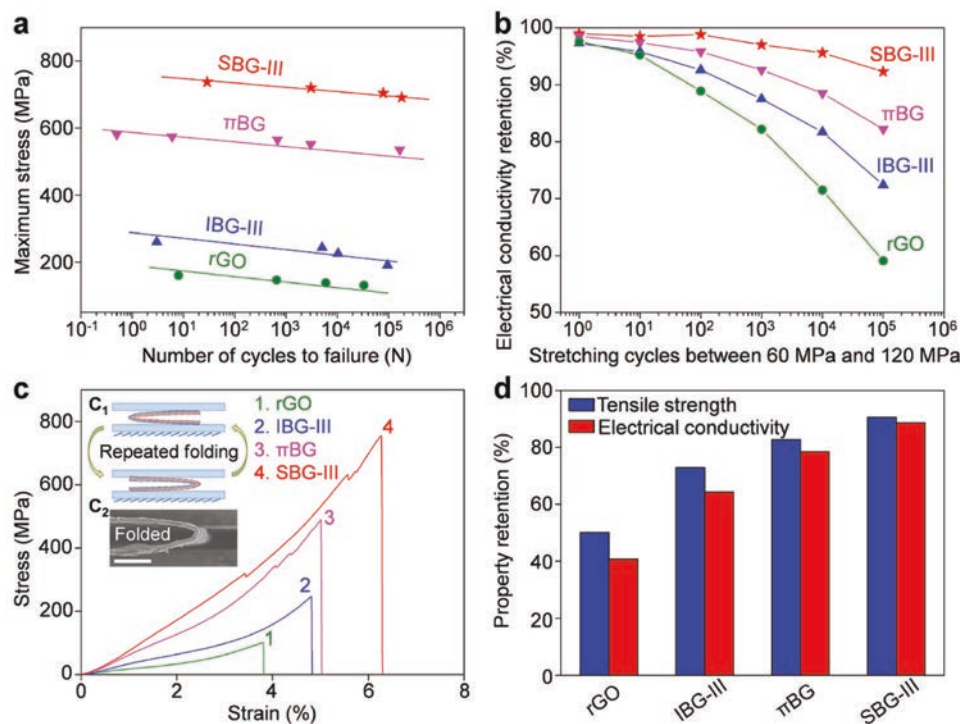


Figure 4. The effects of mechanical cycling on the mechanical and electrical properties of rGO, IBG-III, π BG, and SBG-III sheets. a) The dependence of the number of cycles to failure on the maximum stress level for sheets of rGO, IBG-III, π BG, and SBG-III. b) Conductivity retention percentages as a function of cycle number for sheets of rGO, IBG-III, π BG, and SBG-III that were cycled between 60 and 120 MPa. c) Typical stress–strain curves of the rGO, IBG-III, π BG, and SBG-III sheets after repetitive folding for 100 cycles. The inset c_1 schematically illustrates the repeated folding process, while inset c_2 is an SEM image of a folded SBG-III sheet. Scale bar: 50 μ m. d) Retention percentages for the strength and electrical conductivity of rGO, IBG-III, π BG, and SBG-III sheets after repeated 360° folding for 100 cycles.

and electrical conductivity from 415.8 to 550.2 S cm^{−1}, respectively.

In addition to providing outstanding static mechanical properties and useful electrical properties, sequential interlayer bridging improves the fatigue resistance of SBG sheets to both cyclic tensile stretch and cyclic 360° folding. The dependence of cycle life on the maximum applied stress is shown in **Figure 4a**. The fatigue resistance for tensile stretch of the SBG-III sheet is higher than previously reported for sheet structures derived from rGO, such as a rGO-poly(dopamine) complex that contains Ni²⁺ ions^[39] (which has synergistic ionic and covalent bonding) and rGO-tungsten disulfide (WS₂)-10,12-pentacosadiyn-1-ol^[70] (which contains WS₂ and rGO nanosheets, as well as polydiacetylene chains). The fatigue resistance is highest for SBG-III sheets, and π BG sheets have much higher fatigue resistance than either IBG-III or rGO sheets. The improved fatigue resistance of π BG sheet likely results from the ability of the π – π bonds to break and reform dynamically during cyclic stretching and therefore absorb more energy than rigid ionic bonding. Considering that sheet toughness varies for the different types in the same order as does fatigue resistance, the same explanation likely pertains to sheet toughness. Stress–strain curves during cyclic stretching, as well as the fracture morphologies after fatigue tests, are shown in Figure S12 (Supporting Information).

As a result of the exceptional fatigue crack suppression of SBG-III, the electrical conductivity of the SBG-III sheets

decreases by a smaller percentage during repeated tensile stretch than do the π BG, IBG-III, and rGO sheets (Figure 4b). More specifically, the electrical conductivity of the SBG-III sheet maintains $\approx$ 92% of its original value during 100 000 stretch cycles between 60 and 120 MPa, while the π BG, IBG-III, and rGO sheets retain only $\approx$ 82%, $\approx$ 72%, and $\approx$ 59% of their original value, respectively.

The SBG-III sheets also have higher stability in mechanical and electrical properties during cyclic folding tests than do π BG, IBG-III, and rGO sheets. Figure 4c shows the stress–strain curves of these sheets after 360° folding for 100 cycles between two flat steel plates, whose total weight is $\approx$ 2 $\times$ 10⁵ times that of the sheets. The repeatedly folded SBG-III sheet provides property retention percentages for strength ($\approx$ 91%) and conductivity ($\approx$ 89%) that are higher than for repeatedly folded π BG ($\approx$ 83% and $\approx$ 79%), IBG-III ($\approx$ 73% and $\approx$ 64%), and rGO ($\approx$ 50% and $\approx$ 41%) sheets (Figure 4d). In addition, the SBG-III sheets display high structural integrity after this cyclic deformation (as shown in Figure S13 in the Supporting Information), while the rGO sheets show obvious cracks. Thus, interlayer bridging suppresses delamination of neighboring rGO interlayers and resists folding-induced irreversible shear deformation. Moreover, π BG and SBG-III sheets have higher structural integrity after the folding tests than do the IBG-III sheets.

To evaluate structural stability in harsh environments, electrical resistances for rGO, IBG-III, π BG, and SBG-III sheets

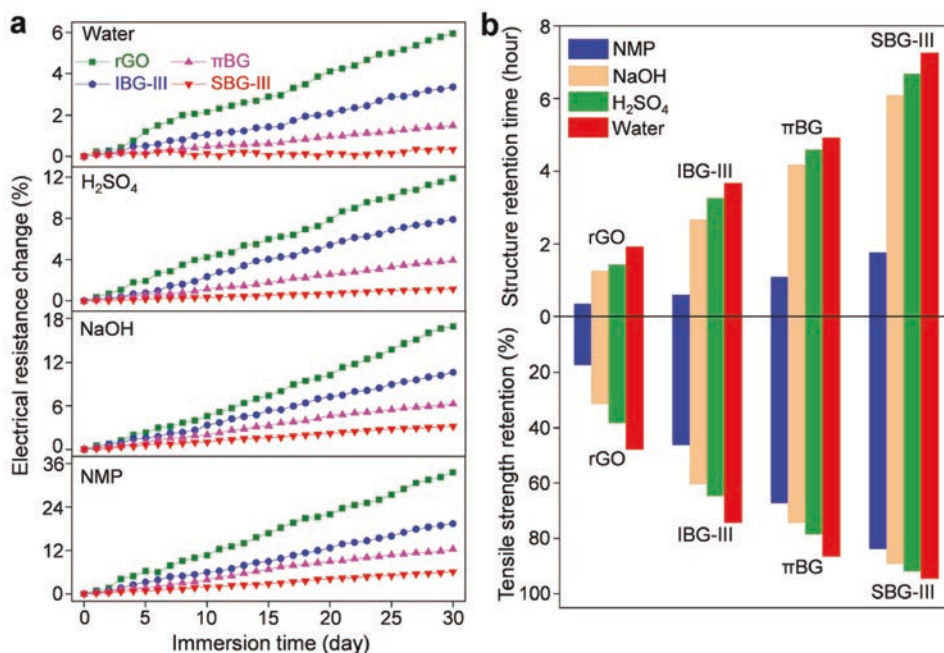


Figure 5. Stability of sheet structures in harsh environments. a) Change of electrical resistance as a function of time for rGO, IBG-III, π BG, and SBG-III sheets during 30 d immersion in NMP, NaOH (with OH^- concentration of 8 mol L^{-1}), H_2SO_4 (with H^+ concentration of 8 mol L^{-1}), and water. b) Structure retention time (top) for rGO, IBG-III, π BG, and SBG-III sheets during ultrasonication (100 W at 40 kHz) in NMP, NaOH, H_2SO_4 , and water, which was estimated using the time when the sharp increase of electrical resistance occurred. The retention percentages for tensile strength (bottom) for the sheets after ultrasonication in NMP, NaOH, H_2SO_4 , and water for 0.33, 1.25, 1.42, and 1.92 h, respectively. These times correspond to the structure retention time of rGO sheet during ultrasonication in these solutions.

