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Nano silica sulfuric acid catalyzed facile synthesis of azothiadiazoles under co-grinding and solvent-free technique

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An efficient method for the use of nano silica sulfuric acid as a heterogeneous catalyst in the synthesis of thiadiazole-containing azo dyes *via* diazo coupling of substituted amino thiazole under solvent-free conditions is described. The method presented is effective, green, inexpensive, and satisfactory to give the products in high yield with an excellent purity in short times under mortar–pestle grinding. The environmental friendliness and re-usability of the catalyst make this protocol attractive in organic synthesis.

Keywords: Azo dyes, Nano silica sulfuric acid, Thiodiazole, Rice husk, Mortal-pestle grinding

Over the past decade, substantial progress has been achieved in the organic colour chemistry. Principally aromatic compounds holding ‘azo/diazenyl’ (R−N=N−R) as a chromophoric functionality are found to be important class in the fields of colour industry and have great applications in high technology domain like linear and non-linear optics, reprography, electronic devices, sensors and biomedical uses[1-4]. Moreover they are well known for their use as colorants in the digital printing and photography[5] textile industries[6], chiral receptors[7], chiral switches in photochemistry[8], new glassy materials[9], liquid crystals[10], in dying of food, cosmetic, drug, biomedicine[11], and molecular recognition[12]. Therefore, due to their versatile skeleton and uses in many practical applications, the development of such compounds received much attention. In fact, it is the area of current research interest where researchers are paid attention to synthesizing these compounds *via* simple and eco-friendly methodologies.

Routine acid-base catalyzed processes are effective for near quantitative formation of the desired azo derivative *via* diazotization of arylamines in the presence of nitrous acid or sodium or potassium nitrites. But the homogeneous characteristics and environmental incompatibility of harmful acidic material limit their usage in conventional processes. Nowadays, heterogeneous solid acid reagents have resolved these problems and improved activity and selectivity rather than individual reagents in the synthesis of azo dyes[13–15]. They also assist to boost the fundamental research and industrial potential of heterogeneous catalysis due to their inexpensive and eco-friendly character. Further, these reagents help to simplify purification processes as well as prevent release of reaction residues into the environment[16]. In this regard, nano structure solid acids such as nano-silica sulfuric acid (nano-SSA), have attracted great interest of scientific community due to their adequate catalytic performance, stability under intense conditions, and extraordinary physical as well as chemical properties, like large surface to volume ratio[17], renders a plurality of active sites. Alternatively, it has excellent activity and selectivity on an industrial scale as well. So, in most cases, it can be recovered from reaction mixtures and reused. In addition, the physicochemical properties such as inertness under the reaction progression and tunable pore structures believe that nano-SSA becomes the best solid support for the organic transformations[17e].

While designing new chemical processes, besides using heterogeneous catalysts we also try to focus one of the thrust areas under the green chemistry principle is to explore alternative reaction media or reaction conditions to furnish the desired chemical transformations with minimized hazardous waste or to control the use of conventional organic solvents, wherever possible. Accordingly, compared to several newer strategies, the solvent-free and co-grinding technology could ameliorate their efficiency from an economic as well as an ecological point of view[18]. Hence in continuation of our efforts towards the synthesis of heterocyclic azo compounds[19], we report here the use of nano-SSA in the synthesis of azothiazole *via* diazo coupling reaction of anilines with substituted amino thiazoles.

