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RESEARCH ARTICLE

Effect of nanoscale TiO_2-activated carbon composite on *Solanum lycopersicum* (L.) and *Vigna radiata* (L.) seeds germination

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Abstract The extensive use of nanoparticles under different industrial processes and their release into the environment are of major concerns in the present global scenario. In the present study, the effects of activated carbon-based TiO_2 (AC-TiO_2) nano-composite on the seed germination of *Solanum lycopersicum* (tomato) and *Vigna radiata* (mungbean) were investigated. The size of nanoparticles used in the study ranged from 30 to 50 nm, and their concentrations were from 0 to 500 mg L^{-1}. The composites were synthesized by sol–gel method and further characterized by scanning electron microscopy, Energy-dispersive X-rays spectroscopy (EDX), Raman spectroscopy, Fourier transform infrared spectroscopy and X-ray diffraction to investigate all the surface structural and chemical properties of AC-TiO_2 nano-composite. The results showed that increase in nano-composite concentration improves the germination rate and reduces germination time up to a certain concentration. Therefore, employing AC-TiO_2 nano-composites in suitable concentration may promote the seed germination and also reduce the germination time in *Solanum lycopersicum* and *Vigna radiata*. Further, it may help to understand the interface of TiO_2 nanoparticles with the environment and agriculture before its application to the field.

Keywords Activated carbon–TiO_2 · Nano-composite · Root elongation · Seed germination

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1 Introduction

Nanotechnology is a rapidly growing and leading discipline of science and technology based industries, by playing a significant role in revolutionizing the agriculture field (Kumar et al. 2012; NAAS 2013; Srivastava et al. 2015a, b), economy, society and environment. It includes almost all branches of science and technology. The nanotechnology-based products are expected to be increased in the global market by US$ 1 trillion (Roco and Bainbridge 2001) including their synthesis processes (Maynard et al. 2006; Dawson 2008; Rejeski and Lekas 2008; Husen and Siddiqi 2014). As a consequence, it is generating both positive and negative responses from governments, scientists and social media throughout the world (Service 2000, 2003; Brumfiel 2003; Bai 2005; Yang et al. 2006). Due to its wide range of applications in various fields such as synthesis process, environmental remediation, cosmetic, agriculture sector, medicine and materials synthesis, it has been made a thrust area of research and development. However, its effects on the environment are mostly unexplored.

Nano-materials are found in both natural and engineered tailor forms. Engineered nano-materials have different physical and chemical properties as compared to the naturally occurring nanoparticles and thus have different effects on environment (Husen and Siddiqi 2014). USEPA (2010) categorized the different natural and engineered nano-materials into seven groups, viz. (1) carbonaceous (natural or engineered, e.g., fullerenes/buckyballs and nanotubes); (2) metal oxides [natural or engineered, e.g., titanium oxide (TiO_2) and cerium oxide (CeO_2)]; (3) zero-valent metals [engineered, e.g., nanoscale zero-valent iron (nZVI) and emulsified zero-valent iron (EZVI)]; (4) quantum dots [engineered, e.g., quantum dots made from cadmium selenide (CdSe) and cadmium telluride (CdTe)]; (5) dendrimers (engineered, e.g., hyperbranched polymers and dendrigraft polymers); (6) composite nano-polymers (engineered, e.g., made with two different nano-materials or resins); and (7) nano-silver (engineered, e.g., colloidal silver and polymeric silver).

Engineered nanoparticles has various applications in agricultural research, such as in reproductive science, transfer of agricultural and food waste to energy, nano-bioprocessing of enzymatic activity, disease prevention and other plant treatments using nanocides (Carmen et al. 2003). For instance, titanium dioxide (TiO_2) is widely used in many process industries (including agrochemicals, cosmetic medicines, textiles, electronics, pharmaceutics and environmental remediation), due to its low cost, abundance, amphoteric nature and catalytic activities (Feizi et al. 2012). The release of nanoparticles in the environment through various routes including synthesis processes is hazardous from environmental point of view. Therefore, proper recycling and disposal of nano-based products are imperative. Further, the disposal of nano-materials after use in the agricultural systems and understanding of its effect on the same are of vital importance.

