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Tellurium Nanowire-Induced Room Temperature Conversion of Graphite Oxide to Leaf-like Graphenic Structures

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A simple nanomaterial-based reduction strategy that can form leaf-like graphenic structures from graphite oxide (GO) at room temperature is described. Mixing of Te nanowires (Te NWs) with GO at room temperature was found to reduce GO while Te NWs are oxidized to TeO_3^{2-} . The reaction was followed time-dependently with use of UV/vis spectroscopy, fluorescence spectroscopy, and transmission electron microscopy (TEM). Raman spectroscopy was used to characterize the graphenic material. The G band, which was blue-shifted (with respect to graphite) in the case of GO, came back to the original position confirming the reduction. From IR spectroscopy, it was confirmed that the carboxylic acid groups in the GO are not getting reduced and the product gets stabilized electrostatically because of the repulsion between the negatively charged carboxylic acid groups. Reduction was confirmed by X-ray photoelectron spectroscopy (XPS) also. The reaction showed strong pH dependence and was found to be happening only in basic pH. In acidic medium, GO aggregates, making reduction difficult, while at higher temperature, the reaction was faster and at lower temperature it was retarded considerably.

Introduction

Carbon-based nanomaterials such as carbon nanotubes,¹ fullerenes,² and carbon onions³ have attracted a great deal of interest in the scientific community. The new member of this family is graphene. Graphene is the two-dimensional (2D) counterpart of naturally occurring 3D graphite, in which the carbon atoms are sp^2 hybridized.⁴ We can visualize graphite as a 3D macrostructure composed of several π -stacked graphene layers with an interlayer separation of 3.44 Å. The interlayer cohesive force, which holds these layers together, has been calculated to be 61 meV/C atom.⁵ Because of the inherent 2D structure and associated unique band structure, in conjugation with open surfaces and sharp edges, graphene offers great promise for potential applications in many emerging fields such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors, and gas storage.⁶ But for exploiting most of the proposed applications, there is a need to synthesize bulk quantities of graphene, as it is not a naturally occurring form of carbon. Several strategies are reported for its synthesis. One method is to mechanically peel off graphene layers by using a “Scotch” tape from naturally occurring graphite,⁷ until a single or a few layers of graphene are left behind on the parent structure. Even though most of the experimental studies done on graphene are produced by this method, the low productivity is a problem when considered for large-scale applications.

Chemical conversion from the thermodynamically most stable form, namely graphite, is being considered as the most viable and cost-effective strategy for the bulk production of graphene.⁸ Most of these reports are based on the oxidation and exfoliation of graphite to graphite oxide (GO) and subsequent production of graphene from GO through chemical conversion or thermal expansion/reduction. The work by Bordie in 1859 to produce individual graphene sheets by exfoliation is believed to be the

first attempt in this direction.⁹ Since then, several attempts have been made to synthesize graphene in the solution phase.⁸ Several of them were successful in making a few layers of graphene,^{8c,e} but the synthesis of a single layer of graphene has been largely unsuccessful. Graphene sheets have a very high specific surface area. So they tend to form irreversible agglomerates or even restack to form graphite through van der Waals interactions unless they are well-separated from each other. This has been found to be the reason for the failure of most of the solution-based routes to produce single-layer samples. The attachment of other molecules or polymers onto the sheets^{8c} is being projected as a way to avoid this aggregation. But these external molecules are undesirable for most applications. The high surface-to-volume ratio and sharp edges of the 2D graphite sheets, whether it is a single layer or a few layers, is considered to be useful for fuel cells and microelectronic applications.¹⁰ Individual graphite sheets could act as a good catalyst support or an efficient edge emitter for electron field emission. Recently graphite nanoplatelets attracted substantial interest as a feasible and inexpensive filler substitute for carbon nanotubes in nanocomposites,¹¹ given the predicted excellent in-plane mechanical, structural, thermal, and electrical properties of graphite.¹²

Recently, Li et al. reported a solution-phase methodology to produce processable aqueous dispersions of graphene nanosheets.^{13a} They reported that, from natural graphite, stable aqueous colloids of graphene nanosheets can be readily formed by chemical reduction methods which are believed to be stable due to electrostatic stabilization. Gilje et al. also reported a chemical route to produce graphene.^{13b} In this report also, GO was prepared from graphite by oxidation, which is dispersible in water as individual platelets. This upon deposition onto Si/SiO₂ substrates, followed by chemical reduction produces graphene sheets. In most of the reports, the reduction of GO was brought about by using a very common chemical reducing agent, namely hydrazine.

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More recently, a nanoparticle-based reduction process for production of graphene was reported by Williams et al.¹⁴ They succeeded in carrying out UV-induced photocatalytic reduction of graphene oxide by TiO₂ nanoparticles, giving well-separated graphene–semiconductor composite sheets. One-dimensional (1D) semiconductor nanostructures, such as nanowires (NWs),^{15a–c} nanorods (NRs),^{15d,e} and nanotubes (NTs),^{15f} have attracted a lot of interest because they can be used as model materials to investigate the dependence of various physical properties on dimensionality and size reduction. Also they are potential candidates for many applications in diverse fields.¹⁵ Trigonal Te (t-Te) is a well-known p-type narrow band gap semiconductor. It has good photoconductivity and has properties such as photoelectricity, thermoelectricity, catalysis, nonlinear optical properties, and high piezoelectricity.¹⁶ Also, t-Te NWs are being utilized as a template to synthesize new composite nanomaterials.¹⁷ Metals like gold and platinum are known to be reduced from the ionic state to the atomic form by Te NWs.¹⁸

All the synthetic strategies involving the chemical reduction of GO are tedious, and have to be done with care. The possibility of using nanomaterials to bring about reduction of GO is a comparatively new strategy. Also, reduction without the aid of any external stimuli such as UV irradiation or thermal aids has never been accomplished. In this article, a simple reaction between GO and Te NWs that can bring about the reduction of GO to leaf-like reduced graphite oxide (RGO) structures resembling graphene in water is reported. The resulting material is highly dispersible in water. We found that simple mixing of GO and Te NWs can bring about the reduction at room temperature. The reaction was followed by UV/vis spectroscopy, fluorescence spectroscopy, Raman spectroscopy, IR spectroscopy, and transmission electron microscopy.

Experimental Section

Materials. Sodium dodecyl sulfate (SDS, C₁₂H₂₅O₄Na, 99%) was obtained from Acros. Tellurium dioxide powder (99.9%) was purchased from Alfa Aesar. Natural graphite was purchased from Active Carbon India Pvt. Ltd., India. Sulfuric acid (H₂SO₄, 95–98%) and hydrochloric acid (HCl, 36%) were purchased from Ranbaxy chemicals, India. Phosphorus pentoxide (P₂O₅), hydrazine monohydrate (N₂H₄·H₂O, 99–100%), and hydrogen peroxide (H₂O₂) were purchased from SD Fine chemicals, India. Potassium peroxydisulfate (K₂S₂O₈) was purchased from Sisco Research Laboratories Pvt. Ltd., India. Potassium permanganate (KMnO₄) was purchased from Merck, India. All chemical were used as received without any additional purification. Triply distilled water was used all through this study.

Synthesis of Te Nanowires (Te NWs). Synthesis of Te NW followed the reported method by Lin et al.^{16k} In short, TeO₂ powder was slowly reduced with hydrazine hydrate in a beaker under constant stirring. After 1 h the color changed from colorless to blue indicating the formation of Te NWs. SDS was added to this solution to arrest the reaction and to protect the Te NWs formed. The as-prepared dispersion was centrifuged at 8000 rpm for 15 min to remove excess hydrazine and SDS. The centrifugation was repeated two more times and the residue was redispersed in equal amounts of triply distilled water to make the dispersion to the initial volume.