were monitored in real time during immersion or ultrasonication in various solutions. Compared with rGO sheets, the bridged rGO sheets show higher stability in mechanical and electrical properties during long-term (30 d) immersion or ultrasonication (100 W at 40 kHz) in various solutions, such as *N*-methyl-2-pyrrolidone (NMP), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and water. Specifically, for both immersion and ultrasonication in all solutions, the changes of electrical resistance as a function of time for these sheets decrease as follows: $\text{SBG-III} < \pi\text{BG} < \text{IBG-III} < \text{rGO}$ (Figure 5a; Figure S14, Supporting Information), indicating the strongest resistance of SBG-III sheets to structural damage in harsh environments. The sharp increase in electrical resistance after a period of ultrasonication indicates disintegration of sheet structure (Figure S14, Supporting Information), and the structure retention time for these sheets to the mechanical abuse by ultrasonication increases as follows: $\text{SBG-III} > \pi\text{BG} > \text{IBG-III} > \text{rGO}$ sheets (Figure 5b). Note for each of these solutions show that the retention percentage for sheet tensile strength after ultrasonication increases monotonically with increase of sheet structure retention time. The tensile stress–strain curves for rGO, IBG-III, π BG, and SBG-III sheets after ultrasonication in these solutions are shown in Figure S15 (Supporting Information) and the corresponding detailed mechanical properties are tabulated in Table S11 (Supporting Information). Note that NMP, which has a surface energy that is well matched to that of graphene, more effectively generates ultrasonication-produced structural damage than do the other liquids.^[74,75]

In summary, we have shown that synergistic successive application of ionic bonding and π – π bonding agents provides optimal enhancement of tensile strength, toughness, and resistance to mechanical abuse. When only one bonding agent is used, the π – π bonding agent is much more effective than the ionic bonding agent for improving both the mechanical and electrical properties of graphene sheets. In fact, the ionic bonding agent degrades electrical conductivity, while it improves mechanical properties. For all of these differently bonded rGO sheets, strength, toughness, long-term electrical stability in different corrosive solutions, and resistance to mechanical damage, ultrasonication disintegration, and conductivity loss vary in the following order: $\text{SBG} > \pi\text{BG} > \text{IBG} > \text{rGO}$. Hence, while the use of the ionic bonding agent augments the mechanical property improvements that result from π – π bonding, the largest property increases result from π – π bonding. Especially since these bonding agents can be applied to conveniently fabricated GO sheets by using an inexpensive low-temperature process, and the realized properties are high, practical applications might result.

Experimental Section

Materials: GO was synthesized by using a modified Hummer's method^[23] and dried at 45°C in a vacuum oven for ≈ 12 h. NMP ($\geq 99.0\%$), dimethylformamide (DMF, $\geq 99.5\%$), H_2SO_4 , NaOH, and ethanol ($\geq 99.7\%$) were purchased from Sinopharm Chemical Reagents Co., Ltd., and PSE, AP, and CrCl_3 (anhydrous) were obtained from Sigma-Aldrich. HI (57 wt%) was purchased from Adamas-beta.

Deionized water, having a resistivity of above 18 M Ω cm was collected from a Milli-Q Biocel system.

Fabrication of IBG, π BG, and SBG Sheets: CrCl₃ and as-prepared GO were dispersed in DIW at a concentration of 0.8 and 2 mg mL⁻¹, respectively, by continuous stirring and ultrasonication. Then, the freshly prepared CrCl₃ solution was added to the GO dispersion to obtain a Cr³⁺ content of 0.2, 0.5, 0.7, and 1 wt%, respectively. To obtain IBGO-I, IBGO-II, IBGO-III, and IBGO-IV sheets, these dispersions were stirred for 2 h, filtered under vacuum, washed with DIW, and vacuum dried at 45 °C for 24 h. Subsequently, these sheets were reduced to provide IBG sheets by immersing them into HI solution for 6 h, washing 5 times with ethanol, and vacuum drying at 45 °C for 2 h. Next, the IBG sheets were soaked in a premixed DMF/PSE solution (24 mmol L⁻¹) for 48 h to absorb PSE molecules, washed 5 times with DMF, and vacuum dried at 45 °C for 2 h. Finally, the SBG sheets were obtained by soaking the IBG sheets in a premixed DMF/AP solution (24 mmol L⁻¹) for 48 h, washing 5 times with DMF, and vacuum drying at 45 °C for 2 h. The π BG sheet was fabricated analogously by eliminating the addition of CrCl₃.

Characterization: SEM images were obtained by using a field-emission scanning electron microscope (JEOL-7500F) at an acceleration voltage of 5 kV. Atomic force microscopy (AFM) images of GO nanosheets were obtained using a Leica TCS SP5 in the contact mode. TGA was performed under nitrogen atmosphere using a TG/DTA6300 (NSK, Japan) with a temperature scan rate of 10 °C min⁻¹ from room temperature to 1000 °C. Mechanical properties were measured at a loading rate of 1 mm min⁻¹ by using a Shimadzu AGS-X Tester. To avoid uncertainties in the measurement of sample cross-sectional area, gravimetric strengths were calculated as the ratio of force at break to the sample weight per sample length. The samples used for mechanical testing were 3 mm wide, 10 mm long strips, and at least three measurements were conducted for each sample type. In order to evaluate the effects of sheet bending on sheet tensile strength and electrical conductivity, sheets were repeatedly folded and unfolded in opposite directions along one fold line for 100 cycles to provide a maximum angle change of 360°. Tensile fatigue tests were performed at a frequency of 1 Hz using an Instron ElectroPulseE1000 mechanical apparatus. The samples used for fatigue testing were 5 mm wide, 25 mm long strips. The samples used for structural stability testings (immersion or ultrasonication in various solutions) were 3 mm wide, 35 mm long strips, where the two ends of the samples were placed outside of the solutions to ensure reliable electrical connections for real-time monitoring of electrical resistance. Electrical conductivities and resistances were measured using a Keithley 2400 multiple-function source meter. Gravimetric electrical conductivities were calculated by dividing the reciprocal of electrical resistance per sample length in the electrical conduction direction by the weight per sample length in this direction. EMI shielding effectiveness was measured in the frequency range between 0.3 and 12 GHz using an AV3629 vector network analyzer. XRD curves were recorded on a Shimadzu XRD-6000 using Cu K α radiation and a scanning speed of 4° min⁻¹. XPS measurements were conducted on an ESCALab220i-XL (ThermoScientific) using a monochromatic Al K α X-ray source. Raman spectra were measured on a LabRAM HR800 (Horiba Jobin Yvon) using 633 nm excitation. FTIR spectra were performed using a Thermo Nicolet NEXUS-470 FTIR instrument in the attenuated total reflection mode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

ionic bridging, π bridging, rGO sheet, sequential bridging

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Supporting Information

Strong, Conductive, Foldable Graphene Sheets by Sequential Ionic and π Bridging

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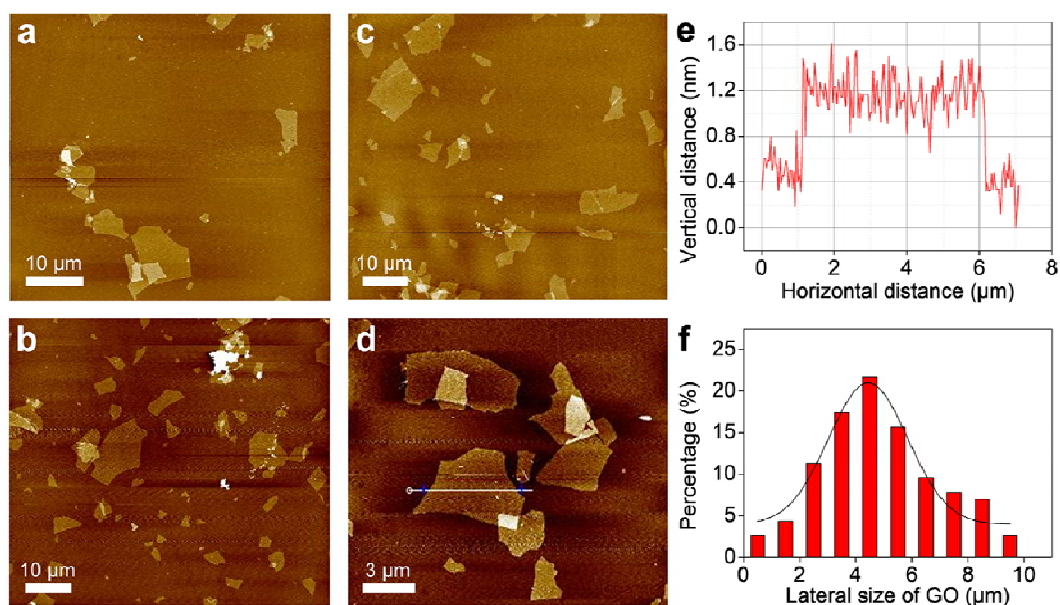


Figure S1. Atomic force microscopy (AFM) characterization of exfoliated graphene oxide (GO) nanosheets. a-d) AFM images of GO nanosheets. e) The height profile of GO nanosheets in (d), indicating that the thickness of GO nanosheets is about 0.8 nm. f) The width distribution of GO nanosheets, indicating that the average width of GO nanosheets is about 4.4 μm .

