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Microwave induced electric discharges on metal particles for the synthesis of zero-, one- and two-dimensional inorganic nanomaterials under solvent-free conditions

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Abstract

Microwave irradiation of metals generates electric discharges (sparks). These sparks are used to generate metallic nanoparticle of Cu and Ni and one-dimensional nanorods of CuS, ZnF_2, and NiF_2 protected with fluorinated amorphous carbon. We have also synthesized reduced graphene oxide and graphene partially rolled into scrolls by this method.

Keywords

keyword; Microwaves; nanomaterials; electric discharges; transmission electron microscopy

Introduction

Synthesizing nanomaterials in short time intervals with fewer chemicals have become increasingly important in material science. Traditional routes of synthesizing nanomaterials include sol-gel, solvothermal, arc-discharge or laser ablations, etc. require either excessive chemicals or longer durations or both.[1] Microwave synthesis has become popular in the last three decades as an alternative route for making molecules and materials in a significantly shorter time scale.[2-8] Dielectric heating under microwaves both in solution state and solid-state rapidly increases the reaction temperature and helps to improve reaction kinetics significantly, thus drastically reducing the reaction time.[9, 10] Non-thermal effects, may also influence, on the reaction kinetics is still a subject of discussion.[9, 11] On the other hand, bulk metals generally reflects the microwaves, whereas fine metal powders or thin films can couple with microwaves (penetration depth of microwaves in metals are in the range of 1-2 μm) thereby increasing the temperatures quickly due to conduction mechanism, which allow them to use to sinter metals under microwaves.[12-14] It is found that the sintering of metal powders by microwaves produces denser and mechanically superior products than obtained by conventional heating.[14] Other than reflection and conduction, metal particles usually produce electric discharges (arcs) when subjected to microwaves due to the formation of high electric field gradients at the sharp edges on the metal surfaces.[12] The generation of the arcs caused might be the reason for not utilizing metal particles under microwaves to generate different nanomaterials and limited only to sintering experiments. However, there are some studies in the literature that treatment of metals under microwave with organic solvents can carbonize organic solvents forming carbon-coated metallic nanoparticles.[15, 16] Recently, Pentsak et al. have shown metals such as Cu, Fe, Mo, etc. on carbon under microwave heating

transforms to the nanoscale.[17] However, the microwave discharge technique, which is fast, solvent-free, and apparatus, is easy to set up has not been explored to its fullest potential to synthesize different nanomaterials and judiciously control of their morphology.

In this communication, we report microwave-induced electric discharge (arc) on metallic particles can be used to synthesize inorganic nanomaterials, especially for making nanoparticles of Cu, Ni in zero oxidation state. Also, we could able to control the morphology of the nanomaterial, which is not able to achieve earlier. Synthesis of ZnF_2, NiF_2, CuS nanorods, which are covered with amorphous fluorinated carbon, is achieved. We have also extended this procedure to synthesize of reduced graphene oxide and graphene without using any solvents or additional surfactants.

Results and Discussion

Smooth surfaces on the commercially available metal particles do not create arcs under microwave conditions instead gets heated up or reflects the microwaves. Thus, activating metal surface by acid treatment is essential before using metal particles for further microwave arc experiments. All the metal powders are treated with 0.5 M nitric acid under sonication for 10 min to create the rough surfaces. Scanning electron microscope (SEM) images of copper powder before and after acid-treatment are shown in Figures 1b and 1c, respectively. SEM image clearly shows the sharp edges on acid-treated copper as compared to the untreated one. Copper partially gets oxidized under acidic treatment to Cu_2O. X-ray diffraction (XRD) patterns (Figure 1a) are indexed to Cu_2O after acid treatment and the majority of the Cu still remains as Cu metal (Figure 1a). Graphitic-carbon nitride (g-C_3N_4) or graphite powder (commercially available) is used as a carbon source. g-C_3N_4 is synthesized and characterized according to the

reported literature.[18] X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) confirms the formation of g-C_3N_4 (see Figure S1 in supporting information (SI)).