Experimental Details

Materials and Methods

Chemicals were purchased from the local supplier Spectrochem (Mumbai, India) and Merck, India and were used without any additional purification. Melting points were determined on a open capillary and are uncorrected. All reactions were monitored by thin-layer chromatography (TLC) using Merck pre-coated silica gel F254 plates. Respective starting material thiazoles[24] and silica nanoparticles (from rice husk ash)[20] were prepared as per known method and used. IR spectra were recorded with a Perkin-Elmer one FTIR spectrophotometer in which samples were examined as KBr discs~5% *w/w*. The SEM analysis was carried out using a JEOL model JSM with 5 kV and 20 kV accelerating voltage. XRD pattern was taken in the 2θ range of 0–80° with a scan rate of 4°/min on a Bruker D2 Phaser X-ray diffractometer at a wavelength of 1.55060 Å. ^{1}H NMR spectra were recorded on a BRUKER AVANCE (400) spectrometer using TMS (δ = 0 ppm) as an internal standard and DMSO-d_6 as solvent. Chemical shift (δ) values are expressed in parts per million (ppm) units with respect to TMS, coupling constants are expressed in hertz (Hz). C.H.N elemental analyses were performed on EURO EA3000 vectro model. The products were characterized by comparison of their spectral and melting point data with reference.

Synthesis of nano-silica from rice husk ash (RHA) [20]

The raw material, rice husk, was obtained from a rice mill and washed thoroughly with distilled water tap water to remove sand, dust, soluble substances, and other contaminants. It was then dried at 60 °C in air oven. The cleaned RH was burned in open environment to collect rice husk ash (RHA). 50 g of RHA was refluxed with 500 ml of HCl 1N for 2 h and allowed to stand overnight in order to remove metallic impurities in RHA. The acid treated RHA was filtered and thoroughly rinsed with distilled water and dried at 60 °C in air oven. Further it was converted into its sodium salts by stirring with 2.5 N NaOH solution for 14 h to form sodium silicate. Again on neutralized with H_2SO_4 (Merck GR) until the pH equal to 8 gives nanosilica gel. Finally, the received gel was turn into powdery form by pursuing calcination at 700 °C for 2 h in muffle furnace with a ramp rate of ~20 °C/min. The obtained product was nono-silica as a white powder.

Synthesis of nano-SSA[20]

To a clean and dry 500 mL round bottom flask containing nano-silica (90.0 g) in dichloromethane (200 mL), was added drop wisely chlorosulfonic acid (35.0 g) with a constant pressure dropping funnel over a period of 30 min at room temperature. HCl gas was evolved from the reaction vessel immediately. After the addition was complete, the mixture was shaken for 30 min and a white solid of nano-SSA (115.0 g) was collected by filtration and dried.

Typical experimental procedure for solvent-free diazo-coupling by co-grinding of reactants in a mortar with pestle

The mixture of aniline (10 mmol) derivative, $NaNO_2$ (10 mmol) and 0.05 gm of nano-SSA was ground for 3 min., at room temperature. To the obtained diazonium salt, added solution of 2-amino thiazole (10 mmol) coupler in 20% caustic solution (1 mL) and ground vigorously for 2 min. until completion of reaction, monitored on TLC. The obtained dye was dissolved in acetone and filtered to isolate the catalyst. By evaporation of solvent and crystallization in ethanol, the solid dye product was obtained in good to excellent yields (71-91%). The products were identified by characteristic spectroscopic data.

Spectral data for the selected compounds

(1) 2-Amino-5-phenylazo-thiazole (3a) [26a]:

Reddish brown solid. yield 89%; mp 268–270ºC. IR (KBr): 3420, 3271 (NH_2), 1640 (C=N), 1240 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.20-7.38 (m, 6H, C4-H, thiazole & -PhH), 8.28 (bs, 2H, NH_2); Anal. Calcd. for $C_9H_8N_4S$ (mol. wt.: 204.24): C 52.92, H 3.95, N 27.43%; Found: C 52.85, H 3.90, N 27.47%.

(2) 2-Amino-5 (4-chloro phenyl) azo-thiazole (3b) [26a]:

Brown Solid. yield 87%; mp: 168–171ºC. IR (KBr): 3357 (NH_2), 3051, 1633 (C=N), 1491(N=N), 1367, 1231, 1146, 1011, 830 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$,): δ 7.26 (s, 1H, C–H thiazole), 7.38 (d, 2H, *J* = 7.5 Hz, Ar–H), 7.44 (d, 2H, *J* = 7.5 Hz, Ar–H), 8.42 (bs, 2H, NH_2); Anal. Calcd. for $C_9H_7ClN_4S$ (mol. wt.: 238.69): C 45.29, H 2.96, N 23.47%; Found: C 45.11, H 2.95, N 23.57%.