Generally, the effects of nano-materials on plant and soil depend upon their particle size and nature of crystalline structure (Feizi et al. 2012, 2013; Clément et al. 2013; Dehkourdi and Mosavi 2013; Song et al. 2013b). For example, the effect of nano-sized TiO_2 on various plants' seed germination and growth showed ambiguous results, because of its positive and negative effects ranging from strong toxicity to the root–shoot systems to growth-stimulating effects (Song et al. 2013b). Various positive and negative effects of TiO_2 nanoparticle associated with the seed germination and plant growth are summarized in Table 1. However, various researches found the negative effects of TiO_2 nanoparticles on a few plant species (García et al. 2011; Mushtaq 2011; Jośko and Oleszczuk 2013; Song et al. 2013a). Moreover, various other effects of nano-materials on the plants and soil ecology interaction are still unknown (Lin and Xing 2007). However, other studies supported that TiO_2 application to soil enhances the chlorophyll content and enzymatic activities such as peroxidase, catalase and nitrate reductase which positively affects on the growth and production by improving essential element content in plant tissue in various crops (Hruby et al. 2002; Feizi et al. 2012). The use of TiO_2 nanoparticles may possibly be a new approach to overcome problems with seed germination in some plant species, particularly medicinal plants which have lower germination rate dormancy period (Feizi et al. 2013).

Understanding of the degree at which nanoparticles affect seed germination and plant development is an important issue. It depends upon the concentration, nature and size of nanoparticles. This could also have economic significance for agriculture (Ju-Nam and Lead 2008; Gong et al. 2011; Gottschalk and Nowack 2011; Jośko and Oleszczuk 2013). Presently, carbon-based TiO_2 nano-materials (Mattle and Thampi 2013), carbon nano-tubes (Ouyang et al. 2013), Fe_2O_3–TiO_2 composite (Ouyang et al. 2013) and N-doped TiO_2 (Sun et al. 2008) catalysts are widely used for the remediation of various environmental contaminations. During processing, a few amounts of these composites are released in the environment and reached the agriculture systems through various processes. However, the environmental impacts of TiO_2 and other such semiconductors used as catalysts have not been studied extensively. Therefore, in the present study, effect of TiO_2 and activated carbon nano-composite (AC-TiO_2) on the seed germination of two important agricultural crops, viz. *Solanum lycopersicum* and *Vigna radiata*, is studied. To check out its effect on agricultural system, this work aims to achieve following objectives dealing with synthesis, characterization and germination effects as:

1. Synthesis of activated carbon-based TiO_2 (AC-TiO_2) nano-composite through sol–gel method and its characterization using various instrumentation techniques and
2. Evaluation of effect nano-composite on the seed germination, root and shoot length and weight of two important agricultural crops

2 Materials and methods

2.1 Chemicals

Titanium tetraisopropoxide (TTIP) and activated carbon (<20 µm) were procured from Sigma-Aldrich. Distilled water was used for all the synthesis processes and for the preparation of nanoparticle suspension.

2.2 Preparation of AC-TiO_2 nano-composite

Activated carbon-based titanium dioxide (AC-TiO_2) nano-composite was synthesized using the sol–gel method by using titanium tetraisopropoxide (97 %) as a binder and commercially available activated carbon (Inoue et al. 1994; Horie et al. 1998; Singh et al. 2015). During the preparation process, 35.8 g of TTIP (97 %) was dissolved in 180 mL of 99.9 % propanol and 20 mL of 34 % HCl (*w/v*) and sonicated for 1 h (h) for homogenization. The resulting solution was diluted to 1000 mL by adjusting pH (pH = 3)

Table 1 Effect of TiO_2 and related nano-composites on seed germination of different vegetable crops

S. no.	Materials	Seed	Effect	References
1.	TiO_2	*Brassica campestris* ssp., *napus* var. *nippo-oleifera* Makina (oilseed rape), *Lactuca sativa* L. (lettuce), and *Phaseolus vulgaris* var. *humilis* (kidney bean)	No effect on seed germination. Positive effects on root elongation in some species. No differences in enzyme activities or chlorophyll	Song et al. (2013a)
2.	Anatase TiO_2	(*Petroselinum crispum*)	Significant increase in the percentage of germination, germination rate index, root and shoot length, fresh weight, vigor index and chlorophyll content of seedlings	Dehkourdi and Mosavi (2013)
3.	TiO_2	Tomato, onion and radish seed	Most positive effect on germination	Haghighi and da Silva (2014)
4.	TiO_2	Spinach	During the growth stage, the plant dry weight was increased, as was the chlorophyll formation, the ribulosebisphosphate carboxylase/oxygenase activity and the photosynthetic rate	Zheng et al. (2005)
5.	TiO_2	*Vicia narbonensis* L. and *Zea mays* L	Induced genotoxic effect for both species	Castiglione et al. (2011)
6.	TiO_2	Wheat seed	Promote the seed germination of wheat in comparison with bulk TiO_2 but in high concentrations had inhibitory or no effect on wheat	Feizi et al. (2012)
7.	AC/TiO_2	*Solanum lycopersicum* and *Vigna radiate*	Promote the seed germination in both species	Present study

with NaOH. Ten grams of activated carbon and 10 g of P25 TiO_2 particles were mixed together and stirred both on magnetic and mechanical stirrer for 3 h in the presence of the above TTIP, HCl and propanol solution. Obtained gel solution was then filtered through membrane filter (0.45 µm) and oven-dried at 80 °C for 24 h. The dried samples were crushed and calcinated at 350 °C temperature for 3 h as suggested by Kubo et al. (2007).