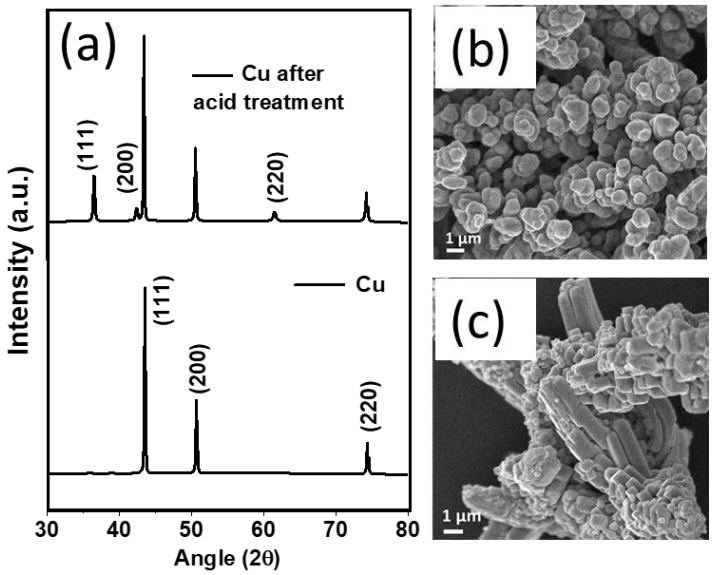

Figure 1: (a) XRD patterns of commercially available Cu powder and Cu powder after 0.5 M HNO_3 treatment. (b) SEM images of pure Cu powder and (c) acid-treated Cu powder.

To generate nanoparticles by microwave-induced discharge technique, the reaction is conducted either in quartz or Teflon beaker. Teflon beaker also served as a carbon and fluorine source for the experiments. Typically, 100 mg of acid-treated metal powder mixed either with graphite powder or g-C_3N_4 (50 mg) and placed inside the domestic kitchen microwave (2.54 GHz, power 700 W) and treated for 5 sec to 2 min. Activated metals under microwave generate arcs and evaporate the metal along with carbon and form carbon-coated metallic nanoparticles on the above lid of a reaction vessel. For synthesizing nanorods, sulfur is used as a growth promoter. Typically, a mixture of activated metal (100 mg), sulfur powder (25 mg) and g-C_3N_4 (50 mg) are taken in Teflon beaker irradiated with microwaves. It is important to note that in the absence of carbon

(graphite/g-C_3N_4), metal arcs produce a mixture of metal and metal oxides nanoparticles and particle sizes are found to be difficult to control.

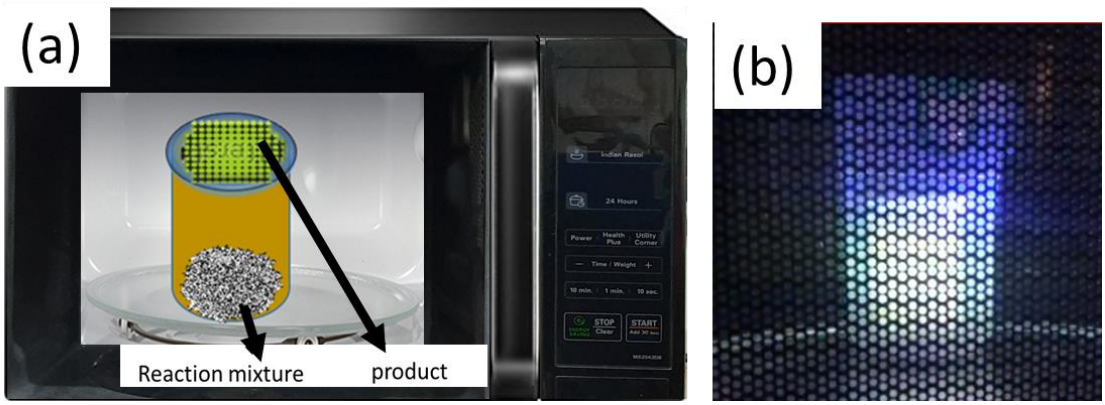

Figure 2: (a) Scheme is showing the formation of products from the reaction mixture placed in a microwave reactor, (b) plasma generated with metal particles under microwave conditions.