Synthesis of Graphite Oxide (GO). GO was synthesized from graphite powder by a modified Hummers method^{8f} as originally presented by Kovtyukhova et al.^{8g} To ensure the complete oxidation of graphite to GO, a preoxidation step prior to the actual oxidation step is usually done.¹³ This preoxidized

graphite is reported to become completely oxidized to GO during the oxidation step.^{8g,13}

Preoxidation of Graphite. Concentrated H₂SO₄ (50 mL) was heated to 90 °C in a 500 mL beaker and 10 g of K₂S₂O₈ and 10 g of P₂O₅ were added with stirring until all the reactants were completely dissolved. The reaction temperature was decreased to 80 °C. Then 12 g of graphite powder was added slowly to the H₂SO₄ solution. This resulted in bubbling that subsides within 30 min. This reaction mixture was kept at 80 °C for 4–5 h. After 5 h, the heating was stopped and the mixture was diluted with 2 L of distilled water and left overnight. The mixture was then filtered and washed to remove all traces of acid. The resulting solid was dried in air overnight.

Oxidation to Graphite Oxide (GO). Concentrated H₂SO₄ (460 mL) was kept in an ice bath maintained at 0 °C. The preoxidized graphite was then added to the acid and stirred. KMnO₄ (60 g) was added slowly and allowed to dissolve. The addition was done carefully so that the temperature of the reaction mixture never went beyond 10 °C. This mixture was allowed to react at 35 °C for 2 h. After 2 h, 1 L of distilled water was added. Water addition was done in such a way that the temperature did not exceed 50 °C. The mixture was stirred for an additional 2 h. Then 3 L of distilled water and 50 mL of 30% H₂O₂ were added. The mixture was kept undisturbed for a day and then the supernatant was decanted. The remaining solution was centrifuged and washed with 10% HCl solution several times, followed by washing with distilled water. The resulting solid was dried in air and diluted to make a 2% (w/w) dispersion. It was then put through dialysis for 3 weeks to remove any remaining metal contamination. This 2% dispersion was diluted to 0.5%.

Reduction of GO to Reduced Graphite Oxide (RGO) Structures by Te NWs. Twenty-seven milliliters of the 0.5% dispersion of GO was taken in a beaker and 3 mL of the purified Te NWs dispersion was added. The dispersion was then kept undisturbed for 36 h. The volumes used in the synthesis were optimized, as discussed later.

Methods. The UV/vis spectrum of each sample was measured time-dependently by using a Perkin-Elmer Lambda 25 UV/vis spectrophotometer. Simultaneously small aliquots of the reaction mixture were dropped onto a carbon-coated copper grid at various time intervals and dried in ambient conditions. These samples were examined with a JEOL 3011, 300 kV transmission electron microscope (TEM) with a UHR polepiece. Detailed control experiments involving UV/vis and HRTEM were performed. For the infrared spectra, vacuum-dried samples were made in the form of KBr pellets, and the spectra were measured with a Perkin-Elmer Spectrum One FT-IR spectrometer. Raman spectra were measured with a WiTec GmbH confocal micro Raman. Fluorescence spectra were measured with a Nanolog HORIBA JOBINYVON spectrofluorimeter with a 100 W xenon lamp as the excitation source at a scan speed of 240 nm/s. The band-pass for both excitation and emission monochromators was kept at 5 nm. X-ray diffraction (XRD) data were collected with a Bruker AXS, D8 Discover, U.S.A diffractometer, using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). A scan step of 1 s and step size (2θ) of 0.1° were applied to record the patterns in the range from 5° to 90° (2θ). A software database published by the Joint Committee on Power Diffraction Standards (JCPDS) was used to analyze the X-ray diffractogram. X-ray photoelectron spectroscopy (XPS) measurements were done with a Omicron ESCAProbe spectrometer with monochromatized Al K α X-rays ($h\nu = 1486.6 \text{ eV}$). Six spectra in the desired binding energy range were averaged. The samples were spotted as drop cast

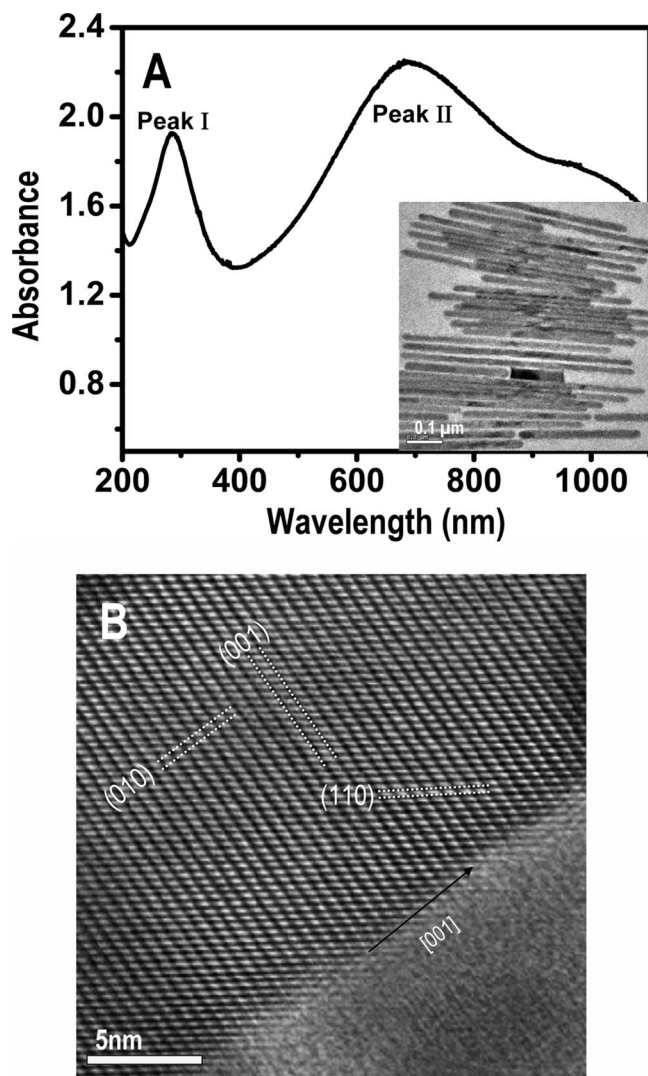


Figure 1. (A) UV/vis spectrum of pristine Te NWs after three centrifugation/redispersion cycles. The inset shows a large area TEM micrograph of the pristine Te NWs. (B) Lattice resolved image of the body of a single Te NW with lattice planes marked with dotted lines.

films on the sample stub, and the surfaces were scraped in situ to remove any surface contamination that could arise from components of the atmosphere such as water and CO_2 . X-ray flux was adjusted to reduce the beam-induced damage of the sample. The energy resolution of the spectrometer was set at 0.1 eV at a pass energy of 20 eV for typical measurements. SEM images were taken with FEI quanta 200.

Results and Discussion

Figure 1A shows the UV/vis spectrum of pristine Te NWs after purification by centrifugation and redispersion. t-Te NW is known to have two characteristic peaks in the UV/vis spectrum.¹⁶ Peak I centered around 280–300 nm is believed to be due to the transition from the p-bonding valence band (VB_2) to the p-antibonding conduction band (CB_1). The second peak centered around 650–695 nm (peak II) is due to the transition from the p-lone-pair valence band (VB_3) to the p-antibonding conduction band (CB_1).^{16k} In a particular synthesis, peak I was centered at 286 nm and peak II was centered at 680 nm. The inset of Figure 1A shows a large area TEM image of the as-prepared Te NWs sample. All the wires were straight. Most of