2.3 Characterization of nano-composite

Various characterization techniques were used to study and analyze the nature, surface and structural properties and phase composition of the nano-composite used. Surface characteristics were observed using scanning electron microscopy (FEI QUANTUM 600F). Phase composition of samples being used, their crystalline nature and size were determined using X-ray diffraction (XRD) carried out in a SIEMENS D500 with Cu-Kα radiation in region varying from $2\theta = 10°–80°$. The functional groups of the composite material were analyzed by Fourier transform infrared (FTIR) spectroscopy (Thermo NICOLET 5700, USA) spectra of samples (with KBr) in the spectral range of 4000–500 cm^{-1}. Raman spectra of samples were obtained using Jobin–Yvon Horiba HR800 Raman spectrometer.

2.4 Preparation of composite suspensions

The AC-TiO_2 nano-composites were suspended directly in deionized water and dispersed by ultrasonic vibration for 30 min. Small magnetic bars were placed in the suspensions for stirring before use to avoid aggregation of the particles.

2.5 Seeds

Seeds of important agricultural crops (viz. *Vigna radiata* and *Solanum lycopersicum*) were collected from the Institute of Agricultural Science and Technology, Banaras Hindu University, Varanasi, India.

2.6 Seed germination and exposure

The collected seeds were washed in tap water initially, immersed in a 10 % sodium hypochlorite solution for 10 min and then rinsed three times with deionized water to ensure surface sterility. Then, the seeds were soaked in nano-composite suspensions solution for about 12 h. One piece of filter paper was put into each 100-mm petri dish, and 5 mL of a test medium was added. Seeds were then transferred onto the filter paper, with 10 seeds per dish with about 1 cm distance between seeds (Yang and Watts 2005). Petri dishes were covered and sealed with paraffin and placed in the dark in a growth chamber at 25 °C. After 24 h, the germination of seeds was checked, on regular basis. The root length and shoot length were measured after 3 days when germination was halted, and seedling root length was measured by a millimeter ruler to observe the different effects between seed soaking and incubation process on the root and shoot elongation.

3 Results and discussion

3.1 Scanning electron microscopy

Surface morphology of composite was characterized by SEM as shown in (Fig. 1). The rough porous surface of activated carbon is resulted from the growth of TiO_2 nanoparticles on it. Most of the TiO_2 nanoparticles were entirely filled into interstitial pores of activated carbon particles (Fig. 1a, b). Presence of TiO_2 along with activated carbon has been also inferred by EDX analysis results shown in Fig. 1c. This revealed that the TiO_2 nanoparticles get adsorbed on the surface of activated carbon to form AC-TiO_2 nano-composites.

3.2 Raman spectra analysis

The Raman spectra of activated carbon, bare TiO_2 nanoparticles and TiO_2 adsorbed on the surface of activated carbon (AC-TiO_2 nano-composite) are shown in Fig. 2. As per the observation, spectra of activated carbon (Fig. 2a) exhibit two well-resolved bands, D (1332 cm^{-1}) and G (1585 cm^{-1}), which clearly indicates vibration in C–C bond in activated carbon (Cuesta et al. 1994). Further, Fig. 2b showed the Raman spectra of bare TiO_2 with each unit cell possessing tetragonal structure (Hyun et al. 2005). Raman spectra of single crystal indicate the four modes which appear at 133, 190, 386, 506 and 630 cm^{-1} (Šćepanović et al. 2009). The first peak appearing at 133 cm^{-1} is slightly broader and shifted than that of a bulk TiO_2 crystal (Zhang et al. 2000). As compared to short-range order of anatase phase in weak broader phase in high-frequency region, certain degree of long-range order exists at 133 cm^{-1} peak (Arora et al. 2007). Figure 2c showed the Raman spectra of AC-TiO_2 nano-composites having peaks at same wave numbers as that of spectra of TiO_2. The variation in intensity at given described peaks reflected that activated carbon is successfully exfoliated and incorporated in the nano-composite.