Microwave irradiation of activated metals generates sparks due to high electric field gradients created on top of the metal surfaces at the sharp edges. In Figure 2a, we have shown the image of a microwave reactor with a schematic reaction vessel. Figure 2b shows the optical image of plasma generated in the reaction vessel due to the treatment of metals under the microwave. Microwave irradiation of activated metals mixed with either graphite or graphitic carbon nitride (g-C_3N_4) yields carbon-coated/nitrogen-doped carbon-coated metallic nanoparticles. When these reactions are conducted in a Teflon reactor, the product with external carbon is further functionalized with fluorine. Figure 3a shows XRD patterns of Cu and Ni nanoparticles generated by microwave treatment of activated Cu and Ni powders in the presence of g-C_3N_4. XRD patterns show the pure phase of Ni and Cu. The formed nanoparticles are covered with

fluorinated amorphous carbon. Figure 3b shows the SEM images of Cu nanoparticles covered with amorphous fluorinated carbon with an average size of 80 nm. C-F bond can be functionalized on top of metallic nanoparticles, which can be further useful for different applications such as drug-delivery.[19] Contrary to Cu and Ni, microwave irradiation of zinc metal in the presence of Teflon and g-C_3N_4 creates ZnF_2 nanorods inside fluorinated carbon (from XPS, carbon to fluorine ration found to be 3:2). The high electropositive nature of Zn reacts readily with fluorine in Teflon and forms ZnF_2. XRD patterns in Figure 3a confirms the presence of ZnF_2 phase. Figure 3d shows the energy dispersive spectroscopy (EDS) mapping of Zn and F, which confirms the presence of Zn and F in the nanorod. Product yields both nanorods and nanoparticles of ZnF_2 as can be seen from the SEM image (Figure 3c). The average diameter of nanorods is 100 nm and lengths ranging from 2 -3 µm. The formation of external amorphous fluorinated carbon nanotube would help as a template in the formation of ZnF_2 in nanorod morphology.

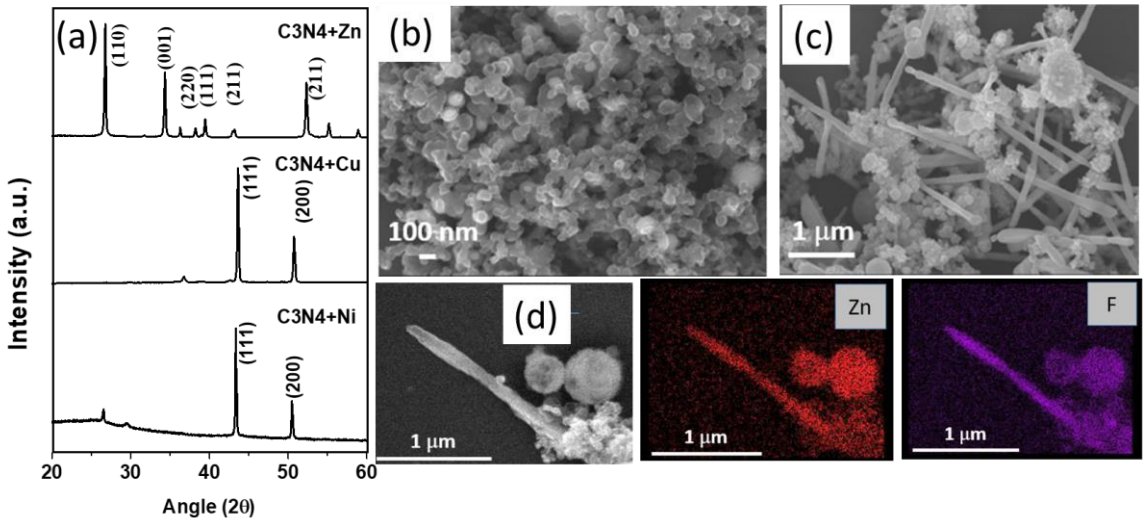

Figure 3: (a) XRD patterns of carbon-coated Cu and Ni nanoparticles and ZnF_2 nanorods. (b) SEM images of carbon-coated Cu nanoparticles and (c) ZnF_2 nanorods. (d) SEM image and EDS elemental mapping on single ZnF_2 nanorod.