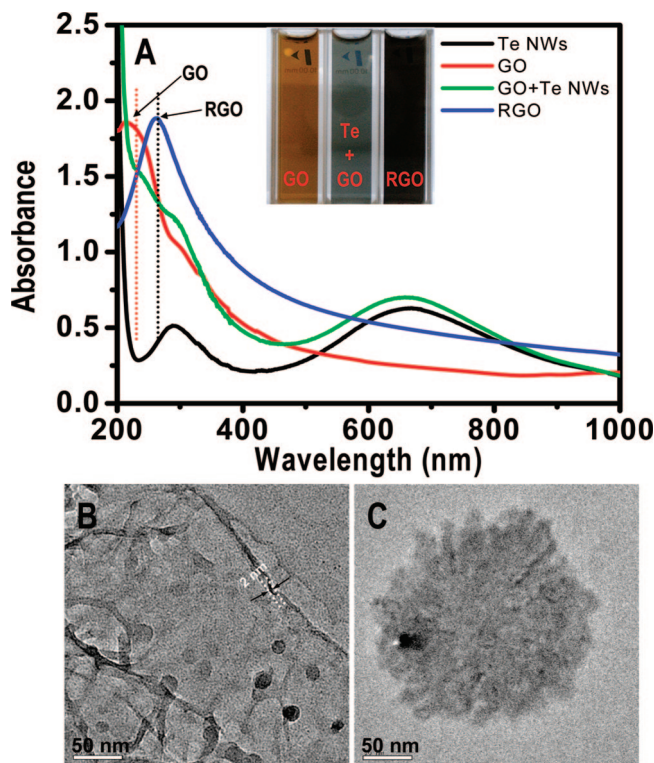


Figure 2. (A) UV/vis spectra showing the characteristic spectral changes at various stages of the reaction. The inset shows a photograph of the different dispersions taken in the UV/vis cuvette. The peak positions of GO and RGO are marked with red and black dotted lines, respectively. TEM image of (B) starting GO showing a folding of the sheet, marked with dotted lines, and (C) leaf-like graphenic structure.

them have the same size with an average diameter of 20 nm and length around 590 nm. The high magnification image in Figure 1B showed three representative planes of t-Te NWs, with interplanar spacings of 0.59, 0.39, and 0.22 nm which correspond to (001), (010), and (110), respectively.^{16k} The crystals were structurally uniform and there were no defects or dislocations indicating that the t-Te NWs are single crystals.

Figure 2 shows the spectral changes observed during the reaction between GO and Te NW. The black trace shows the UV/vis spectrum of t-Te NW before the reaction. Peaks I and II were centered at 286 and 680 nm, respectively. GO is known to show an absorption centered around 230 nm.¹³ When GO and Te NW were mixed, only peak II of the NW and that due to the GO around 230 nm were visible. Due to the higher absorbance of GO, peak I may be getting masked in the spectrum. As the reaction was complete, there was a red shift for the GO peak from 230 to 268 nm (marked by dotted lines). This indicates the reduction of GO to reduced graphitic or graphene-like structures (RGO). The red-shift in the spectrum is explained as due to the restoration of conjugation in the reduced structure, which was disrupted in the case of GO.¹³ The absorption features due to Te NWs (peaks I and II) were completely absent from the spectrum, implying that the Te NWs are reacted during the reduction of GO. The reaction was complete in 36 h. No further spectral changes were observed after this, pointing to the completion of the reaction. The inset photograph in panel A shows the color changes accompanying the reaction. The brownish yellow GO changes to bluish green upon the addition of Te NWs and after the completion of the reaction; we obtain a black dispersion characteristic of graphene dispersion.

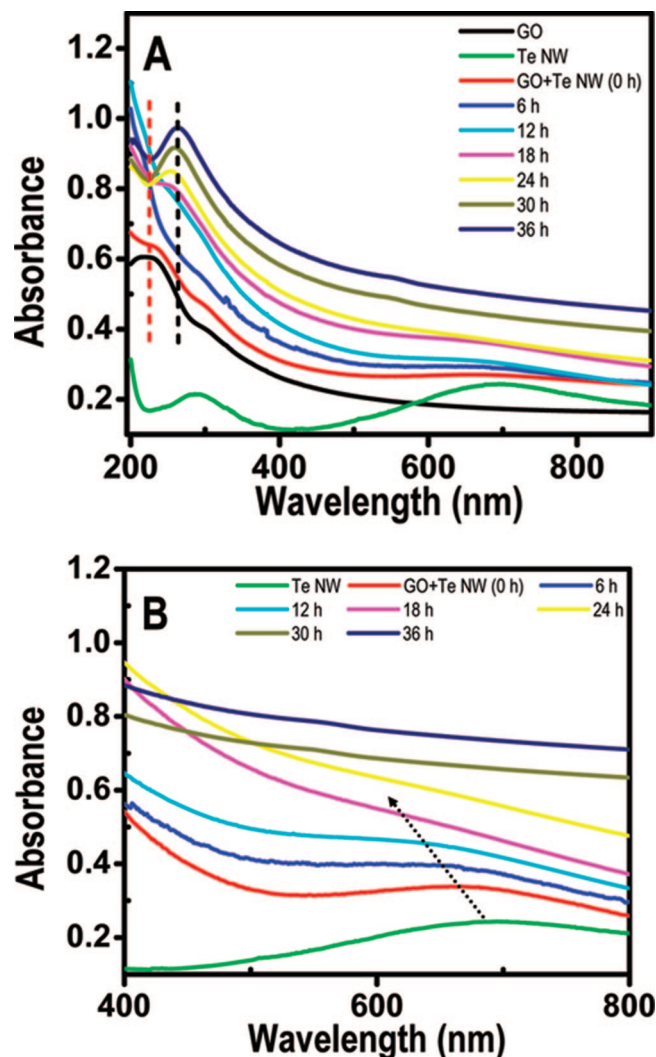


Figure 3. (A) Time-dependent UV/vis spectra of the reaction between Te NW and GO. Spectra were taken every 6 h of the reaction. The initial peak position of GO and that after the formation of RGO structures are marked with red and black dashed lines, respectively. (B) Expanded view of the spectral changes around peak II. The gradual shift in peak position is marked.

Figure 2B shows the TEM image of the starting GO. A sheet-like structure can be seen in the image. The edge of the GO sheet was found to be curled. One such edge was measured to be 2 nm in width (marked in Figure 2B). The GO films were better visible in SEM (Supporting Information, Figure S2). SEM showed sheets of GO over a micrometer in area. They were found to be almost transparent emphasizing the proposition that the sheets are really thin, which is seen from the TEM image also (Figure 2B). The sheet was found to be very thin consisting of a few layers. GO is known to form stable dispersions in water medium, once it is fully oxidized, because of electrostatic stabilization.^{13,19} Carboxylic acid and phenolic hydroxyl groups are known to exist in GO,²⁰ which upon ionization are known to give negative ζ -potential to the GO surface.¹³ This negative surface charge induces electrostatic repulsion and as a result, GO becomes stabilized in a water dispersion. Figure 2C shows a leaf-like 2D structure, which is the product obtained after the completion of the reaction. This is quite different from the starting GO. This will be explained later in the text.

Time-Dependent Study of the Reaction. The reaction was followed in a time-dependent manner by using UV/vis spectroscopy, TEM, and fluorescence spectroscopy. Figure 3 shows