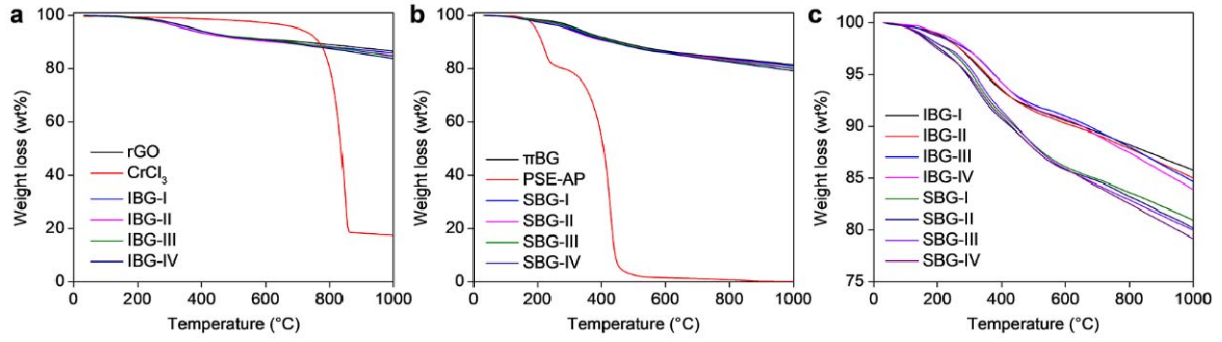


Figure S2. Thermogravimetric analysis (TGA) curves. a) As-received chromium trichloride (CrCl_3), reduced GO (rGO), and ionically bridged rGO (IBG) sheets. b) 1-pyrenebutyric acid N-hydroxysuccinimide ester and 1-aminopyrene (PSE-AP), π - π bridged rGO (π BG), and sequentially bridged rGO (SBG) sheets. c) High resolution TGA curves for IBG and SBG sheets. The TGA measurements were performed under nitrogen atmosphere from room temperature to 1000 °C using a temperature rising rate of 10 °C $\cdot$ min $^{-1}$. IBG-I, IBG-II, IBG-III, and IBG-IV designate that the precursor IBGO-I, IBGO-II, IBGO-III, and IBGO-IV sheets were prepared using a solution in which the Cr^{3+} content was 0.2 wt%, 0.5 wt%, 0.7 wt%, and 1 wt% of the GO- Cr^{3+} weight, respectively.

The weight fraction of PSE-AP in π BG sheets was estimated from the weight loss curve over the temperature range from 100 °C to 1000 °C. The PSE-AP weight fraction (w_1) in π BG sheets is calculated by equation 1:

$$w_1 = \frac{M_{\pi BG} - M_{rGO}}{M_{PSE-AP} - M_{rGO}} \quad (1)$$

where M_{PSE-AP} , M_{rGO} , and $M_{\pi BG}$ are the fraction of weight loss for PSE-AP, rGO, and π BG sheets, respectively, between 100 °C and 1000 °C.

Similarly, the weight fraction of trivalent chromic ion (Cr^{3+} , w_2) in the IBG sheets and PSE-AP weight fraction (w_3) in the SBG sheets are calculated by equations 2 and 3, respectively:

$$w_2 = \frac{M_{IBG} - M_{rGO}}{M_{CrCl_3} - M_{rGO}} \times \frac{52}{158.4} \quad (2)$$

$$w_3 = \frac{M_{SBG} - M_{IBG}}{M_{PSE-AP} - M_{IBG}} \quad (3)$$

where M_{CrCl_3} , M_{PSE-AP} , M_{rGO} , M_{IBG} , M_{SBG} are the fraction of weight loss for $CrCl_3$, PSE-AP, rGO, IBG, and SBG sheets, respectively, between 100 °C and 1000 °C.

Since the Cr^{3+} /rGO weight ratio in the SBG sheets is the same as in the corresponding IBG sheets, the weight fraction (w_4) of Cr^{3+} in the SBG sheets is estimated using equation 4:

$$w_4 = (1 - w_3) \times w_2 \quad (4)$$

The detailed data for Cr^{3+} and PSE-AP weight percentage in IBG, π BG, and SBG sheets are tabulated in Table S1 (Supporting Information).

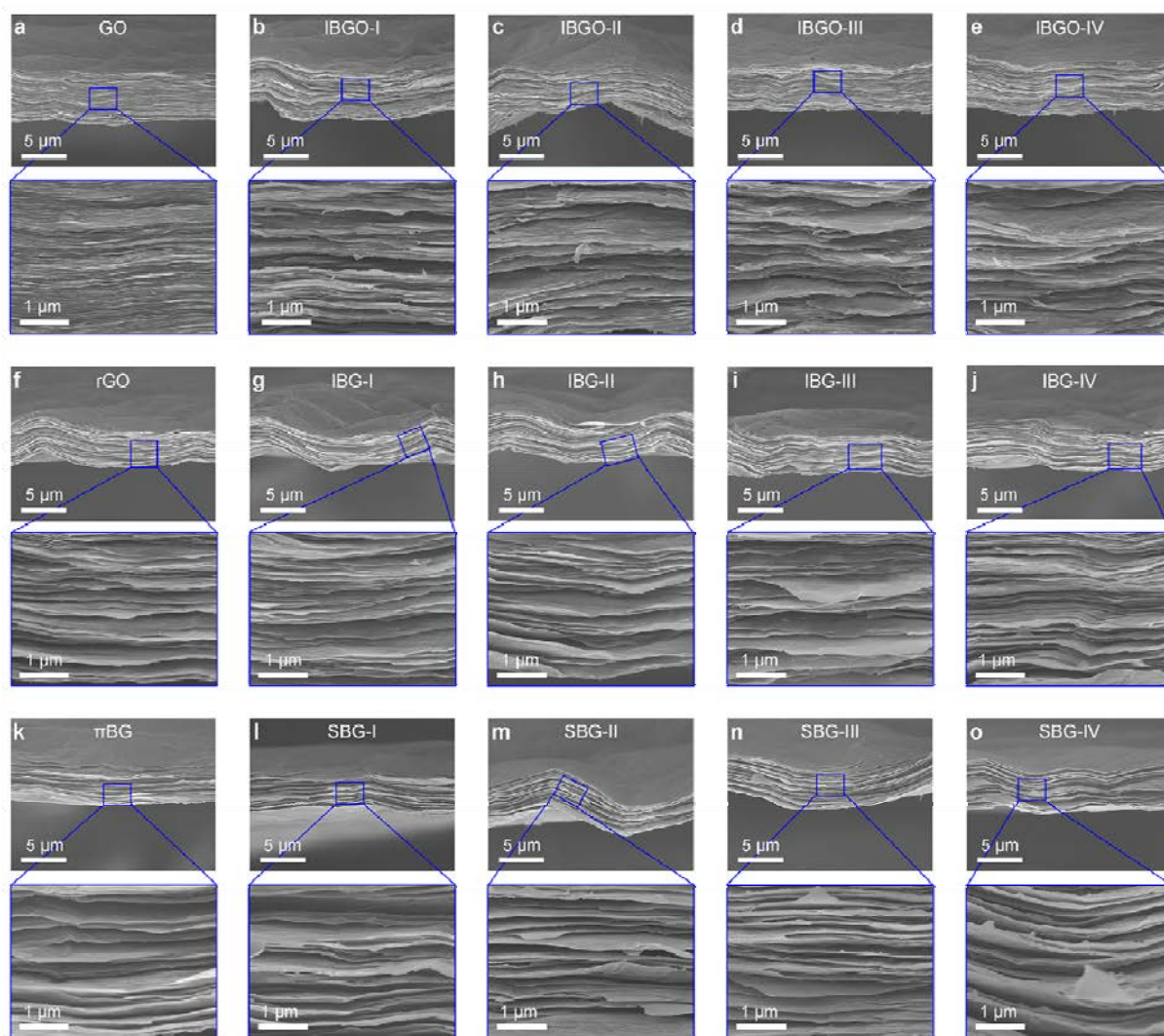


Figure S3. Scanning electron microscope (SEM) images of the fracture surface of sheets. a) GO, b-e) IBGO-I to IBGO-IV, f) rGO, g-j) IBG-I to IBG-IV, k) π BG, and l-o) SBG-I to SBG-IV sheets. These images display the layered structure of the sheets.