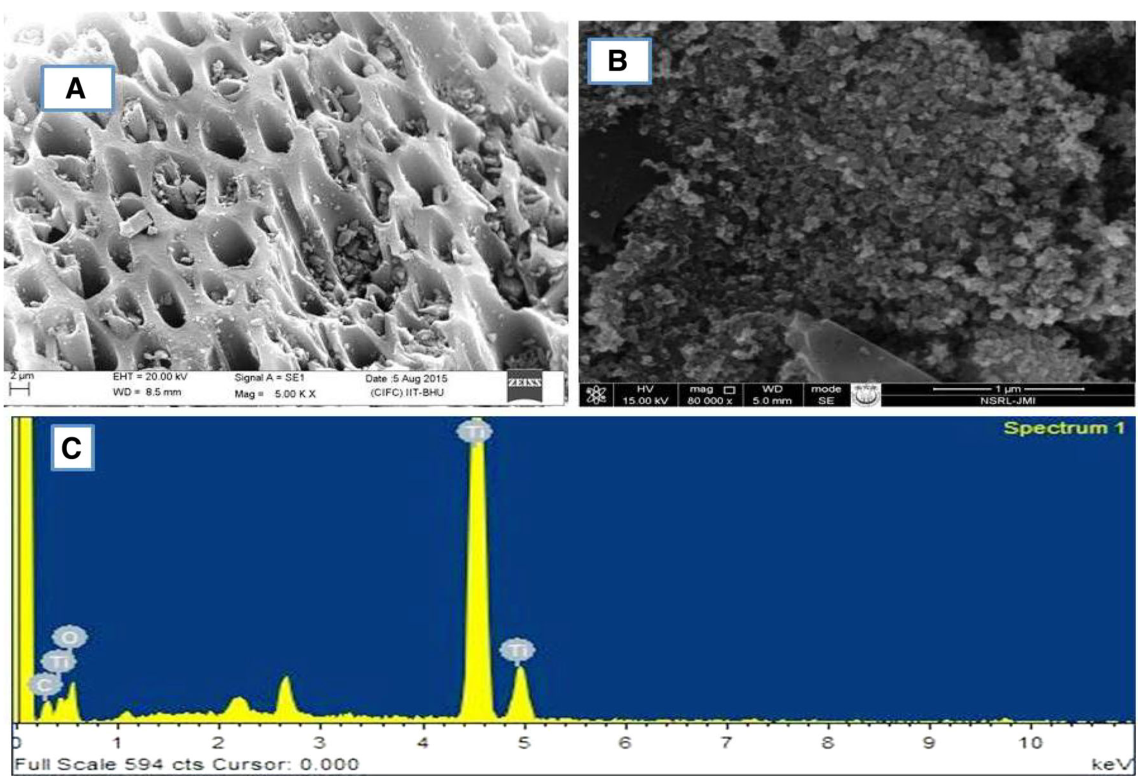

Fig. 1 Scanning electron microscopy (SEM) of AC-TiO_2 nano-composite. **a** SEM image of activated carbon-based TiO_2 at magnification $x = 5000$, **b** AC-TiO_2 nano-composite SEM–EDX image at $x = 60{,}000$ and **c** EDX analysis AC-TiO_2 nano-composite