(3) 2-amino-5-(4-acetylphenylazo)-thiazole (3e)[26b]:

Brown solid. yield: 91%; m.p. 152–154°C. IR (KBr): 3348, 3232 (NH_2), 1669 (C=O), 1348, 1282 cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.43 (s, 3H, $COCH_3$), 7.24 (d, 2H, *J* = 7.8 Hz, Ar-H), 7.34 (s, 1H, thiazole C4-H), 7.38 (d, 2H, *J* = 7.8 Hz, Ar-H), 8.21 (bs, 2H, NH_2); Anal. calcd. for $C_{11}H_{10}N_4OS$ (mol. wt.: 246.29): C, 53.64; H, 4.09; N, 22.75%. Found: C, 53.50; H, 4.11; N, 22.71%.

(4) 2-amino-5-(4-anisylazo)-4-phenylthiazole (3g) [26d]:

Brown Solid. yield: 86%; m.p. 252-254°C. IR (KBr): 3420 (NH_2), 3105 (C-H), 1505, 1478, 1310, 1251, 1179 cm^{-1}; ^1H-NMR (DMSO-d_6): δ 3.86 (s, 3H, -OCH_3), 7.05 (dd, 2H, *J* = 7.6 Hz, -ArH), 7.41-7.44 (m, 7H, -PhH/ArH), 7.85 (bs, 2H, -NH_2); Anal. calcd. for $C_{16}H_{14}N_4OS$ (mol. wt.: 310.37): C, 61.92; H, 4.55; N, 18.05%. Found: C, 61.86; H, 4.51; N, 18.11%.

(5) 2-amino-5-(4-nitrophenylazo)-4-phenylthiazole (3i) [26f]:

Brown Solid. yield: 80%; m.p. 242-244°C. IR (KBr): 3433 (NH_2), 3057 (C–H), 1559, 1503, 1488, 1410, 1319, 1257, 1079 cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.25 (d, 2H, *J* = 8.5 and 1.6 Hz, –PhH), 7.39–7.45 (5H, m, ArH), 7.63, (d, 2H, *J* = 8.5 Hz, - PhH), 8.09 (bs, 2H, NH_2); Anal. calcd. for $C_{15}H_{11}N_5O_2S$ (mol. wt.: 325.34): C, 55.38; H, 3.41; N, 21.53%. Found: C, 55.30; H, 3.51; N, 21.50%.

(6) 2-Amino-4-methyl-5-(4-nitrophenylazo)thiazole (3k) [26g]**:**

Dark violet solid. yield = 82%; m.p. = 168-170℃; IR (KBr): 3443, 3270 (NH_2), 1609, 1528, 1375, 1209 cm^{-1}; ^1H NMR: 2.17 (s, 3H, thiazole-CH_3), 7.13 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.36 (d, 2H, *J* = 8.8 Hz, Ar-H), 8.42 (bs, 2H, NH_2); Anal. calcd. for $C_{10}H_9N_5O_2S$ (mol. wt.: 263.27): C, 45.62; H, 3.45; N, 26.60%. Found: C, 45.60; H, 3.51; N, 26.63%.

(7) 2-Amino-5-(4-anisylazo)-4-methylthiazole (3l)[26g]:

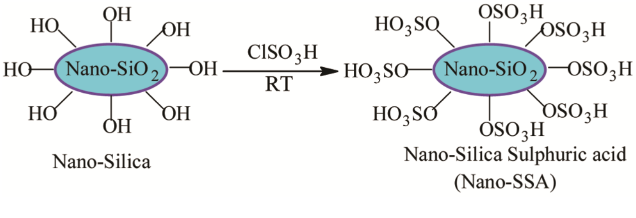
Orange solid, yield = 88%; m.p. = 210-212℃. IR(KBr): 3441, 3273 (NH_2), 2202, 1403, 1380 cm^{-1}; ^1H NMR: 2.13 (s, 3H, thiazole-CH_3), 3.43 (s, 3H, -OCH_3), 7.25 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.36 (s, 2H, NH_2); Anal. calcd. for $C_{11}H_{12}N_4OS$ (mol. wt.: 248.30): C, 53.21; H, 4.87; N, 2.56%. Found: C, 53.26; H, 4.91; N, 22.60%.