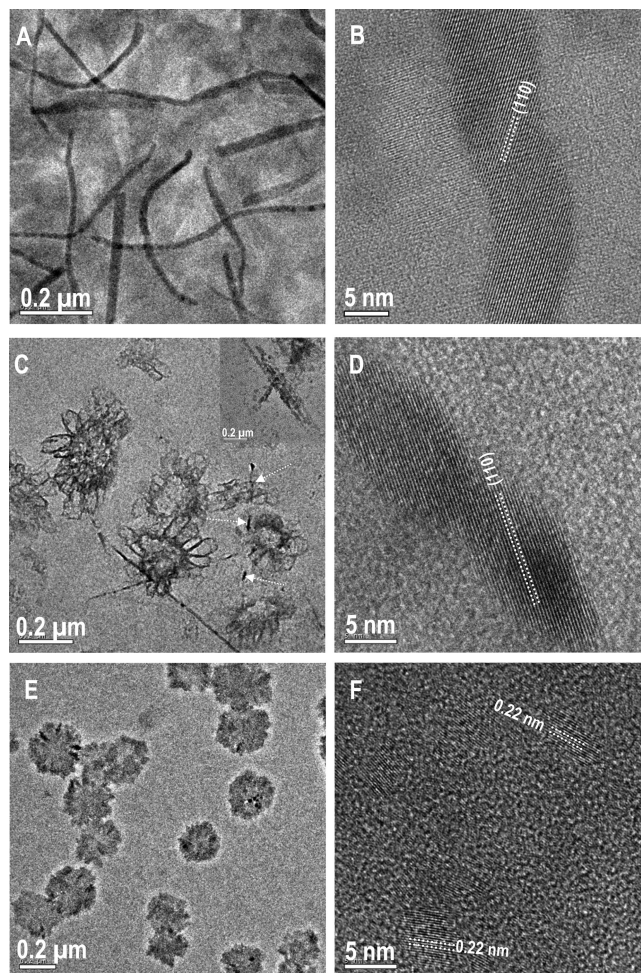


Figure 4. TEM images (A) after 12 h of the reaction showing the bent NWs, (B) lattice resolved image of a bent NW showing the (110) plane (dotted lines), and (C) after 30 h of reaction showing the flower-like structures and broken Te NW (dotted arrows). The inset shows a bunch of broken Te NW found in some other area. (D) Lattice resolved image of a broken NW showing the (110) plane with dotted line, (E) low-magnification image of leaf-like structures formed after the completion of the reaction (36 h), and (F) high-magnification image of a single leaf-like structure. We can see small areas showing the lattice structure, which corresponds to the (110) plane of t-Te.

the time-dependent UV/vis spectrum of the reaction. Spectra revealed a galvanic-like reaction between GO and Te NWs. As the peak at 230 nm corresponding to GO red-shifts, showing the reduction to graphenic structures, peak II of Te NWs blue-shifted. The blue shift was accompanied by a flattening of the peak also. The blue-shift in peak II of Te NW and the red-shift of the GO feature occurred together, implying that both processes are related. In Figure 3A, we see that the GO feature at 230 nm vanishes after 6 h of reaction, leaving behind a small hump around the same spectral range. After 12 h of reaction, the hump red-shifts to 242 nm. After 24 h of reaction, a well-defined peak appears around 255 nm that red shifts to 264 nm after 30 h. After 36 h, the peak was centered at 268 nm. After this, there was no further shift in the peak position, implying the completion of the reaction.

Figure 3B shows the spectral changes of peak II of Te NWs time-dependently. Initially, it was centered at 680 nm. Immediately after the addition of GO into Te NWs, there was a blue shift of 17 nm, and the peak was centered at 663 nm. This can be considered as due to the interaction of GO with Te NWs. After 6 h of reaction, it shifted to 648 nm and after 30 h of

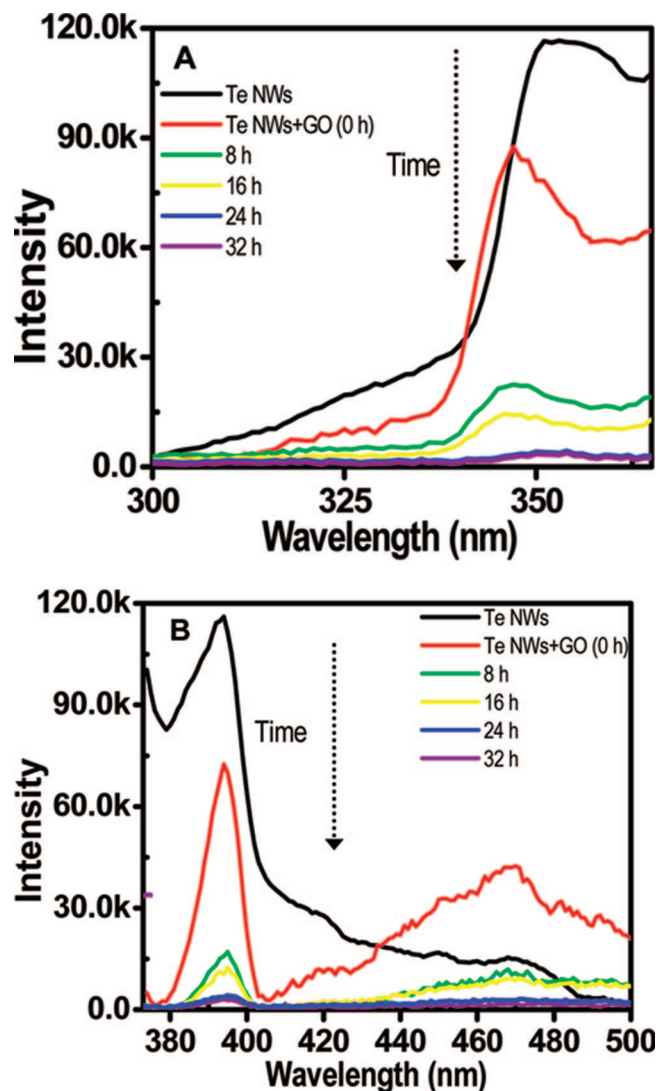


Figure 5. Time-dependent fluorescence spectra of Te NWs during the reaction: (A) excitation spectra and (B) emission spectra.

reaction it disappeared completely. It is already reported that changes in peak I correspond to diameter changes and a blue-shift in peak II corresponds to a decrease in aspect ratio.^{16k} In our case, the blue-shift continues until 30 h, where it completely

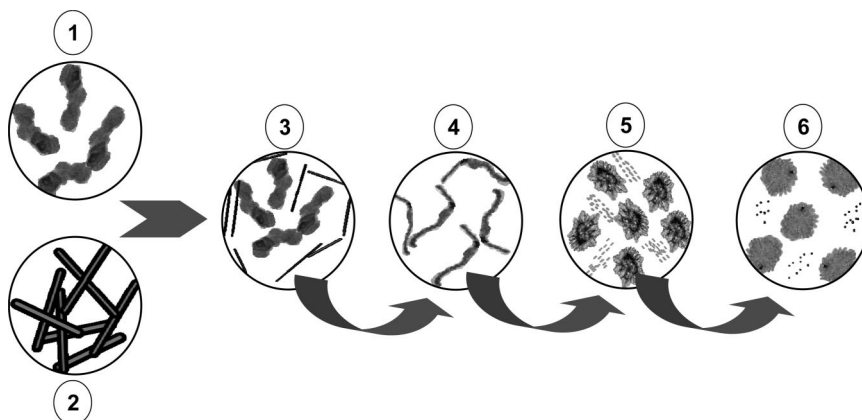
vanishes. This can be directly correlated to a decrease in the aspect ratio of the Te NWs due to reaction with GO. We can also see a flattening of the peak as the reaction goes on before it finally disappears. There was a concomitant change in GO features also. We can see the gradual red-shift of the GO peak from 230 to 268 nm confirming the reduction, which is marked by dashed lines in Figure 3A.

When the reaction starts, Te NWs starts to react with GO. After 12 h of reaction, we found that the NWs are mostly bent and because of the reaction, they tend to break into smaller NWs (Figure 4A). During the reaction, the sides of the nanowires are etched away, giving them a bent morphology (Figure 4B). Figure 4B shows a high-magnification image of a bent NW. We can see even the defect sites produced on the NW due to the reaction. The lattice spacing in the NW was found to be 0.22 nm, which corresponds to the (110) plane of t-Te. Figure 4C was taken from the sample after 30 h of reaction. Te NWs were barely visible and some flower-like structures were seen all through the grid. Very few broken Te nanostructures were seen (denoted by dotted arrows). The inset of Figure 4C shows a bunch of broken t-Te NW after 30 h of the reaction. This indicates that most of the NWs have reacted with GO, in the process reducing them to these flower-like structures. Figure 4D shows a lattice resolved image of a piece of a broken NW. From the lattice spacing, it was attributed to t-Te.