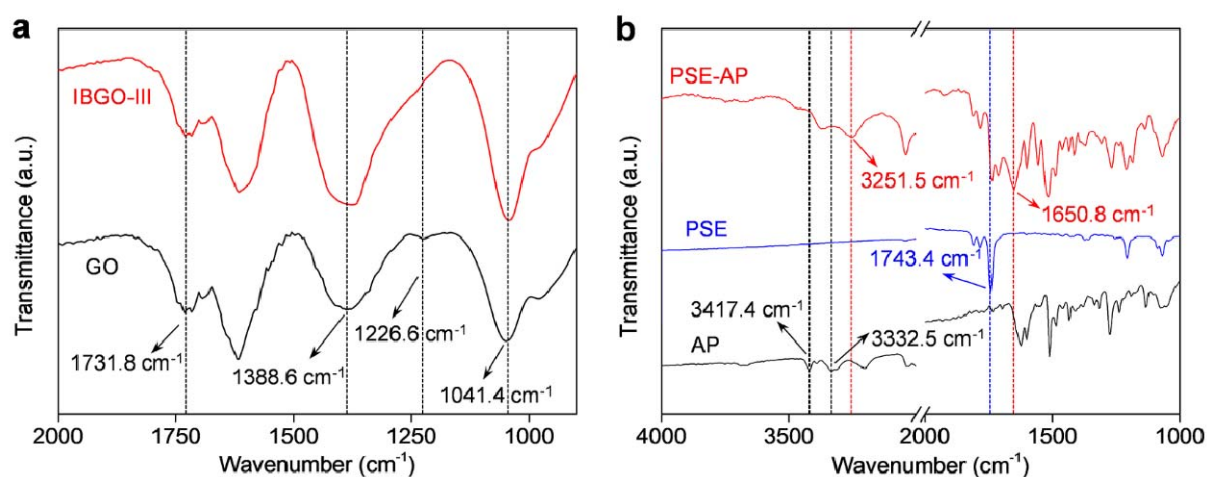


Figure S4. Fourier transform infrared (FTIR) spectra. a) GO and IBGO-III sheets. b) Neat AP, PSE, and PSE-AP. Compared with GO sheet, the IBGO-III sheet has a weaker epoxy/ether C–O peak at 1226.6 cm^{-1} , but a stronger hydroxyl C–O peak at 1041.4 cm^{-1} , indicating the epoxide ring-opening between Cr^{3+} and GO nanosheets.^[38] In addition, the IBGO-III sheet has a weaker carboxyl C=O peak at 1731.8 cm^{-1} and a stronger carboxyl C–O peak, which is red shifted from 1388.6 cm^{-1} for GO sheet to 1377.0 cm^{-1} .^[38] The peaks around 3251.5 cm^{-1} and 1650.8 cm^{-1} in PSE-AP molecules correspond to the stretching vibrations of N–H and C=O, respectively, of amide groups, indicating that the PSE and AP have reacted to form an amide linkage.

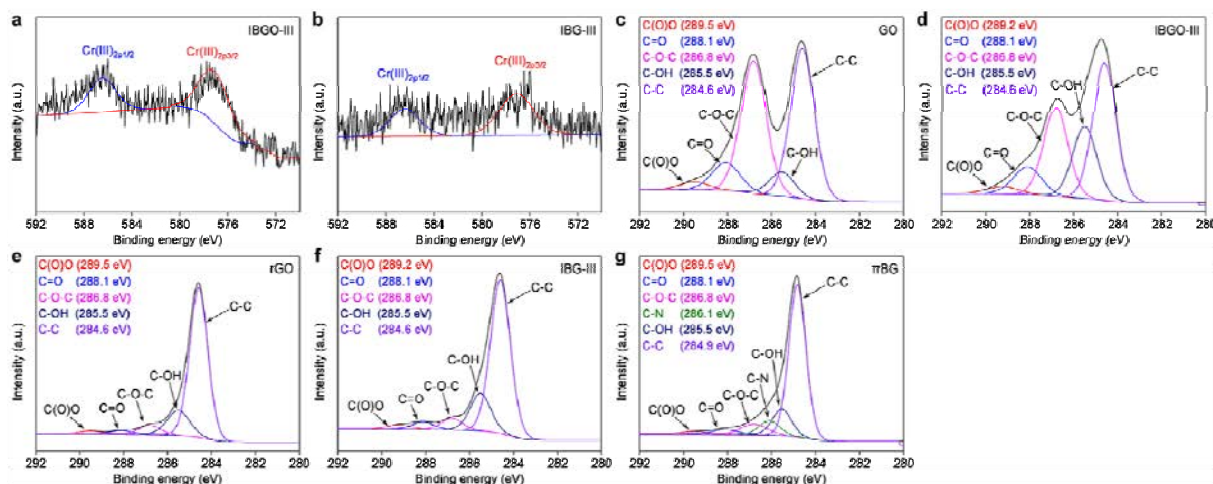


Figure S5. X-ray photoelectron spectroscopy (XPS) spectra. The broad Cr_{2p} peak of a) IBGO-III and b) IBG-III sheets. The broad C_{1s} peak of c) GO, d) IBGO-III, e) rGO, f) IBG-III, and g) π BG sheets. The peaks around 586.7 eV ($\text{Cr}_{2p1/2}$) and 577.1 eV ($\text{Cr}_{2p3/2}$) in the IBGO-III and IBG-III sheets indicate the presence of Cr^{3+} .^[57] Compared with GO sheet, the IBGO-III sheet has a decreased intensity C–O–C peak and an increased intensity C–OH peak, indicating the epoxy ring-opening reaction between Cr^{3+} and GO nanosheets.^[38] Moreover, the C(O)O peak is slightly down-shifted from 289.5 eV for sheets of GO, rGO, and π BG to 289.2 eV for sheets of IBGO-III and IBG-III, which suggests coordination between Cr^{3+} and carboxylic acid groups on the GO nanosheets.^[38] Additionally, the $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ peak is slightly up-shifted from 284.6 eV for sheets of GO, rGO, IBGO-III, and IBG-III to 284.9 eV for π BG sheet, suggesting π - π interactions between PSE-AP and rGO nanosheets.^[58]

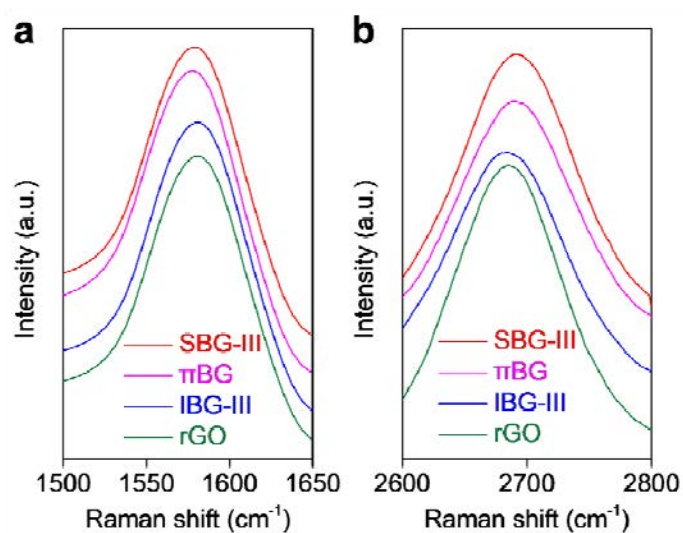


Figure S6. High resolution plots of the Raman spectra (shown in Figure 2d) for the rGO, IBG-III, π BG, and SBG-III sheets for Raman shift ranges of a) from 1500 cm^{-1} to 1650 cm^{-1} and b) from 2600 cm^{-1} to 2800 cm^{-1} . Compared with the rGO and IBG-III sheets, the π BG and SBG-III sheets have a slightly down-shifted G band frequency from 1581 cm^{-1} to 1578 cm^{-1} and a slightly up-shifted 2D band frequency from 2684 cm^{-1} to 2690 cm^{-1} , which suggests π - π interactions between PSE-AP and rGO nanosheets.^[62]