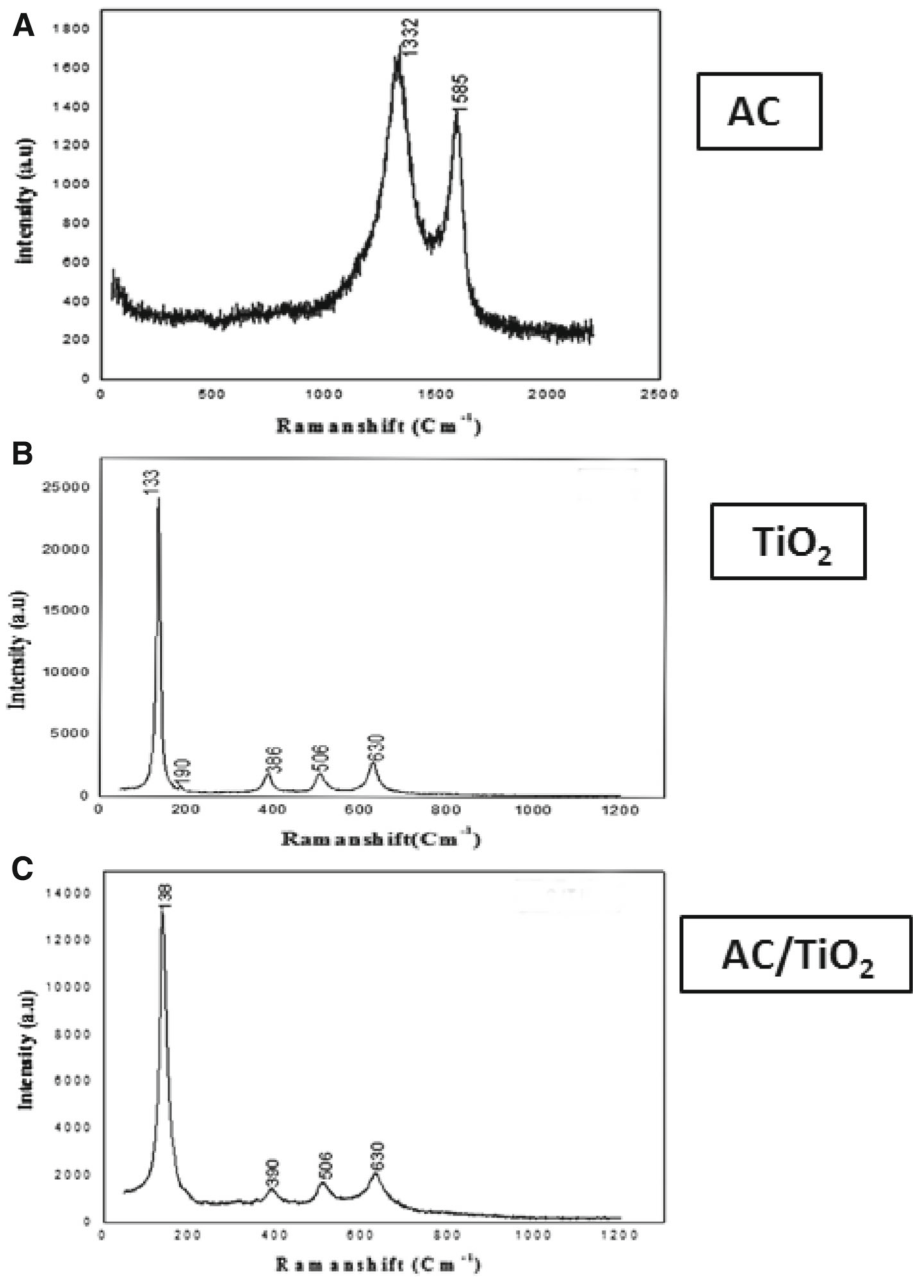

Fig. 2 Raman spectra of **a** activated carbon **b** bare TiO_2 and **c** AC-TiO_2 nano-composite

3.3 Fourier transform infrared (FTIR) analysis

FTIR spectra of AC-TiO_2 nanoparticles showed different peaks at different wave numbers revealing various absorption patterns (Fig. 3). Absorption peak at 3415 cm^{-1} represents the stretching of hydroxyl (–OH) group in water as moisture (Ba-Abbad et al. 2012), whereas peak at 1632 cm^{-1} shows the stretching of titanium carboxylate, which was the product of TTIP and ethanol used in sol–gel method. Further, absorption peak at 757 cm^{-1} represents the stretching of Ti–O bond which is the characteristic attribute of the formation of TiO_2 nanoparticles (Hema et al. 2013). FTIR study of AC-TiO_2 nano-composite shows the shift in the O–H vibration band toward lower wave number (3400 cm^{-1}). These shifts confirm the alteration of acid–base characteristics of –OH group in the used samples. Further, the bands near 600 cm^{-1} are assigned to the stretch vibration of Ti–O bond and prove that the TiO_2 particle is well distributed on the surface of activated carbon (Zhang et al. 2012).

3.4 X-ray diffraction of nano-composite

X-ray diffraction analysis was performed to assay the phase composition, crystalline nature and size of prepared AC-

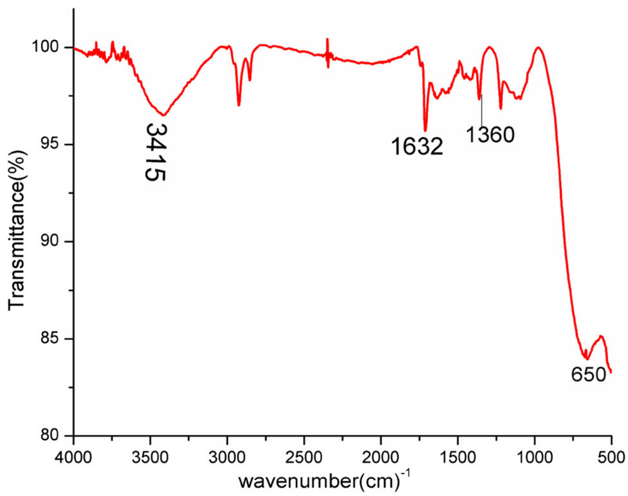

Fig. 3 FTIR analysis of AC-TiO_2 nano-composite

TiO_2 nano-composites (Fig. 4). Various diffraction peaks (Fig. 4) at $2\theta = 25.40°$, $48.02°$, $54.19°$ and $62.72°$ were given by AC-TiO_2 nano-composite, which were assigned to (101), (200), (105) and (103) reflections of anatase phase and peaks at $2\theta = 27.48°$, $36.07°$, $37.80°$ and $69.00°$ being assigned to (001), (021), (210) and (220) reflect the rutile phase of TiO_2. The average intensity of rutile phase is considerably less as compared to that of anatase phase. Average crystalline size can be determined using Scherer's equation (Borchert et al. 2005) as:

$$D = \frac{K\lambda}{\beta \cos \theta} \tag{1}$$

where $K =$ Scherer constant, $\lambda =$ X-ray wavelength, $\beta =$ the peak width of half maximum, and $\theta =$ Bragg diffraction angle.