After the completion of the reaction (36 h), only some leaf-like structures were present. Te NWs were completely absent in the reaction mixture. Figure 4E is a large area TEM image showing several leaf-like graphenic structures. Several dark spots are visible in the graphenic structures, probably due to Te particles. A high-magnification image of a single structure is shown in Figure 4F. It showed some lattice structures inside. The lattice spacing was found to be 0.22 nm, which corresponds to the (110) plane of t-Te. This may be a portion of the Te NW left behind after the completion of the reduction reaction. We tried to take high-magnification images of the edges of the structure. We could not see any graphitic layered structure. This points to the fact that the structure produced after the reaction contains a only very few layers of graphene, if not a single layer.

Te is a p-type semiconductor material known to show fluorescence in the range of 390 to 550 nm depending upon the aspect ratio of the nanowires.^{16k} The reaction was followed time-dependently by using fluorescence. Figure 5 shows the time-dependent fluorescence spectra of the reaction. In a typical

SCHEME 1: Pictorial Representation of Various Reaction Products Formed during the Reaction between GO (1) and Te NWs (2)^a



^a In the scheme, 3 corresponds to a mixture of 1 and 2, 4 represents bent Te NW during reaction, 5 shows flower-like graphitic structures and broken Te NWs, and 6 shows leaf-like graphenic structures after the reaction.

synthesis, the excitation at 350 nm gave emission at 394 nm for a bare Te NWs sample. After the addition of GO into this sample, the excitation spectrum showed a small blue-shift of 3 nm. This small blue-shift may be attributed to the interaction between GO and Te NWs. In the emission spectrum, the maxima did not show any appreciable shift, but a new background peak emerged around 475 nm, attributed to GO, which is known to produce a fluorescence background.^{21c} As the reaction progressed, the fluorescence also decreased showing that the reactant, Te NW, is being used up in the reaction. There was a simultaneous reduction of background fluorescence due to GO. Considering the UV/vis and fluorescence spectral observations, the reduction of GO to graphene-like material by Te NWs can be concluded. It can also be inferred that the reaction is redox-like in nature where Te NW is being oxidized and GO is being reduced simultaneously.

As the reaction goes on, the Te NWs reacted and dissolved in the reaction medium in the form of TeO_3^{2-} and GO was reduced progressively to graphenic structures. Scheme 1 is a pictorial representation of the reaction and the product formed in a time-dependent manner.

Raman intensities of conjugated double bonds are usually very high. Therefore, Raman spectroscopy is considered to be an efficient tool for characterizing carbon materials. Natural graphite has mainly two Raman-active bands. One is called the G-band, which is due to the in-phase vibration of the graphite lattice and is centered at 1575 cm^{-1} . This is known to be the most prominent band in the graphite spectrum. The second one, called the D-band or the disorder or defect band, is due to the defects in the graphite edges and is centered at 1355 cm^{-1} .²¹ Usually, in highly ordered graphite, this peak will be very weak or even absent. The lattice vibration that corresponds to the frequency of the D band is always present in all infinite graphene sheets, but it is forbidden by symmetry rules. When the edges break the symmetry, hence the symmetry rules, this band begins to appear.²¹ Both G and D bands undergo several changes when crystalline graphite changes to amorphous form or to a single layer of graphene. These changes are believed to be due to the fraction of sp^3 carbon present in the amorphous form.²² It is also reported that as the defects in graphite increase, the G band becomes more broadened and the D band increases in intensity and becomes more broad as well.^{21,22} Figure 6 shows the Raman spectra taken from various samples during the reaction. Graphite showed a very sharp G band at 1570 cm^{-1} . There was a very weak D band also located at 1345 cm^{-1} . As expected, both G and D bands broadened and the D band increased in intensity in the case of GO and RGO structures. There was a shift in the position of the G band in the case of GO and RGO compared to graphite. This can be clearly seen in Figure 6B, where an expanded view of the region between 1100 and 1700 cm^{-1} is given. In the case of GO, the position of the G band shifted to higher frequency and was located at 1588 cm^{-1} . As all the measurements were done with the same laser (514.5 nm), this shift compared to the graphite G band is not due to changes in laser frequency, which is reported to affect the D band position in the case of graphite.²²

The blue-shift of the G band is already reported in the case of amorphization of graphite.²² A similar shift has been reported in the case of GO formation also.²¹ It is reported that in graphite with sufficient amount of defects, another band called the D' band arises above the G band due to the presence of nonzero phonon density of states. This will become Raman active only when it is confined inside the defect and is located around 1620 cm^{-1} .^{21a,23} This can merge with the G band and can give rise to

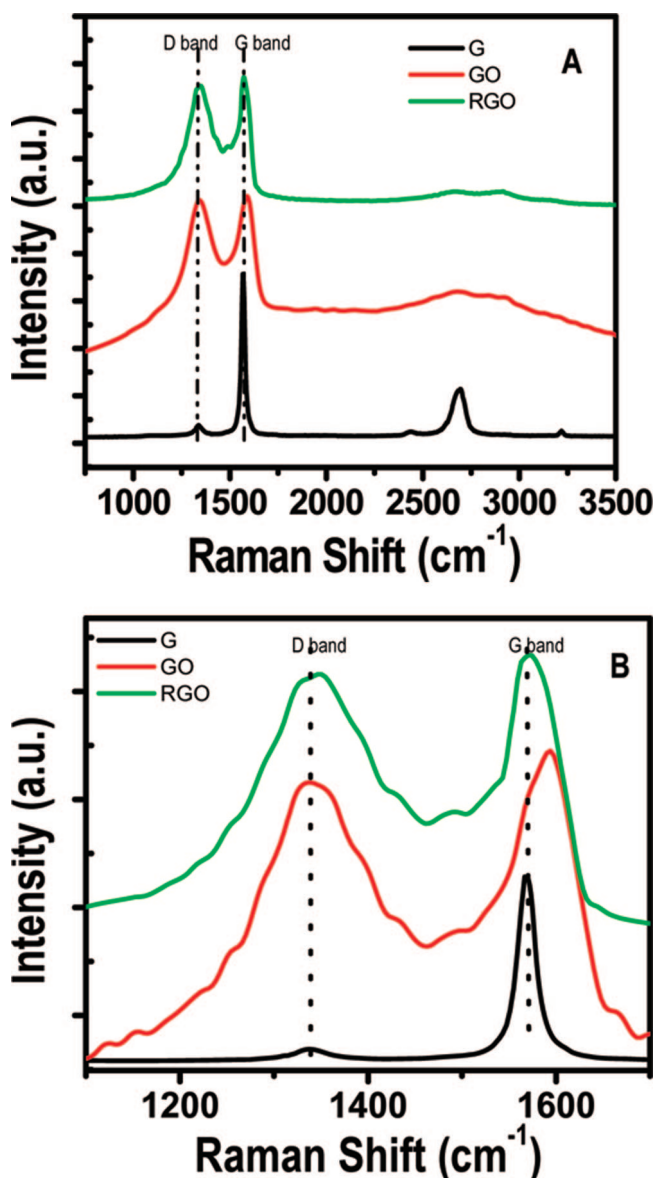


Figure 6. (A) Raman spectra of graphite (G), GO, and RGO. (B) Enlarged view of the same spectra showing the shift in the G-band.

a shift in the G band position. Specific double bonds that are reported to be present in GO¹³ resonate at a higher frequency than the G band. The influence of this resonance also is reported to be the most important reason for this blue shift.^{21b} Both these effects are considered to be the cause of the blue shift observed in GO.