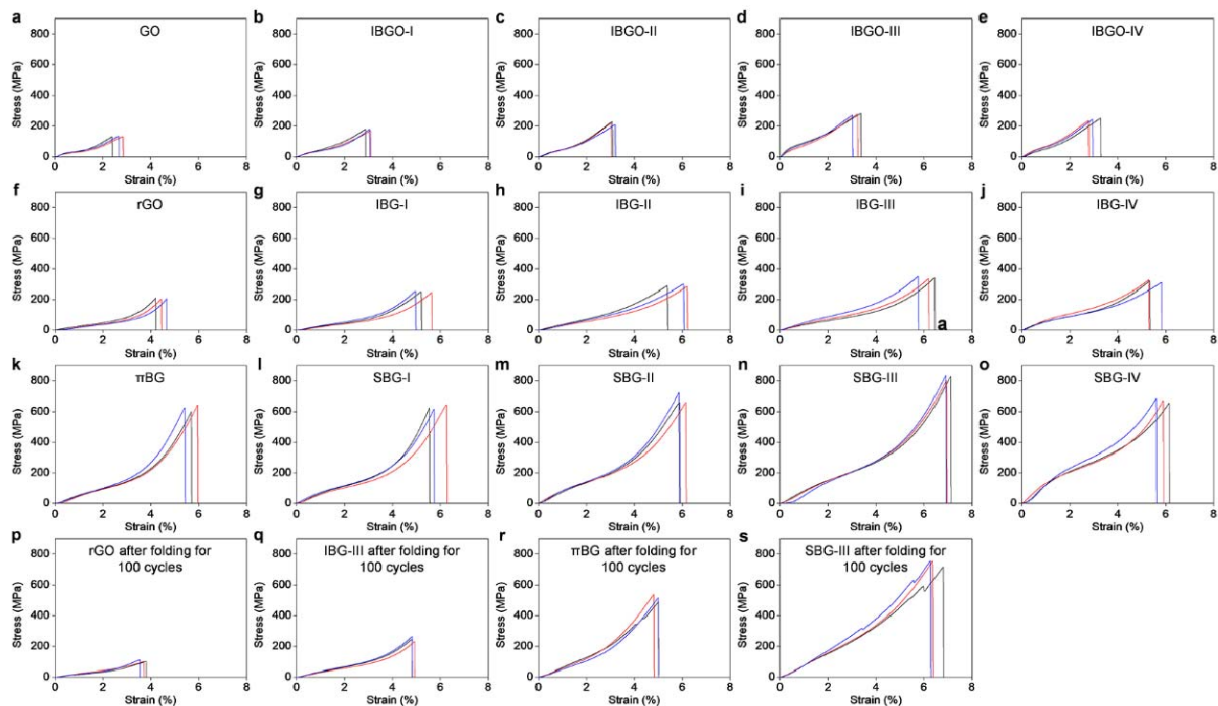


Figure S7. Tensile stress-strain curves of sheets. a) GO, b-e) IBGO-I to IBGO-IV, f) rGO, g-j) IBG-I to IBG-IV, k) π BG and l-o) SBG-I to SBG-IV sheets. p) rGO, q) IBG-III, r) π BG, and s) SBG-III sheets after 100 cycles of 360° folding.

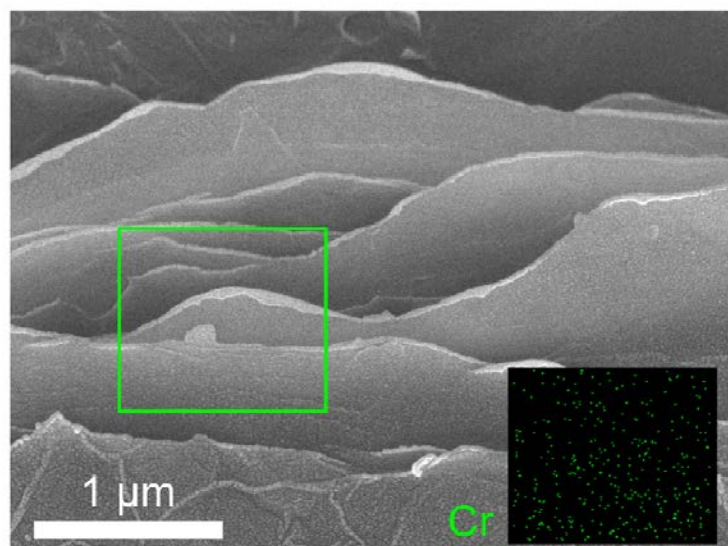


Figure S8. Inclined-view SEM image of fracture edges for the SBG-III sheet and corresponding EDS mapping of Cr^{3+} . The pictured sheet curling is consistent with rupture of bridging bonds. The Cr^{3+} laid on the fracture surface of rGO nanosheets.

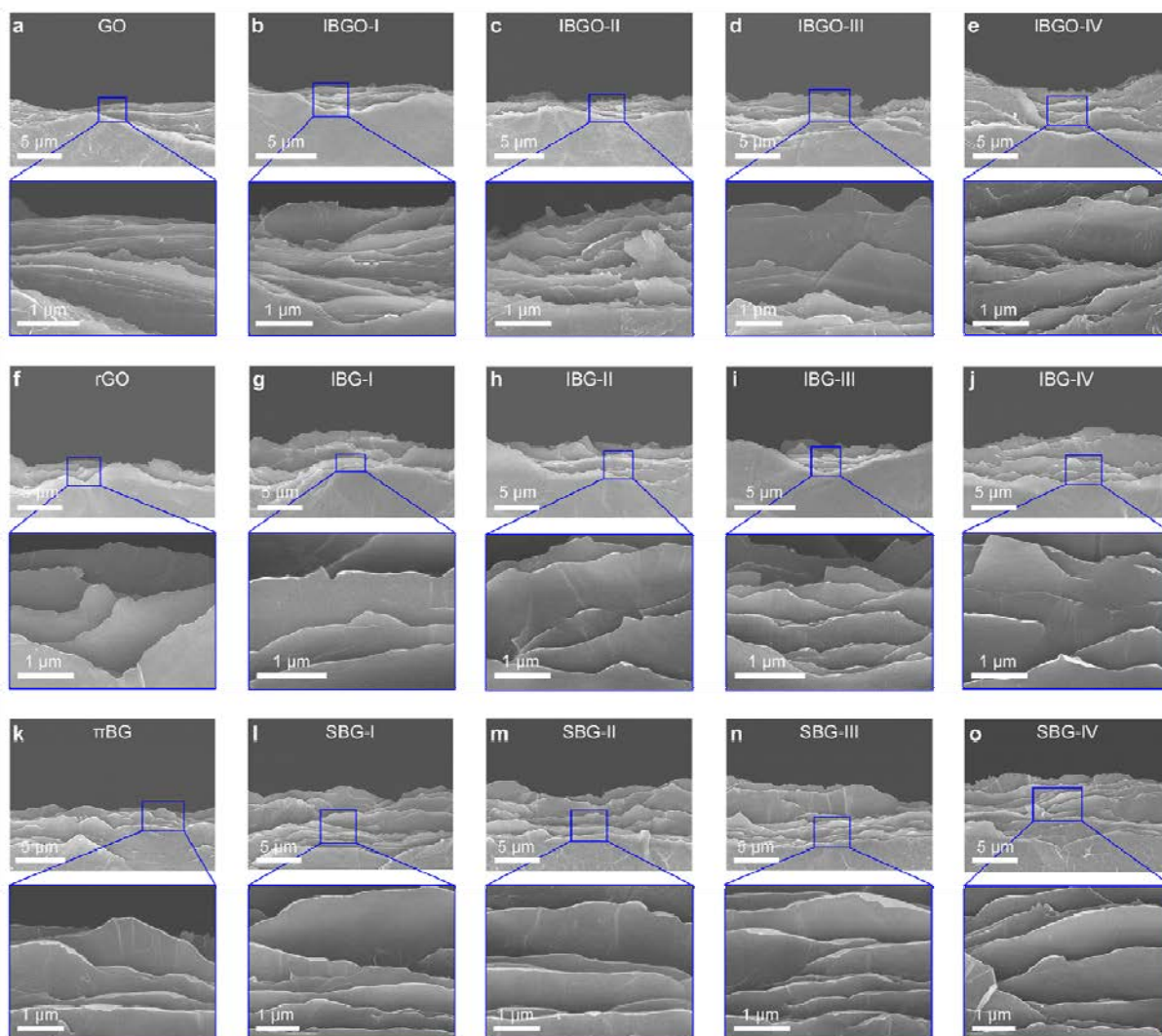


Figure S9. Inclined-view SEM images of the fracture surface of sheets. a) GO, b-e) IBGO-I to IBGO-IV, f) rGO, g-j) IBG-I to IBG-IV, k) π BG, and l-o) SBG-I to SBG-IV sheets. These images show curling of nanosheet edges for the bridged rGO sheets, including IBG, π BG, and SBG, but not for the rGO sheet.

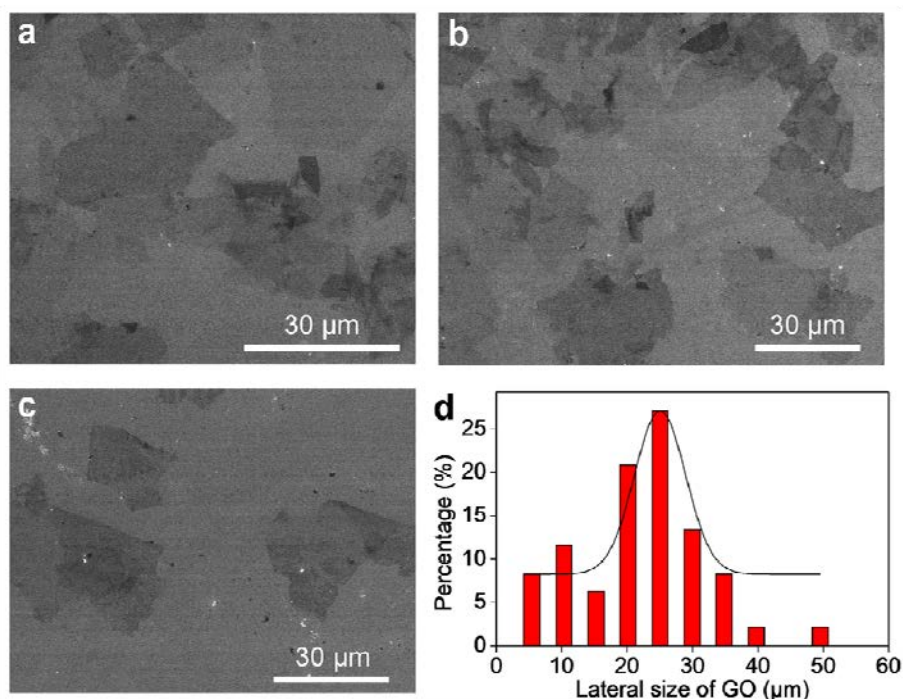


Figure S10. a-c) SEM images of large GO nanosheets. d) The lateral size distribution of large GO nanosheets, indicating that the average lateral size of large GO nanosheets is 25.1 ± 4.6 μm .