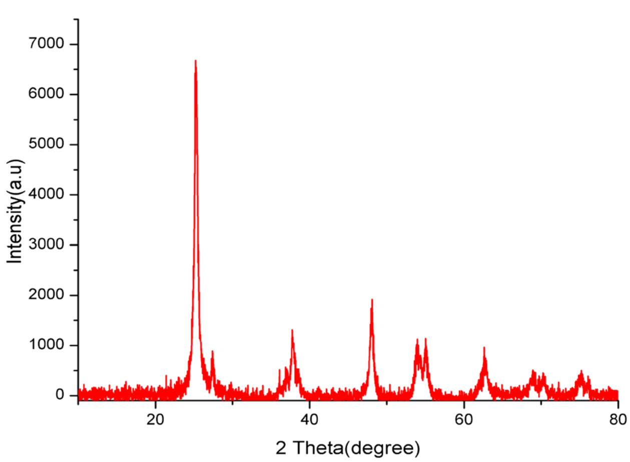

Fig. 4 XRD patterns of AC-TiO_2 nano-composite (JCPDS 894921)

3.5 Effect of AC-TiO_2 nano-composite on seed germination

To test the effect of AC-TiO_2 nano-composite on seed germination and seedling growth, the seeds of *V. radiata* (Mung) and *S. lycopersicum* (Tomato) were placed in petri dish and treated with 5 mL of AC-TiO_2/water mixture of different concentrations. The seeds without AC-TiO_2 suspension treatment were used for control experiments (Fig. 5). After 3 days of incubation, AC-TiO_2 was found to accelerate the process of seed germination and significantly shortened the germination time as compared to the control one. The root-to-shoot lengths of AC-TiO_2-treated seed as shown in Fig. 5 were also found much longer than that of the control seeds. Moreover, the root length of *V. radiata* showed higher value at the lower concentration of AC-TiO_2; however, the overall root length decrease with further increase in the concentration.

Figure 6 shows that germination of lower-concentration-treated *S. lycopersicum* seeds was more than that of control seeds on the second day. During the next few days, the germination rate was dramatically faster for seeds treated with AC-TiO_2 than that of the control seeds. The germination percentage for the control seeds averaged 80 % in 4 days, while germination percentage of the AC-TiO_2-treated seeds averaged 100 % (higher concentration) in 4 days, 100 % (medium concentration) in 4 days and 90 % in lower concentration (Fig. 6). It indicates that the accelerated seed germination could be caused by increasing concentration of nano-composite, which might be due to the penetration of the seed husks by TiO_2. As illustrated in Fig. 6, at stage I, the AC-TiO_2 was found to be densely deposited on the seeds' surface and penetrated seed husks which supports and allows water uptake inside the seeds. In case of *S. lycopersicum*, the germination rate was 0 % in 4 days in control, 10 % in lower concentration, 35 % in medium concentration and 80 % in higher concentration. After 8 days, the germination rate was increased by 0–50 % in control, 50 % in lower concentration, 95 % in medium concentration and 90 % in higher concentration. Zhang et al. (2015) demonstrated that the nano-sized TiO_2 helps the water absorption by the *Spinach* seed which helps in the enhancement of the germination rate. Khodakovskaya et al. (2009) also supported the same in case of carbon nanotube. Water uptake is an important process in the seed germination as mature seeds are fairly dry and need water to initiate the cellular metabolisms and growth.

Generally, these nanoparticles enhance the germination rate in various plant species. Mature seeds are relatively dry and need uptake of significant amounts of water to start their cellular metabolism and growth resume. Nanoparticles may create new pores in the seed coat and therefore facilitate the process of water uptake inside the seed