It can be also observed in Figure 6B that upon reduction, the G band comes back almost to the original position, even though not to the exact value. Upon reduction of GO to RGO, there is a certain amount of restoration of graphitic order. Similar effects were seen in heat-treated graphite samples also with a sharpening of the G band and decrease in intensity of the D band.^{21b,24} This has been termed as graphitic “self healing”.^{21b} So from the spectral changes in Figure 6B, it is clear that the GO is indeed being reduced to graphene-like graphitic structures. In mechanical synthesis, graphene is characterized by a third band, the G' band, centered at $\sim 2700\text{ cm}^{-1}$.^{25a} Comparing the intensities of G and G' bands, it is possible to calculate the number of layers in a graphenic sample.²⁵ But in the case of chemically synthesized graphene, the G' band is not as prominent.¹³ Usually the reduction is characterized by the shift of the G band as

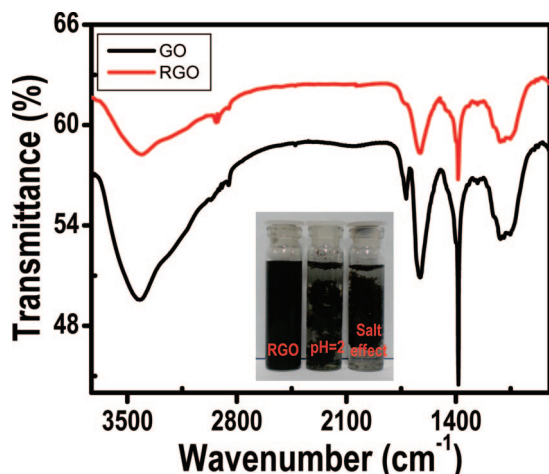


Figure 7. IR spectra of GO and reduced RGO. The inset photograph shows the aggregation of RGO at acidic pH and the salt effect upon addition of sodium chloride, confirming the colloidal nature of the RGO dispersion, which is stabilized electrostatically.

mentioned earlier.^{13b} A prominent G' band was not observed (Figure 6A).

The stabilization of the formed graphenic structures in water was investigated. We found that the dispersion is stable for months and no settling happened even after centrifugation at 8000 rpm. This stability is similar to that of GO. GO is known to have many functional groups like epoxides, esters, carbonyl, hydroxyl, and carboxylic acid groups.^{13,23c} It is well-known that GO is being stabilized in water electrostatically. The presence of carboxylic and phenolic hydroxyl groups makes the GO surface negatively charged and by electrostatic repulsion, they are stabilized in dispersion. We believe that the presence of carboxylic acid groups, which may not be reduced as in some of the earlier reports on graphene,^{8a,13} in RGO may be the reason for its stabilization. In the Raman spectrum, the G band did not come back exactly to the original graphitic position. This may be due to the presence of these carboxylic acid groups. So in our reaction, most of the carbonyl groups other than the carboxylic acids in GO are reduced. These unreduced carboxylic acid groups may be providing stabilization for the RGO structures. We measured the IR spectra to find the presence of such functional groups both in GO as well as in RGO. For this, the samples (both GO and RGO) were dried in ambience and solid powders obtained were used for analysis.

Figure 7 shows the typical IR spectra obtained from GO and RGO. Both spectra are essentially the same. However, when compared to GO, the peak intensities have been considerably reduced in the case of RGO. Four major peaks of interest were seen in GO. The first observable feature in the case of GO was centered at 1715 cm^{-1} and is often related to the C=O stretching of the COOH groups situated at the edges of the GO. It is also reported that functional groups other than COOH, anhydrides, or lactones which are expected to give carboxylates via alkaline hydrolysis will also give a $\nu_{\text{C=O}}$ signal around the same frequency.^{20c} The second prominent feature present in GO was centered at 1670 cm^{-1} . This may be due to the carbonyl groups, other than the carboxylic carbonyl groups, which normally come at lower values. This feature can also be attributed either to oxygen compounds like cyclic ethers or to ring vibrations throughout the carbon skeleton.²⁰ The HOH bending vibrations also appear in a very close range. The third prominent feature was centered at 1370 cm^{-1} , which has a sharp peak and a broad shoulder. Amorphous carbon is known to produce such a sharp

peak in this region.²⁶ The broad shoulder may be due to the O—H deformations of the tertiary C—OH groups as reported in the case of GO.^{26,20d} A fourth strong broadband at 1100 cm^{-1} is attributed to C—O stretching vibrations.²⁶ There were prominent changes in the spectrum of the GO after reduction. In the RGO sample the peak at 1715 cm^{-1} diminished in intensity and became a shoulder of the feature at 1670 cm^{-1} implying the reduction of most of the oxygenated species other than carboxylic acid groups which are difficult to reduce. Importantly, the intensity of the peak around 1670 cm^{-1} is greatly decreased in the RGO sample. This peak is very prominent in the GO sample. This implies the reduction of carbonyl groups. But the peak due to C—O stretching at 1100 cm^{-1} is still prominent in the RGO spectrum. This points to the fact that carboxylic acid groups present in the GO sample are still present in the RGO sample. The intensity of the sharp feature at 1375 cm^{-1} has been reduced, implying reduction in the amorphous character. The inset photograph shows the aggregation of the RGO dispersion upon changing the pH to 2. This can be explained by the fact that at acidic pH, the carboxylic acid groups which gave stabilization to RGO will be in the protonated state. Hence the electrostatic repulsion, which is responsible for the stabilization, will be absent at acidic pH. Therefore, RGO dispersion will aggregate. According to the classical Derjaguin—Landau—Verwey—Overbeek theory,^{27,13a} a colloidal dispersion that is stabilized by electrostatic interaction is known to coagulate upon addition of an electrolyte into the aqueous dispersion. This is commonly known as the “salt effect”. To check this, we added a small amount of sodium chloride into the RGO dispersion. An immediate coagulation was observed. The inset of Figure 7 shows the photographs of various dispersions. From these observations it is clear that the RGO is stabilized electrostatically by the carboxylic acid groups which are not reduced in the reduction reaction. Further studies on this are in progress.

The reduction of GO to RGO was characterized by using XPS as well. The C1s XPS signature has been used to differentiate between GO and RGO.^{8a,c} The C1s XPS spectrum of GO (Figure 8A) indicated a significant degree of oxidation with four major signatures corresponding to carbon atoms in different functional groups, which were also seen in the IR spectra.^{8a,c} They are non-oxygenated ring C at 284.8 eV , C of C—O bonds at 286.7 eV , C of C=O at 288.1 eV , and that of carboxylate (O—C=O) at 289.6 eV . All of these features agree well with the literature values of GO.^{8a,c,28} The C1s XPS of RGO also showed similar spectra but the intensities of oxygenated carbon peaks are considerably decreased implying reduction.^{8a,c} The reduction is incomplete as suggested by the electrostatic stabilization discussed above.

Effect of pH on the Reduction Reaction. GO to begin with was acidic with a pH of 3.8, which is reasonable considering the amount of acids used during the oxidation process. This GO was subjected to dialysis for 3 weeks to remove the excess acids and metal ions present. After dialysis the pH of the sample was increased to 6.2. The pH of the as-prepared Te NWs sample was 9.2 due to the presence of excess hydrazine present after the reduction. After 3 centrifugation and redispersion cycles, the pH reduced to 7.8 showing that most of the unreacted hydrazine has been removed. After the addition of Te NWs to the GO suspension, the pH of the reaction mixture was found to be 7.6. To check whether there is any influence of pH in the reaction, we carried out the reaction at very high pH (10) and also at a very low pH (2).