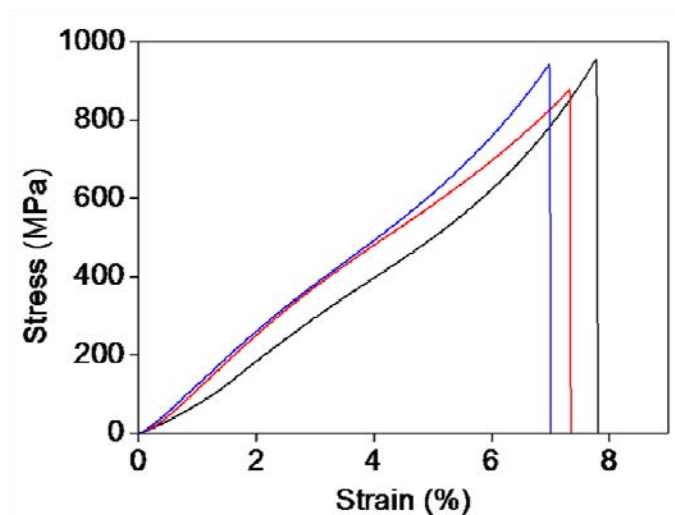


Figure S11. Tensile stress-strain curves of three L-SBG sheet samples.

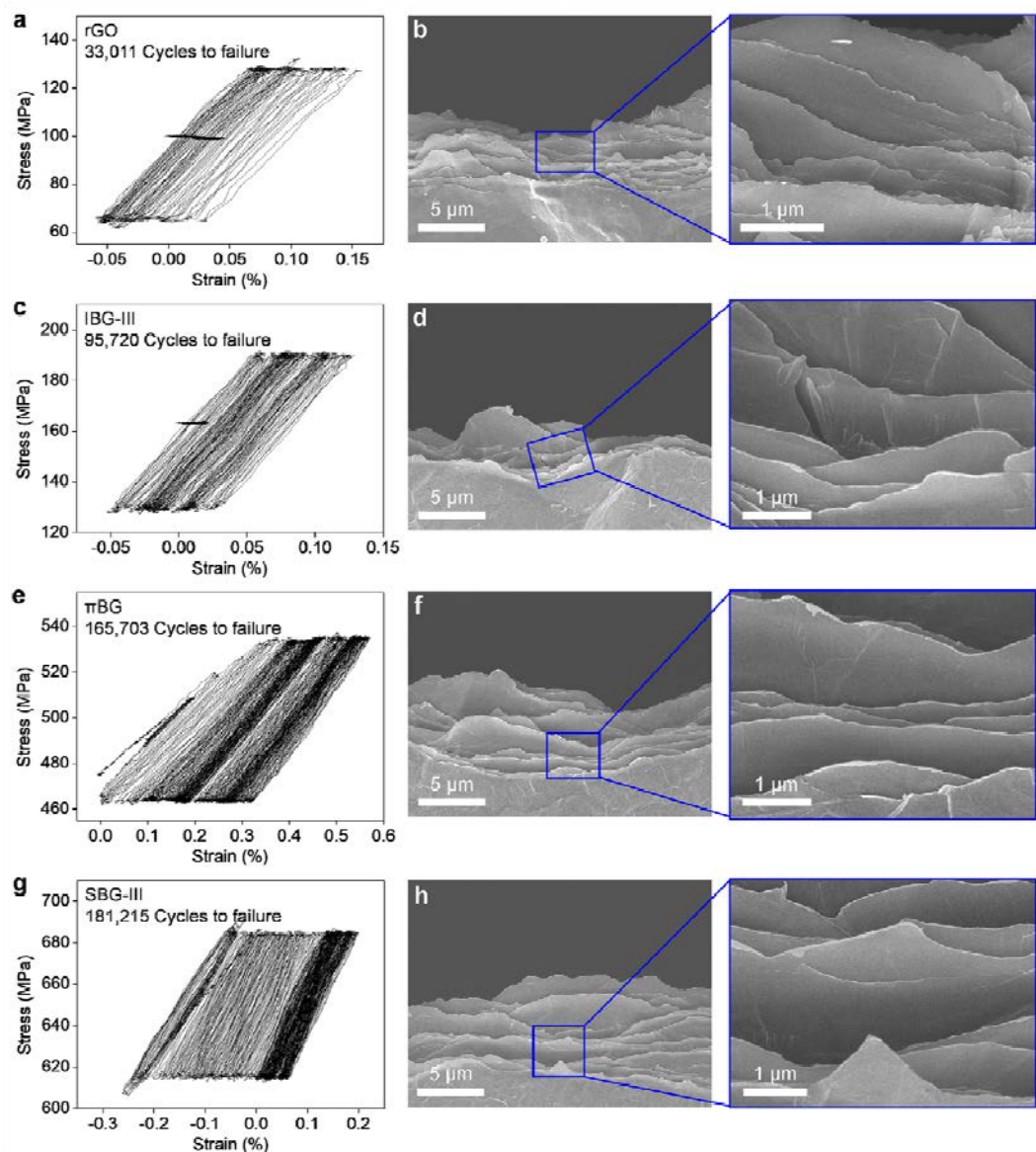


Figure S12. Tensile stress-strain curves during fatigue testing and corresponding SEM images of the fracture surface resulting from tensile failure. a,b) rGO, c,d) IBG-III, e,f) π BG, and g,h) SBG-III sheets. The bridged graphene sheets demonstrate higher fatigue lifetime and sheet curling, which does not appear for fractured rGO sheets.

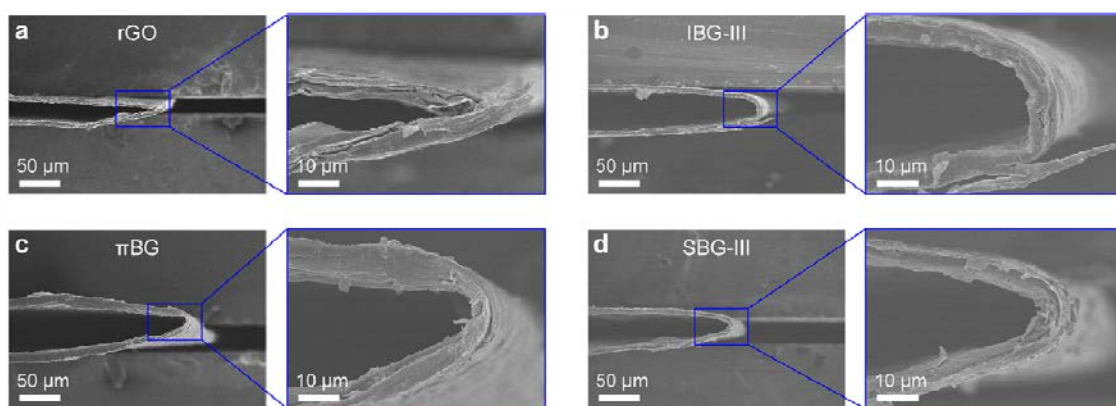


Figure S13. SEM images of sheets after 100 cycles of 360° folding. a) rGO, b) IBG-III, c) π BG, and d) SBG-III sheets. The folded π BG and SBG-III sheets have higher structure integrity than the folded rGO and IBG-III sheets.