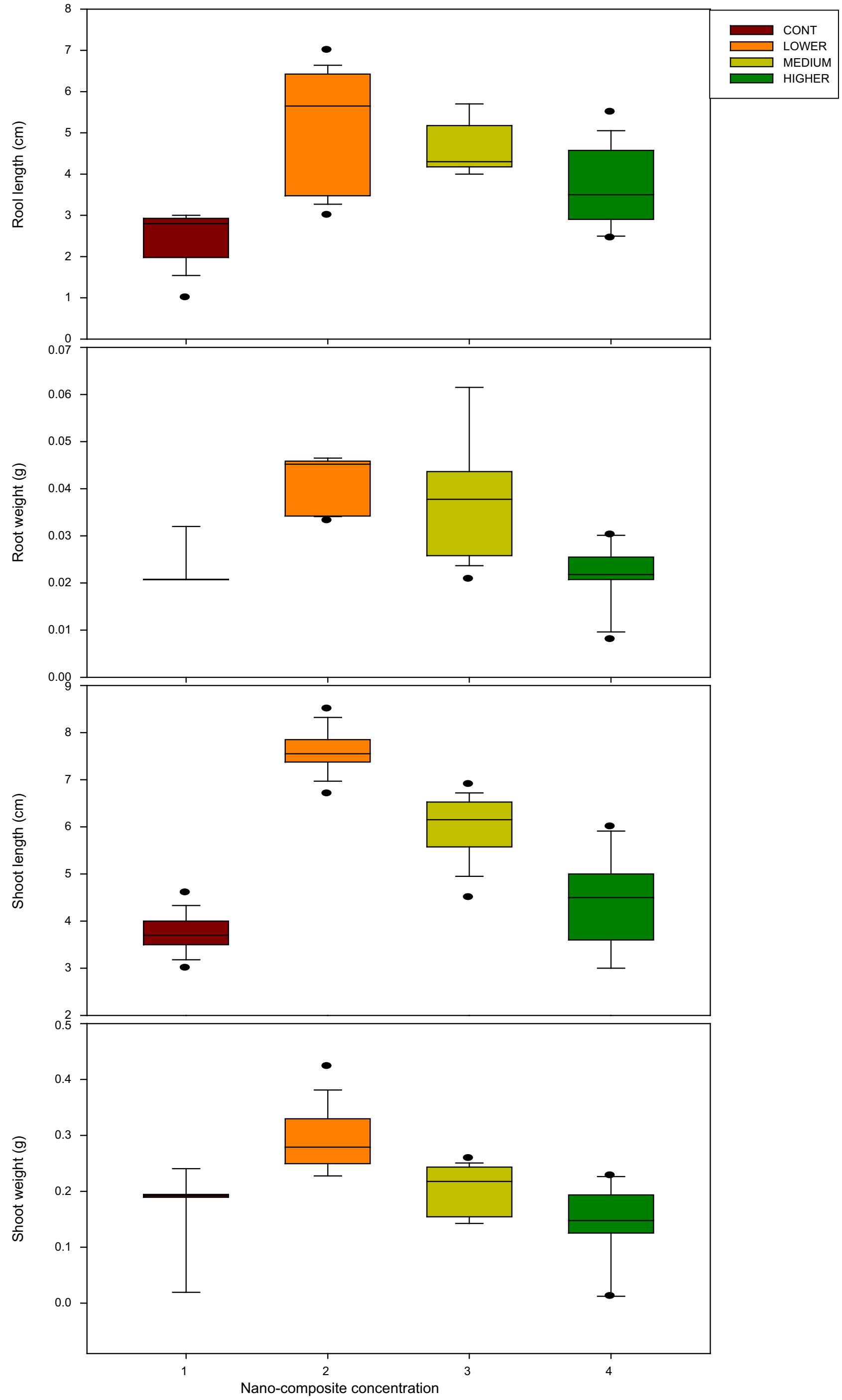

Fig. 5 Shoot and root length and weight of *Vigna radiata* growing under different concentrations of AC-TiO_2 nano-composite

embryo, and therefore, germination rate. Various other studies reported that TiO_2 in the nano-range promotes the seed germination, photosynthetic activity and nitrogen metabolisms which cumulatively promotes the growth of plant species at a suitable range of concentrations (Zheng et al. 2005; Hong et al. 2005; Yang et al. 2007). Further, it increases the activity of several enzymes and promotes the adsorption of nitrate, accelerating the transformation of inorganic into organic nitrogen. However, normal-sized TiO_2 does not have such effects (Ma et al. 2010a, b).

AC-TiO_2 composite had positive impacts on the germination of *V. radiata* seeds, which can be attributed to the fact that TiO_2 was able to penetrate the seed husks (Fig. 7). The penetration might break the husks to facilitate water uptake, resulting in rapid seed germination and higher percentage of germination rates. However, at the stage of