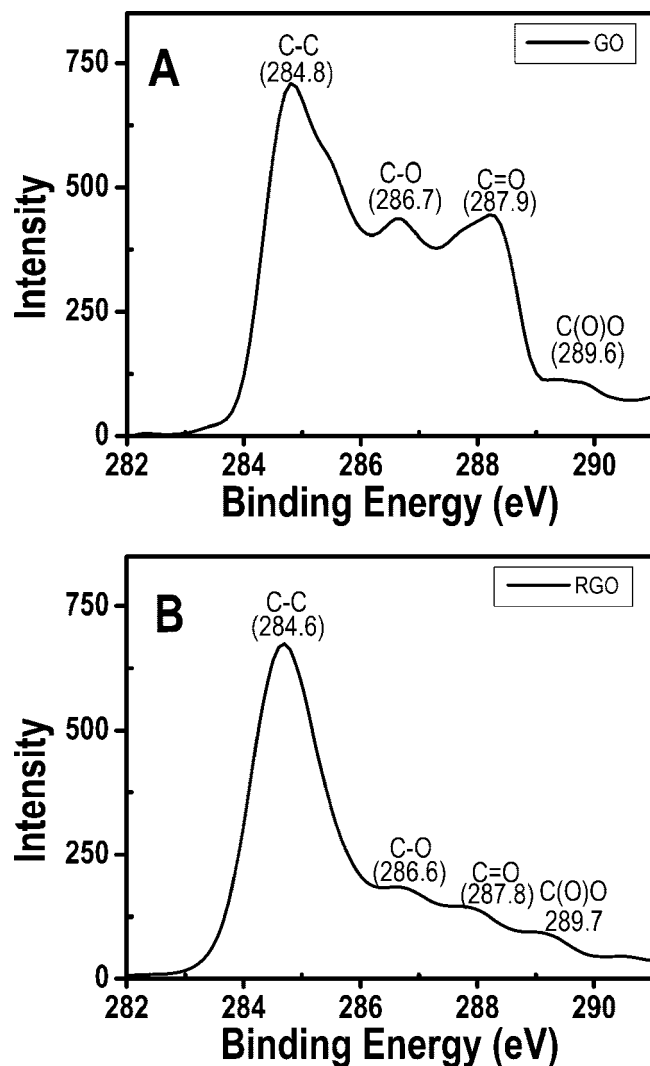


Figure 8. The C 1s XPS spectra of (A) GO and (B) RGO.

Figure 9A shows the reaction carried out at a pH of 10. The reaction followed a similar path and the spectral changes were similar to those of the earlier reaction. This is in the expected line because the normal reaction also was taking place in a slightly alkaline condition itself. So increasing the alkalinity of the reaction medium did not affect the nature of the reaction. The product was found to be more stable, forming a clear dispersion. This is understandable because at higher pH conditions, more and more carboxylic and hydroxyl groups will be in the ionized form giving extra electrostatic stability to the formed product. Figure 8B shows the UV/vis spectra of the same reaction carried out at an acidic pH (pH 2). Here the reaction was not found to be happening at all. Even after 36 h of reaction, there was only a very small shift for the GO peak at 230 nm. Also the sample was found to be agglomerating after some time and started settling. This prevented interaction between Te NW and GO. Thus the reduction reaction did not happen at acidic pH. This aggregation can be explained by the fact that at acidic pH, the carboxylic acid groups present on GO will not be ionized and they will be in the protonated form. In this form, these groups cannot induce any electrostatic repulsion between GO, which is believed to be the primary reason for the stabilization of GO in the solution phase.¹³ Therefore, in the acidic pH, all the GO present in the dispersion separate out. The big particulates formed during the agglomeration of GO, which scatters more, caused an increase in the background of the

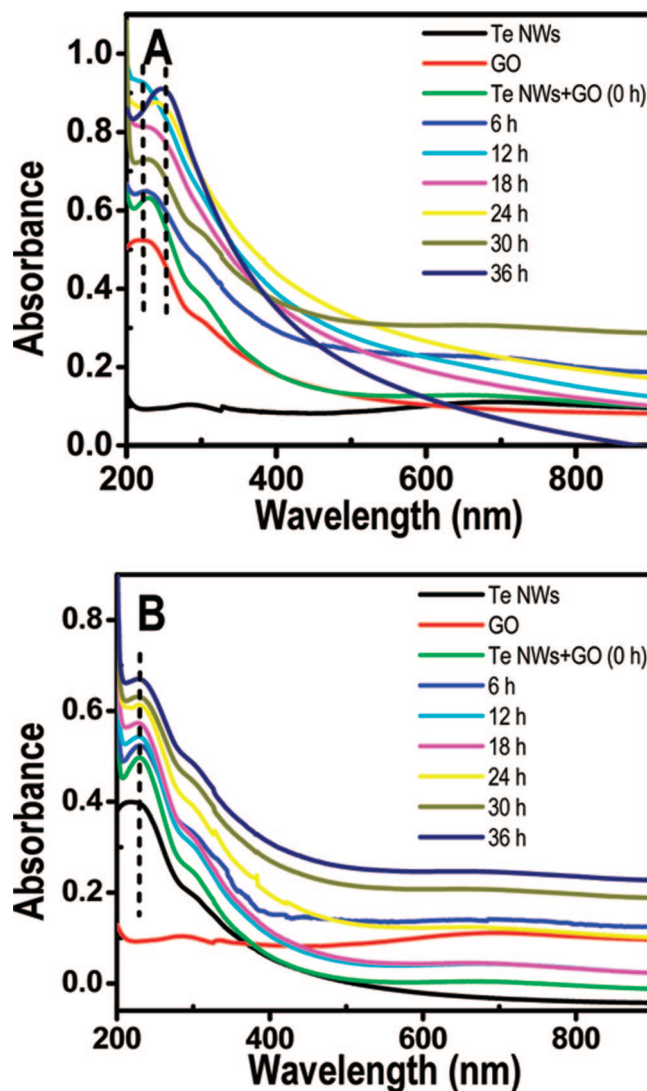


Figure 9. Time-dependent UV/vis spectra of the reaction between Te NWs and GO: (A) at pH 10 and (B) at pH 2. The shift in the spectra (in A) is marked with dashed lines.

spectrum. The curves in Figure 9B have been translated vertically to accommodate them in the same absorbance window as in Figure 9A. The large increase in background is, therefore, not observable in Figure 9B. Thus, a basic pH was found to be necessary to facilitate the reaction and to obtain a stable product. The stability of Te NW at acidic pH was evaluated (Supporting Information, Figure S4). Time-dependent UV/vis spectra showed a small shift immediately after the change in pH. After this there was no change in spectra even after 48 h (Supporting Information, Figure S4A). TEM images taken after 36 h did not show any change in crystal structure or morphology of Te NW (Supporting Information, Figure S4B).

Effect of Temperature on the Reaction. To check the dependence of temperature on the reaction, we carried out the reaction at a higher temperature (50 °C) as well as at a lower temperature (4 °C). Figure 10A shows the reaction done at 50 °C.

The reaction rate was found to be increased with an increase in temperature. The reaction took nearly 36 h for completion at room temperature. It was complete in 6 h, when carried out at 50 °C. After 6 h no additional change was observed even if the temperature was maintained at 50 °C. When the reaction was carried out at 4 °C, no appreciable change in spectra was visible,

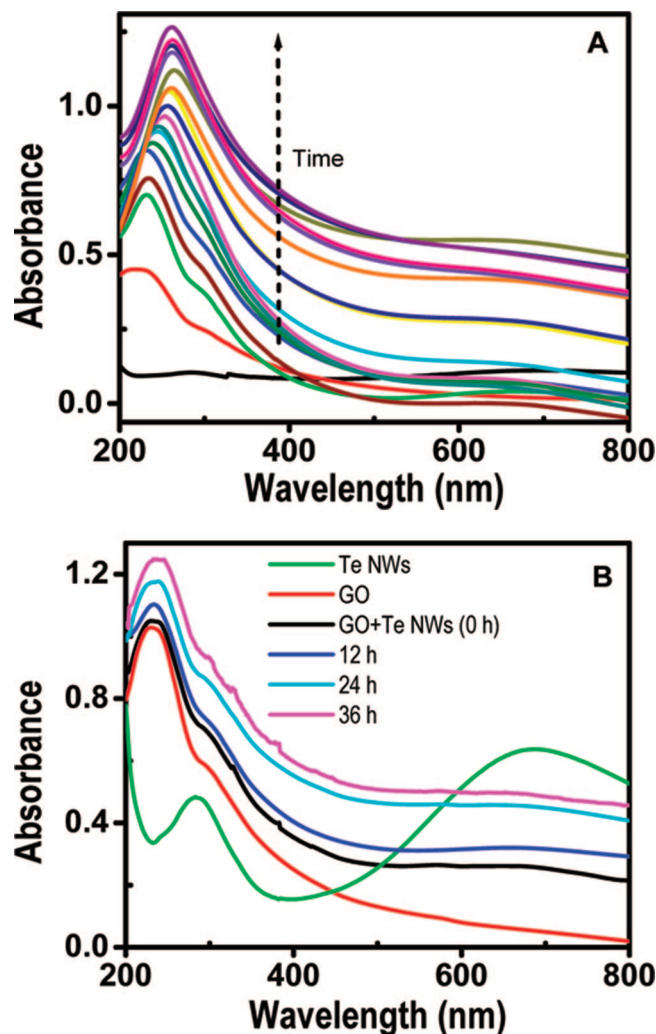


Figure 10. Time-dependent UV/vis spectra of the reaction between Te NW and GO: (A) 50 °C, spectra were taken every 30 min of the reaction, and (B) 4 °C. In panel B, spectra were taken every 12 h of the reaction.

implying that no significant reduction had happened (Figure 10B). Only a 6 nm shift was seen in the 230 nm peak after 36 h of reaction. At higher temperatures, the product formed was found to be not as stable as that formed at room temperature. A film was formed and a precipitate was seen after the reaction, upon storage.