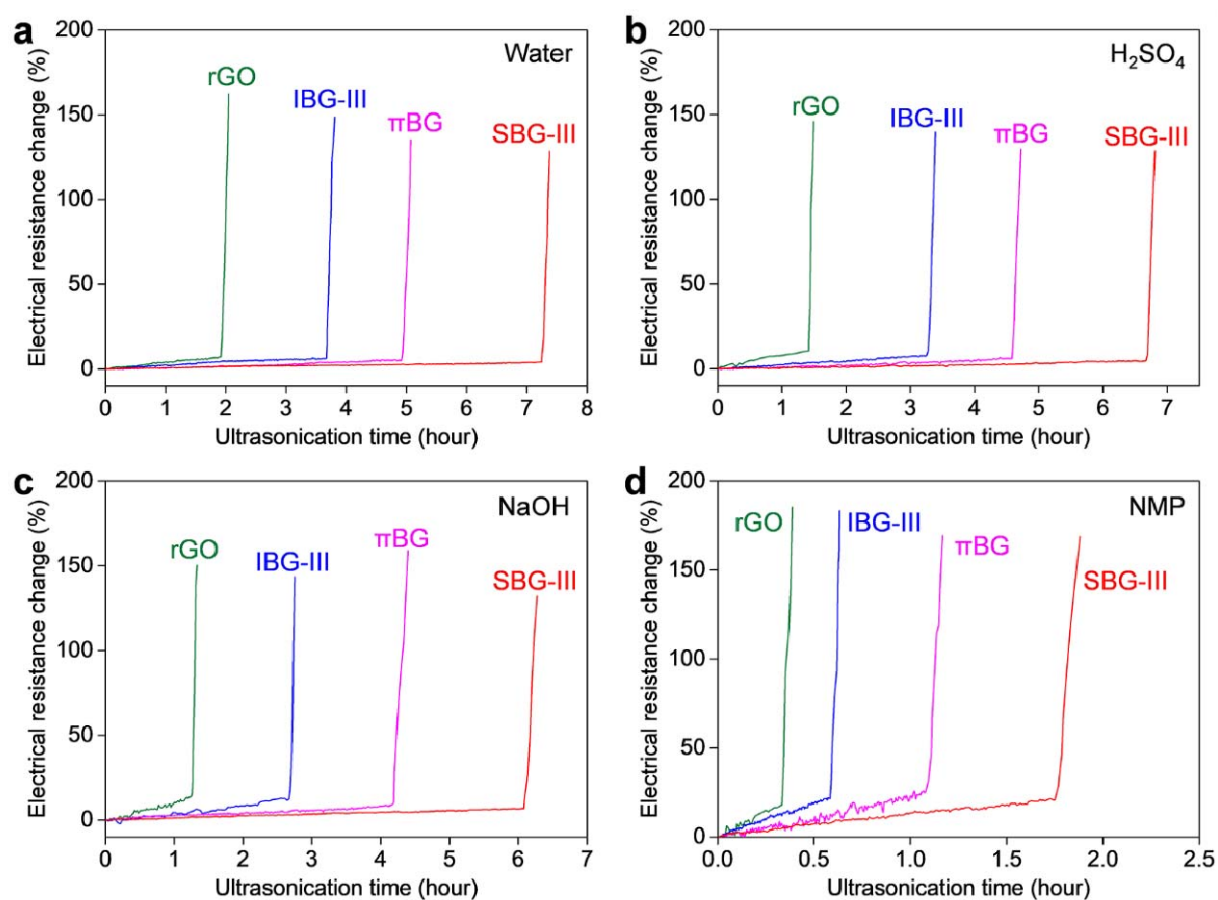


Figure S14. Change of electrical resistance as a function of ultrasonication time (using a 100 W, 40 kHz sonicator) for rGO, IBG-III, π BG, and SBG-III sheets in a) water, b) sulfuric acid (H_2SO_4 , with H^+ concentration of $8 \text{ mol}\cdot\text{L}^{-1}$), c) sodium hydroxide (NaOH, with OH^- concentration of $8 \text{ mol}\cdot\text{L}^{-1}$), and d) N-methyl-2-pyrrolidone (NMP) solutions.

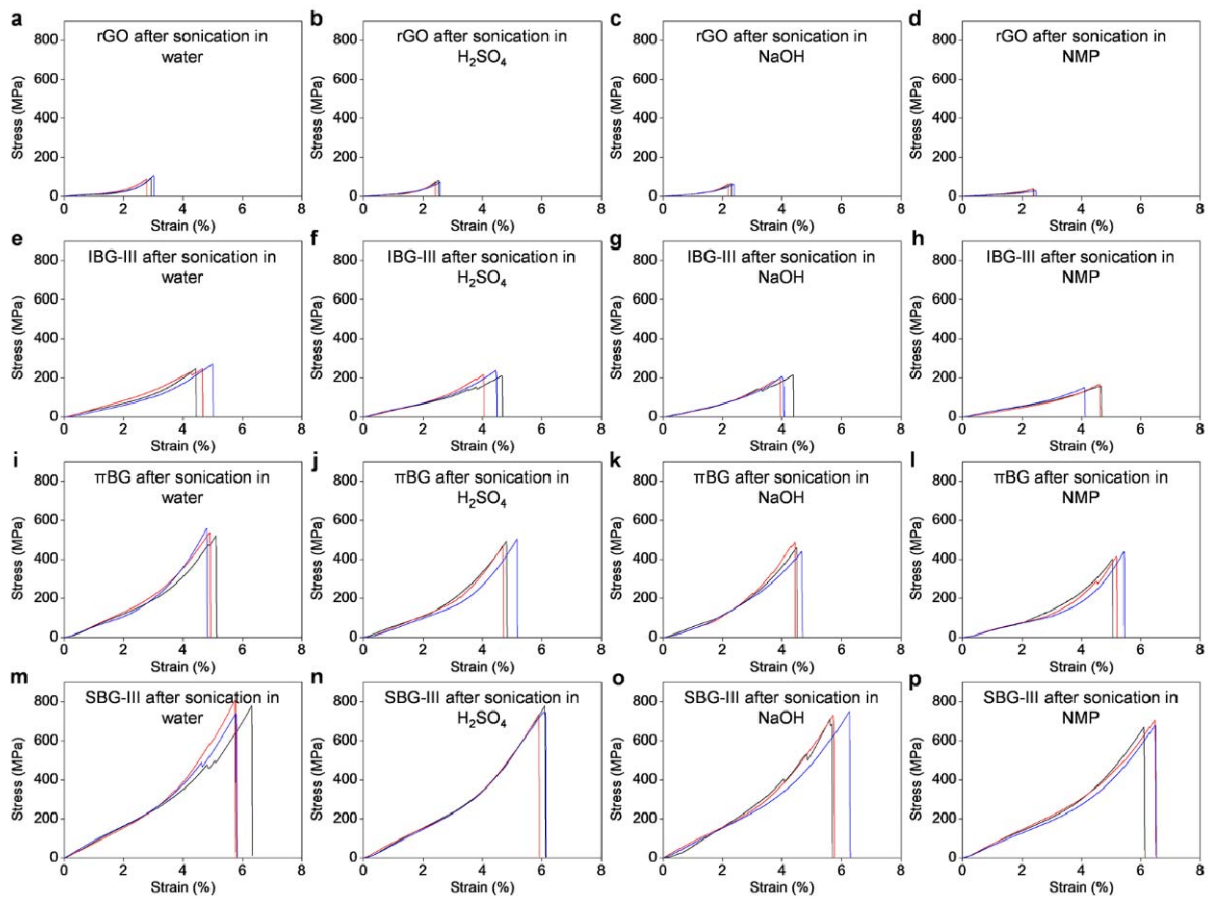


Figure S15. Tensile stress-strain curves for a-d) rGO, e-h) IBG-III, i-l) π BG, and m-p) SBG-III sheets after ultrasonication in water, H_2SO_4 , NaOH, and NMP for 1.92, 1.42, 1.25, and 0.33 hours, respectively.

Table S1. PSE-AP and Cr³⁺ content of IBG, π BG, and SBG sheets.

Sample	Cr ³⁺ content (wt%) by TGA	PSE-AP content (wt%) by TGA
IBG-I	0.27	-
IBG-II	0.68	-
IBG-III	0.83	-
IBG-IV	1.23	-
π BG	-	5.57
SBG-I	0.26	5.54
SBG-II	0.64	5.49
SBG-III	0.78	5.46
SBG-IV	1.16	5.40

Table S2. Normalized content of element C, O, and Cr in SBG-III sheet by energy-dispersive X-ray spectroscopy (EDS).

Element	Content (wt%)
C	83.72
O	15.41
Cr	0.87

Table S3. Interlayer spacing of GO, rGO, IBGO, IBG, π BG, and SBG sheets.

Sample	d (Å)
GO	8.04
IBGO-I	8.13
IBGO-II	8.16
IBGO-III	8.27
IBGO-IV	8.34
rGO	3.62
IBG-I	3.64
IBG-II	3.64
IBG-III	3.66
IBG-IV	3.68
π BG	3.72
SBG-I	3.73
SBG-II	3.74
SBG-III	3.75
SBG-IV	3.76

Table S4. Full width at half maximum (FWHM) for the 002 peak of rGO, IBG-III, π BG, and SBG-III sheets, when using Cu-K α radiation.

Sample	FWHM (°)
rGO	2.72
IBG-III	2.65
π BG	1.98
SBG-III	1.94

Table S5. Normalized content of element C, O, and Cr, and atomic ratios of Cr/C in IBGO-III and IBG-III sheets by EDS.

Sample	Element content (wt%)			Cr/C (atomic ratios)
	C	O	Cr	
IBGO-III	65.15	34.21	0.64	0.00227
IBG-III	83.16	15.99	0.85	0.00236

Table S6. O_{1s}/C_{1s} atomic ratios for GO, rGO, IBGO-III, IBG-III, π BG, and SBG-III sheets.

Sample	O _{1s} /C _{1s} (atomic ratios)
GO	0.42
rGO	0.17
IBGO-III	0.41
IBG-III	0.16
πBG	0.15
SBG-III	0.16

Table S7. *D/G* Raman intensity ratios for GO, rGO, IBGO-III, IBG-III, π BG, and SBG-III sheets.

Sample	<i>D/G</i>
GO	1.12
rGO	1.63
IBGO-III	1.29
IBG-III	1.74
πBG	1.64
SBG-III	1.74

Table S8. The thickness and mechanical properties of GO, rGO, IBGO, IBG, π BG, and SBG sheets and the thickness and mechanical properties of rGO, IBG-III, π BG, and SBG-III sheets after 100 cycles of 360° folding.