It is well established that sulfur acts as a growth promoter for carbon nanotube and carbon fibers.[20, 21] Thus, sulfur is introduced in the present reaction mixture to improve the yield of nanorods. Microwave treatment of activated Zn metal with g-C_3N_4 and sulfur in Teflon container produce nanorods of ZnF_2 with high yield. Figure S2 in SI shows the SEM and transmission electron microscope (TEM) images of ZnF_2 nanorods produced in the presence of sulfur. SEM image indicates the high yield of ZnF_2 nanorods. High-resolution TEM (HRTEM) image in Figure S2d in SI confirms the single-crystalline nature of ZnF_2. XRD patterns in Figure 4a confirms the pure phase of ZnF_2. Similarly, microwave treatment of Ni in the presence of sulfur in Teflon beaker yield NiF_2 nanorods along with Ni nanoparticles (Figure 4a, and Figure S3 in SI). It is important to note that a similar experiment without sulfur yield only Ni nanoparticles. Figure S3 in the supporting information shows SEM and TEM images of NiF_2 nanorods. EDS mapping in Figure S3c in SI confirms the presence of Ni, F and C on NiF_2 nanorod. HRTEM image (Figure S3e) clearly shows the single-crystalline nature of NiF_2 nanorod covered with an amorphous coating. Interestingly, microwave treatment of copper in the presence of sulfur in Teflon yield CuS nanorods instead of CuF_2 nanorods. Reactivity of Cu with sulfur is higher than that of fluorine as soft-soft interactions between Cu and S dominate the product stability compared to soft-hard interaction between Cu and F. XRD patterns in Figure 4a confirms the hexagonal covellite structure of CuS. SEM image in Figure 4C and TEM image in Figure 4d confirms one-dimensional nature. CuS nanorods are single-crystalline as can be seen from the HRTEM image in Figure 4e. CuS nanorods found to have [101] growth direction. The average core diameter of CuS nanorods is about 25 nm and the thickness of the amorphous layer on top of CuS nanorods is about 5 nm.