Effect of the Amount of Te NW on Reaction: Optimization of Te NW Concentration. The amount of Te NW added into the reaction mixture was varied in order to check the effect of the Te NW concentration on the reaction. In the original synthesis, 3 mL of Te NW dispersion was added into 27 mL of GO dispersion. The amount of Te NW was reduced to 2 mL, keeping the volume of GO constant (Supporting Information, Figure S5A). The reduction was not complete even after 36 h. After 30 h of reaction, the GO peak was shifted to 258 nm and peak II due to Te NW was completely absent. One milliliter of Te NW was again added to the above dispersion. After 12 h, the peak was again shifted to 268 nm showing complete reduction. The amount of Te NW added was further increased to 5 mL (Supporting Information, Figure S5B). The reaction was complete in 36 h and GO peaks shifted to 268 nm. But after the reaction (36 h), peak II was clearly visible in the spectrum implying that excess Te NW is left behind in the dispersion.

To confirm whether the reaction is over after 36 h, we added 1 mL of Te NW dispersion into the RGO dispersion after the reaction (Supporting Information, Figure S6A). No spectral changes were observed even after 36 h. Both the RGO peak as well as peak II remained unchanged. This implies that, once the reaction is over, excess addition of Te NW does not have any effect on RGO. The reaction was tried with bulk Te powder also (Supporting Information, Figure S6B). Even after 7 days of stirring, no appreciable spectral change was observed. Only a slight broadening of the GO peak was observed. This broadening was observed in the case of reaction with Te NW also, in the initial stages of the reaction. So this can be taken as an indication of the start of the reduction reaction. But in the case of Te powder, the reaction is very slow compared to that with Te NW. This could be interpreted as a surface area effect.

Predicting the stoichiometry of this kind of reactions, where nanomaterials are used as reagents, is difficult. The exact concentration of Te NW cannot be calculated accurately. The as-prepared sample was centrifuged three times prior to addition to the GO dispersion. During each centrifugation cycle, some amount of Te is always lost. Therefore, the final concentration of Te will be less than the concentration taken initially. Moreover, the number of functional groups that are present on the GO sample and the nature and type of oxygenated functional groups in which they are present cannot be accurately identified. Hence, the number of oxygenated functionalities being reduced cannot be determined accurately. In view of this, an effort to determine the stoichiometry of the reaction was not made. The resulting product, leaf-like graphenic structures, always contained impurities such as TeO_2 (which are converted into TeO_3^{2-} in solution), and cannot be separated from the solution easily. Also, some traces of Te were attached onto the graphenic structures (see Figure 4F). As a result, a calculation of mass balance of the reaction was not attempted.

The mechanism of the reduction reaction is not fully understood at this time. One could argue that the residual hydrazine used for the reduction of Te during the preparation of Te NW is doing the reduction of GO to graphene-like structures. But this can be ruled out since after three centrifugation and redispersion cycles, the amount of hydrazine, if at all present, will be negligible. The pH showed a drop from 9.2 to 7.8, which can be attributed to the removal of excess hydrazine from the Te NW dispersion. If reduction was done only by the residual hydrazine, Te NW would have remained intact during the process. But time-dependent UV/vis, fluorescence, and TEM studies showed a simultaneous destruction of Te NW with the reduction of GO. Therefore, this possibility can be excluded. The second possibility is a redox reaction involving Te NWs and GO. Te NWs have been known to be used as a template for the production of 1D nanostructures, where a redox reaction between Te NWs and the concerned metal gives rise to composite structures. Also, the concurrent reaction, most probably oxidation of Te NWs with the reduction of GO, implies more of a redox-like reaction between Te NWs and GO. The form of Te that can be formed in an alkaline medium is reported to be TeO_2 , which spontaneously is converted to TeO_3^{2-} and Te^{2-} .²⁹ But Te^{2-} is highly unstable in aqueous medium and will readily be converted back to metallic Te.²⁹ It is reported that as the temperature increases, the rate of oxidation of Te increases.²⁹ This may be the reason for the higher rate of reduction reaction in our case when temperature was increased to 50 °C. Considering the spectroscopic and microscopic observations, it is reasonable to consider that this is the most probable case. The reduction reaction was characterized by XPS also. The proposed

mechanism suggests the oxidation of Te NW to TeO₂. The Te 3d region was examined in detail (Supporting Information, Figure S7). Before the reaction the spectrum showed a prominent Te(0) feature (3d at 573.0 eV). There was a small amount of oxidized Te signature ~576.6 eV, which may be due to the surface oxidation of Te NW.³⁰ After the reaction, the signature due to elemental Te was completely absent and only the oxidized peaks are seen in the spectrum, which proves that the Te NWs are being oxidized completely during the reaction. XRD was also used for the characterization of the reactant and products formed. Initial Te NWs before the reaction (Supporting Information, Figure S8A) showed the characteristic reflections which can be indexed to the t-Te. The values are in good agreement with the standard literature data (JCPDF card number 36-1452).¹⁸ After the reaction (Supporting Information, Figure S8B), only peaks due to the carbon (002) plane³¹ (JCPDF card number 75-1621) and those due to TeO₂ were present (JCPDF card number 76-0680). This implies the reduction of GO to graphenic structures and the oxidation of Te to TeO₂, as proposed. This suggests that the reaction is redox-like where reduction of GO happens concomitantly with the oxidation of Te NWs.

Conclusions

A room temperature reduction reaction has been reported for the preparation of leaf-like graphenic nanostructures. The reduction was redox-like between Te NW and GO. The reaction was followed time-dependently by UV/vis spectroscopy, fluorescence spectroscopy, and TEM. TEM images showed a leaf-like morphology for the material. Reduction of GO to graphenic-like structure was confirmed by UV/vis spectroscopy, IR spectroscopy, Raman spectroscopy, and XPS. The reaction showed a strong dependence on the reaction temperature. The reaction rate was found to be increased considerably upon increasing the temperature. No appreciable reaction was found to be happening at 4 °C. Near-neutral or alkaline pH was found to be optimal for a stable product formation. At an acidic pH, the GO was found to be agglomerating and no reaction happened. XRD showed that after the reaction Te is converted to TeO₂ as proposed. Nanoparticle-induced formation of graphene-like structures without the aid of additional stimulants such as UV or heat is likely to have synthetic utility.

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Supporting Information Available: TEM images of GO before the reaction, leaf-like graphenic structures after the reaction, time-dependent UV/vis spectra of the reaction between Te NW and GO, where the amount of Te NW was varied, time-dependent UV/vis spectra obtained after extra addition of 1 mL of Te NW after the completion of reduction, time-dependent UV/vis spectra of the reaction between Te powder and GO, time-dependent UV/vis spectra and TEM image of Te NW at pH 2, showing the stability of the structure and XRD patterns of Te NWs before the reaction and graphenic structures after the reaction, and XPS spectrum of Te 3d before and after the reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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