Sample	Thickness (μm)	Modulus (GPa)	Tensile strength (MPa)	Toughness ($\text{MJ}\cdot\text{m}^{-3}$)	Strain (%)
GO	6.2 ± 0.3	7.0 ± 0.4	132.9 ± 2.6	1.4 ± 0.2	2.6 ± 0.2
rGO	3.8 ± 0.1	2.7 ± 0.2	206.1 ± 3.0	2.7 ± 0.1	4.4 ± 0.2
rGO after folding	3.6 ± 0.2	2.3 ± 0.3	103.3 ± 6.2	1.5 ± 0.1	3.7 ± 0.2
IBGO-I	5.2 ± 0.2	7.2 ± 0.4	177.3 ± 5.5	2.1 ± 0.1	3.0 ± 0.1
IBG-I	3.1 ± 0.1	2.85 ± 0.3	251.4 ± 5.0	4.3 ± 0.1	5.3 ± 0.3
IBGO-II	5.0 ± 0.2	7.1 ± 0.5	218.8 ± 9.8	2.8 ± 0.1	3.1 ± 0.1
IBG-II	3.3 ± 0.1	3.6 ± 0.3	292.0 ± 8.2	6.7 ± 0.5	5.9 ± 0.4
IBGO-III	4.8 ± 0.2	9.1 ± 0.4	276.6 ± 6.0	4.3 ± 0.5	3.2 ± 0.2
IBG-III	3.2 ± 0.1	4.7 ± 0.4	342.5 ± 7.9	7.8 ± 0.2	6.1 ± 0.4
IBG-III after folding	3.5 ± 0.1	3.8 ± 0.4	249.6 ± 16.7	4.3 ± 0.3	4.8 ± 0.1
IBGO-IV	5.6 ± 0.2	11.0 ± 0.9	242.7 ± 7.9	3.1 ± 0.3	3.0 ± 0.3
IBG-IV	3.7 ± 0.2	6.5 ± 0.3	320.1 ± 7.8	7.4 ± 0.4	5.5 ± 0.3
πBG	3.6 ± 0.2	6.2 ± 0.4	623.5 ± 21.4	10.9 ± 0.7	5.7 ± 0.3
πBG after folding	3.8 ± 0.2	5.8 ± 0.5	515.8 ± 24.7	9.3 ± 0.3	4.9 ± 0.1
SBG-I	3.3 ± 0.1	7.4 ± 0.5	629.5 ± 14.7	11.8 ± 1.1	5.9 ± 0.4
SBG-II	3.0 ± 0.1	8.6 ± 0.6	680.5 ± 36.2	14.8 ± 0.4	6.0 ± 0.2
SBG-III	3.4 ± 0.1	9.3 ± 0.6	821.2 ± 17.7	20.2 ± 0.6	7.0 ± 0.1
SBG-III after folding	3.5 ± 0.2	8.6 ± 0.3	743.6 ± 21.3	19.6 ± 0.8	6.5 ± 0.3
L-SBG	3.3 ± 0.2	12.9 ± 1.5	924.8 ± 41.5	31.4 ± 0.5	7.4 ± 0.4
SBG-IV	3.3 ± 0.1	12.2 ± 0.3	670.4 ± 14.1	17.3 ± 0.6	5.9 ± 0.3

Table S9. Electrical conductivity, density, and gravimetric electrical conductivity for rGO, IBG-III, π BG, and SBG-III sheets. Gravimetric electrical conductivities were calculated by dividing the reciprocal of electrical resistance per sample length in the electrical conduction direction by the weight per sample length in the electrical conduction direction. Reflecting the accuracy of the density measurements for these thin sheets, nearly the same gravimetric electrical conductivity was obtained by dividing the electrical conductivity by the sample density.

Sample	Electrical conductivity ($\text{S}\cdot\text{cm}^{-1}$)	Density ($\text{g}\cdot\text{cm}^{-3}$)	Gravimetric electrical conductivity ($\text{S}\cdot\text{cm}^2\cdot\text{g}^{-1}$)
rGO	216.3 ± 18.5	2.02	107.1 ± 9.2
IBG-III	204.9 ± 16.1	2.07	99.0 ± 7.8
πBG	425.6 ± 24.2	2.06	206.6 ± 11.7
SBG-III	415.8 ± 26.3	2.10	198.0 ± 12.5
L-SBG	550.2 ± 23.8	2.04	269.7 ± 11.7

Table S10. Tensile strength and toughness of the SBG-III sheet and previously reported rGO sheets bridged through hydrogen bonding, ionic bonding, π - π bonding, covalent bonding, two building blocks, and two interfacial interactions.

Number	Materials	Tensile strength (MPa)	Toughness (MJ/m ³)	Reference
1	rGO-HPC	244.8	5.4	(36)
2	rGO-PAA	309.6	8.9	(35)
3	rGO-CMC	372.7	5.2	(34)
4	rGO-SF	300.0	2.8	(32)
5	rGO-PVA	188.9	2.5	(29)
6	rGO-Ni ²⁺	277.8	6.8	(39)
7	rGO-Zn ²⁺	355.6	4.2	(40)
8	rGO-Cu ²⁺	247.4	6.0	(36)
9	rGO-PAAP	97.5	1.1	(44)
10	rGO-AP-DSS	538.8	16.1	(42)
11	rGO-PB	8.4	0.01	(46)
12	rGO-PDA	204.9	4.0	(47)
13	rGO-PCDO	129.6	3.9	(52)
14	rGO-CNC	765.0	15.6	(65)
15	rGO-MMT-PVA	356.0	7.5	(73)
16	rGO-MoS ₂ -TPU	235.0	6.9	(68)
17	rGO-NFC-PCDO	314.6	9.8	(66)
18	rGO-DWNT-PCDO	374.1	9.2	(67)
19	rGO-WS ₂ -PCDO	413.6	17.7	(70)
20	rGO-PEI-CNC	655.0	1.8	(71)
21	rGO-Cu ²⁺ -HPC	274.3	6.7	(36)
22	rGO-PAPB	382.0	7.5	(72)
23	rGO-Zn ²⁺ -PCDO	439.1	7.5	(40)

24	rGO-PDA-Ni²⁺	417.2	19.5	(39)
25	rGO-CS	526.7	17.7	(69)
26	rGO-PAAP-Eu³⁺	131.2	1.7	(44)
27	rGO-CMC-Mn²⁺	475.2	6.6	(34)
28	rGO-PCDO-PSE-AP	944.5	20.6	(25)
29	SBG-III	821.2	20.2	This work

Table S11. Mechanical properties of rGO, IBG-III, π BG, and SBG-III sheets after ultrasonication (100 W at 40 kHz) in NMP, NaOH, H₂SO₄, and water for 0.33, 1.25, 1.42, and 1.92 hours, respectively.

Ultrasonication medium	Sample	Modulus (GPa)	Tensile strength (MPa)	Toughness (MJ·m ⁻³)	Strain (%)
NMP	rGO	1.0 ± 0.2	35.5 ± 4.8	0.3 ± 0.1	2.4 ± 0.1
	IBG-III	2.8 ± 0.3	158.1 ± 9.3	2.9 ± 0.3	4.4 ± 0.3
	π BG	4.6 ± 0.2	418.4 ± 18.9	7.0 ± 0.2	5.2 ± 0.2
	SBG-III	7.4 ± 0.3	686.2 ± 19.1	7.4 ± 0.3	6.4 ± 0.2
NaOH	rGO	1.3 ± 0.2	64.6 ± 1.0	0.5 ± 0.1	2.3 ± 0.1
	IBG-III	3.3 ± 0.2	206.5 ± 7.8	3.3 ± 0.4	4.1 ± 0.3
	π BG	5.5 ± 0.4	463.1 ± 24.6	7.6 ± 0.1	4.5 ± 0.2
	SBG-III	8.3 ± 0.5	731.5 ± 20.2	16.7 ± 1.2	5.9 ± 0.4
H ₂ SO ₄	rGO	1.4 ± 0.2	78.7 ± 4.8	0.6 ± 0.1	2.5 ± 0.1
	IBG-III	3.6 ± 0.2	221.2 ± 14.0	3.9 ± 0.4	4.4 ± 0.3
	π BG	5.7 ± 0.4	489.1 ± 17.7	8.2 ± 0.6	4.9 ± 0.3
	SBG-III	8.4 ± 0.3	753.2 ± 22.5	17.3 ± 0.8	6.0 ± 0.1
Water	rGO	1.8 ± 0.2	98.4 ± 9.4	0.7 ± 0.1	2.9 ± 0.1
	IBG-III	3.7 ± 0.4	254.3 ± 14.1	4.7 ± 0.5	4.7 ± 0.3
	π BG	6.0 ± 0.2	538.9 ± 19.3	9.5 ± 0.5	4.9 ± 0.2
	SBG-III	8.6 ± 0.9	775.1 ± 35.5	17.5 ± 1.3	6.0 ± 0.3