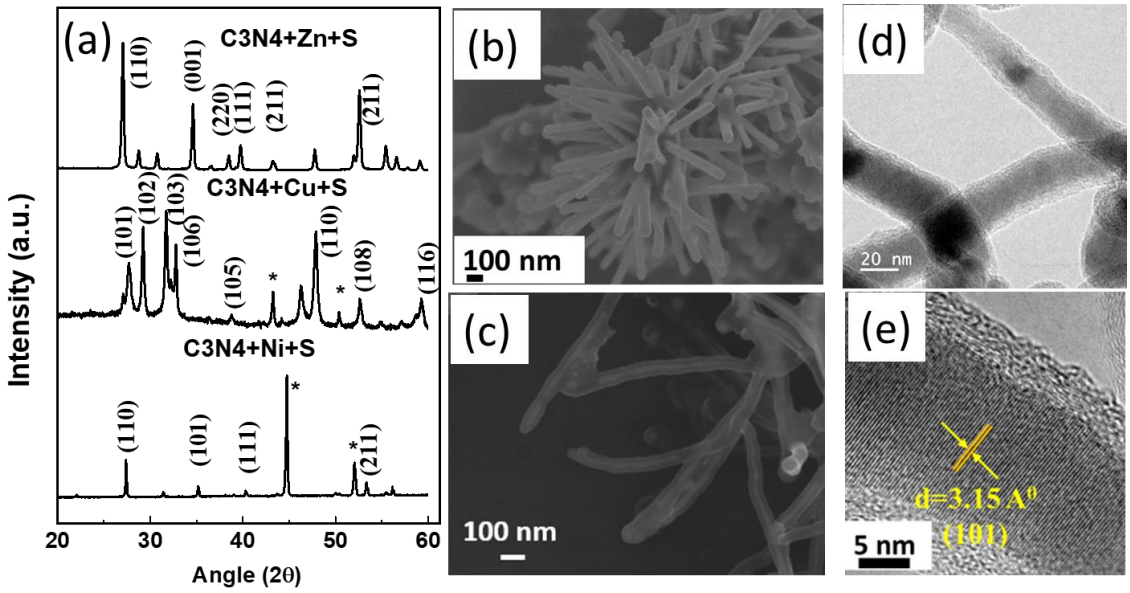

Figure 4: (a) XRD patterns of nanorods of ZnF_2, CuS and NiF_2 synthesized in the presence of sulfur by microwave irradiation of respective metals in the presence of g-C_3N_4 in Teflon beaker. (b) SEM image of NiF_2 nanorods. (C) SEM, (d) TEM and (e) HRTEM images of CuS nanorods. Asterisk (*) in XRD panel indicates the reflection originated from corresponding metals.

The generation of inorganic nanomaterials by metallic arcs under the microwave conditions are rare. Here we have shown that metals can effectively interact with microwaves when metallic particles contain rough surfaces or sharp edges. When conducting rough surfaces is subjected to microwaves, the charge would move to the conductor's surface and distribute unevenly. At tips and sharp edges, the electric field would reach very high values due to an accumulation of high charge densities, thus leading to ionization of material and surrounding gas leading to electric discharge.[12] Local temperatures at this discharges might reach more than the melting point of metals thus the evaporation of metal and surrounding carbon, sulfur as well as fluorine (from Teflon) take place. A chemical reaction between the metal and F/S leads to the formation

of either metal fluorides/ sulfides depending upon the reactivity. On the one hand, Cu and Ni in the presence of graphite/g-C_3N_4 and the absence of sulfur produce metallic nanoparticles. This might be due to the reducing capability of carbon at high temperatures to prevent metals from getting oxidized and stabilize metallic nanoparticles. On the other hand, when sulfur is used in the reaction mixture along with graphite/g-C_3N_4, sulfur helps to produce carbon nanotubes instead of carbon nanoballs. The reactivity of sulfur with end caps of nanotubes doesn't allow carbon nanotubes to close. This amorphous carbon nanotubes, thus formed, would help as a template to intercalate metal fluorides/metal sulfides. As local temperatures are very high, metal fluorides and sulfides are in liquid states and fill in the nanotubes via capillary forces. These liquids solidify as one-dimensional nanorods inside nanotubes.

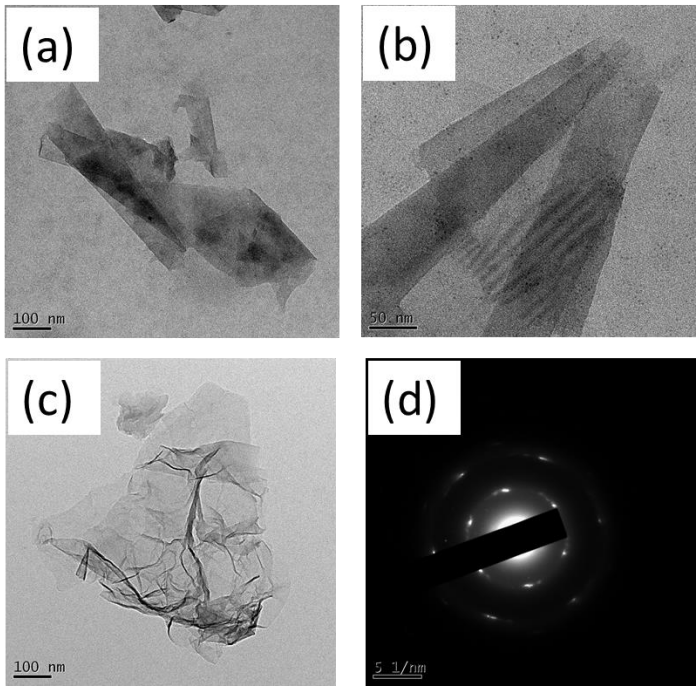

Figure 5: (a) and (b) TEM images of partially rolled few-layered graphene into nanoscrolls synthesized by microwaving graphite in the presence of Zn metal. (c) TEM image of graphite oxide after exfoliation in microwave in the presence of Zn metal and its (d) corresponding selected area electron diffraction pattern.