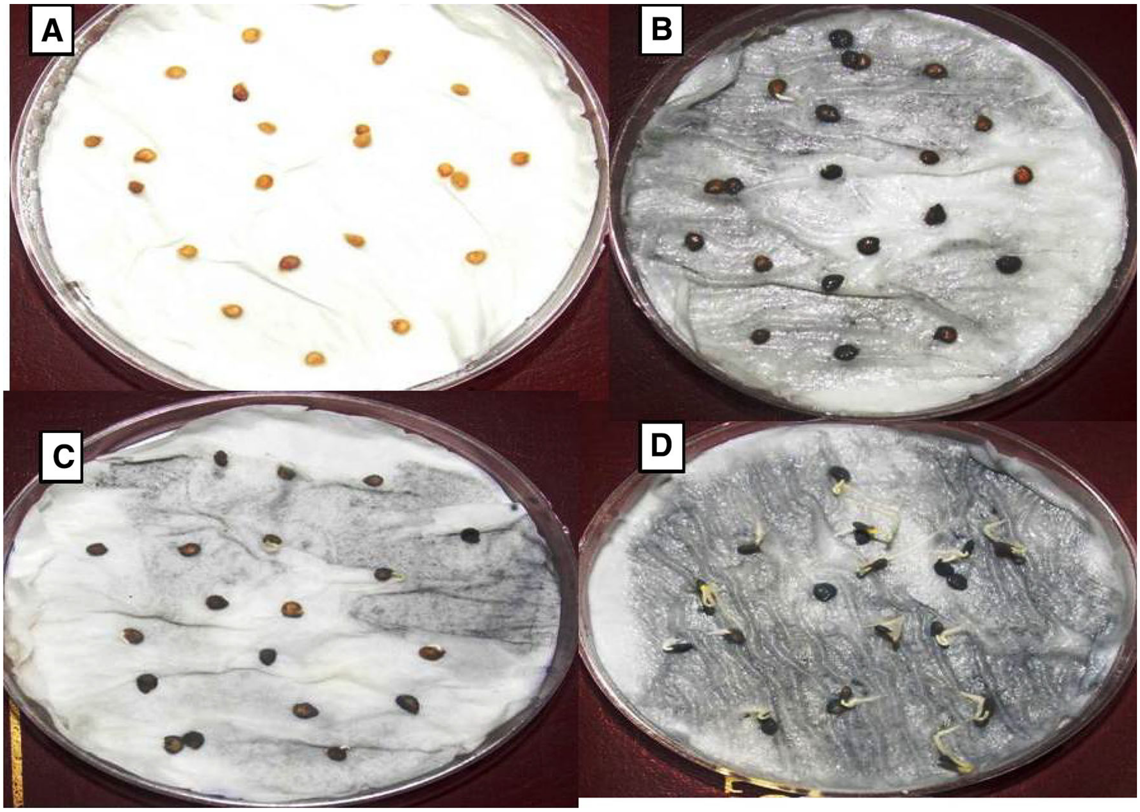

Fig. 6 Germination of *Lycopersicum esculentum*: **a** control, **b** lower concentration, **c** medium concentration and **d** higher concentration

Fig. 7 Seed germination of *Vigna radiata* after 4 days: **a** higher concentration, **b** medium concentration, **c** lower concentration and **d** control

seedling growth, activated carbon may be providing moisture to the seed. Furthermore, stems and roots of the higher-concentration-treated seedlings were longer than those of the control. Zhang et al. (2015) found that in the case of graphene, it penetrates the seed husk which might break the husk to facilitate water uptake, resulting in faster germination as well as higher germination rate. Carbon nano-materials are known for their light weight and extreme conductivity which occupy a unique place in agriculture because of their abilities to enhance the seedling growth and development. Effect of nano-materials on the plant growth also depends upon the type of nano-materials, size-specific area, functional groups, concentration, plant species, soil type and condition (Lin and Xing 2007; Ge et al. 2011; Rico et al. 2011; Josko and Oleszczuk 2013).

Seed germination was higher in lower and medium concentrations of AC-TiO_2, whereas root-to-shoot ratio was found higher in the lower concentration. It showed that the concentration of nano-composite plays a vital role in the plant growth and development. The increase in the seed germination might be due to the photo-generation of active oxygen like superoxide and hydroxide anions which causes re-activation of aged seed. Activated carbon present in the nano-composite provides large surface area and moisture for seed germination. It also enhances the penetrability of seed capsule, facilitating the admission of water and dioxygen into the cell, thereby resulting in an increase in the seed germination. TiO_2 also induces oxidation–reduction via free superoxide radical during the germination. The oxygen produced in such processes could be used for respiration which further promotes the seed germination (Zheng et al. 2005).

4 Conclusions

The release of nano-materials into the environment affects various plant growth mechanisms and development from the seed germination to pollination. We observed that the activated carbon-based TiO_2 (AC-TiO_2) nano-composite had positive impacts on the germination of *Vigna radiata* and *Solanum lycopersicum* seeds, which can be attributed to the fact that TiO_2 was able to penetrate the seed husks. It envisaged that the elongation in root-to-shoot ratio may be related to the concentration of catalysts, but further studies are needed at cellular and molecular level for the best understanding of the mechanisms of reaction of catalysts with seed. The dose of the nano-composites (AC-TiO_2) was studied on the germination of seed and by measuring their root and shoot growth. The results indicated that AC-TiO_2 nano-composite enhanced the seed germination in plants and also enhanced the shoot-to-root ratio depending on the concentration of materials. At increased concentration, the germination is enhanced, but the growth of root and shoot was either decreased or remained stable as compared to the control. Overall, these results will be helpful for further understanding of the mechanisms of interaction of nano-materials with the plants species.

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