We have also studied exfoliation of graphite and graphite oxide under microwaves in the presence of Zn metal. We have observed exfoliation of graphite into few-layered graphene. We have also seen partial rolling of these graphenes into nanoscrolls as shown in Figures 5a and 5b. Formation of ultra-small nanoparticles of ZnO along with graphene is detected. In the case of GO exfoliation, we have observed the formation of nanosheets of reduced graphite oxide (Figure 5c). These nanosheets still keep hexagonal structure under microwave conditions as can be seen from Figure 5d.

Conclusion

In conclusion, we have shown that microwave-induced electric discharge on rough metallic surfaces can be effectively used to synthesize nanomaterials as well as control their morphology. Cu and Ni metallic nanoparticles are stabilized in amorphous carbon. Nanorods of ZnF_2, NiF_2 and CuS are synthesized inside the fluorinated amorphous carbon nanotubes in the presence of sulfur. External C-F bond can be further functionalized readily without disturbing internal materials for further applications. We could also produce reduced graphene oxide and graphene, which is partially rolled into nanoscrolls, from this method. We believe, this work inculcates other researches and opens the possibilities to synthesize other inorganic nanomaterials by microwave electric discharge method in shorter times without using surfactants and solvents.

Experimental

Creating the rough surfaces over metal powders

Commercially purchased micron-size metal powders (Ni, Cu and Zn) are treated with nitric acid to create rough surfaces. In a typical reaction, 100 mg of each metal powder

is transferred to a beaker containing 10 ml of 0.5 M nitric acid and sonicated for 10 min. The resultant powder is washed with water several times to make pH = 7 and dried it in an oven at 50 ^{o}C for 2h before using it in further microwave experiments.

Synthesis of Graphitic-carbon nitride (g-C_3N_4)

g-C_3N_4 is synthesized and characterized according to the reported literature.[18] In a typical reaction, melamine (150mg) and urea (71mg) are physically mixed in a quartz boat and heated at 650 ^{o}C under the nitrogen flow for 2h to obtain orange precipitates of bulk g-C_3N_4.

Generation of nanomaterials using microwave discharge technique

To generate nanoparticles by microwave-induced discharge technique, the reaction is conducted either in quartz or Teflon beaker. Teflon beaker also served as a carbon and fluorine source for the experiments. Typically, 100 mg of acid-treated metal powder mixed either with graphite powder or g-C_3N_4 (50 mg) and placed inside the domestic kitchen microwave (2.54 GHz, power 700 W) and treated for 5 sec to 2 min. The product containing carbon-coated metallic nanoparticles are collected from the above lid of a reaction vessel. For synthesizing nanorods, sulfur is used as a growth promoter. Typically, a mixture of activated metal (100 mg), sulfur powder (25 mg) and g-C_3N_4 (50 mg) are taken in Teflon beaker irradiated with microwaves. Products are collected from the lid of a reaction vessel. The Above experiments are performed in aerobic conditions.

Preparation of few-layer graphene and graphite oxide nanosheets

In a typical experiment, 50 mg of acid-treated Zn metal is mixed with 100 mg of either graphite or graphite oxide in quartz beaker and irradiated with microwaves for 1 min. Products are collected from the reaction vessel and sonicated in ethanol for a minute

and centrifuged it for 5 minutes at 6000 rpm to allowed to settle the big metal particles and unreacted graphite. The solution is collected for further characterization.

Characterization of products

As collected reaction products are characterized by X-ray diffraction (PANanalytical X'pert PRO), field emission scanning electron microscopy (JEOL JSM 7600F, combined with energy-dispersive spectroscopy (EDS)), transmission electron microscopy (JEOL JEM 2100F) and X-ray photoelectron spectroscopy XPS (Thermo VG Scientific MultiLab, ESCA).

Supporting Information

Supporting Information File 1:

Characterization details of g-C_3N_4 by XRD and XPS.

Characterization details of nanorods of ZnF_2 and NiF_2 via SEM, TEM.

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