Results and Discussion

The synthesis of nanosilica particles was carried out *via* incineration, acid leaching process, and particle size reduction through a high-energy milling process. The crude rice husk, samples used in this study were obtained from a rice mill. That was washed to remove adhered soil or dust with distilled water and then burnt in a muffle furnace under an inert atmosphere. The obtained rice husk ash on refluxing with 1 M NaOH and followed by adjusting the pH using 1 M H_2SO_4 yielded desired grain size nano-silica[20]. Further on treatment of nano-silica particles with chlorosulfonic acid afforded the desired nano-SSA (Scheme 1). It is worthy to note that the immediate evolution of HCl gas from the reaction mixture makes this process very easier and cleaner[21].

The precise functionalization of nano-silica was studied by FT-IR spectrum. As shown in Fig. 1, the spectra of nano-silica and nano-SSA with the differential of both catalysts displayed the Si–O–Si symmetric as well as asymmetric vibrations bands in the range of 1000–1250 cm^{-1} and 798 cm^{-1}, respectively, and the related bending vibration is at 466-469 cm^{-1}. The IR peak at 1638 cm^{-1} is associated with bending vibration of water molecules trapped in silica matrix. The bending vibration at 963 cm^{-1} (Fig. 1(B)) was attributed to Si-OH silanol groups. The emergence of fresh peaks at 693 and 1179 cm^{-1} is a good reason for the functionalization of nano-silica by chlorosulfonic acid (Fig. 1(B)) In addition; successful sulfonic acid functionalization of the silica surface was evidenced by the absorption bands at 1312 cm^{-1} and 1179 cm^{-1} related to the stretching of the S–O bonds. The appearance of an intense sharp peak at about 3458 cm^{-1} is due to the stretching of the OH groups in the SO_3H moiety.

The morphology, as well as particle size of the catalyst, was evaluated by SEM technique and it reveals that both nano-silica as well as nano-SSA particles were formed at the nanoscale, typically below 200 nm (Fig. 2). Herein the functionalization was occurred randomly with an irregularity in its shapes on a smooth surface without any specific geometrical shapes. (Fig. 2(b)) Also nano-SSA particles do not show clear boundaries as they are in agglomerate and amorphous form.



Scheme 1 — Synthesis of Nano-SSA

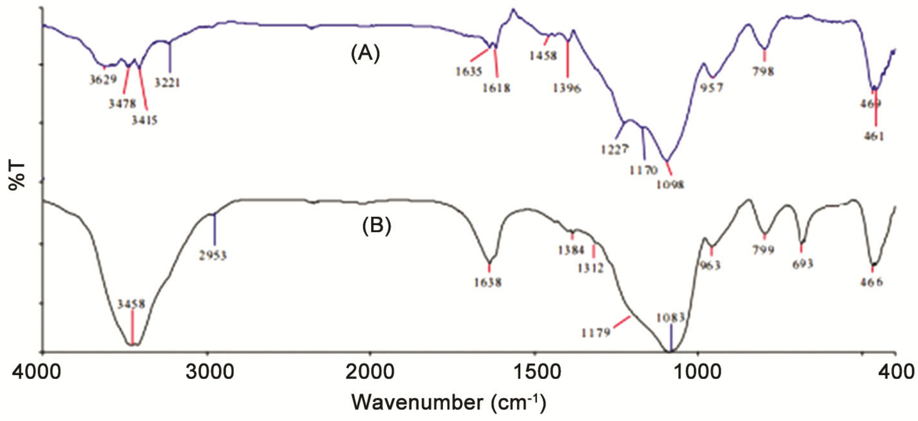


Fig. 1 — FT-IR spectrum of (A) nano-silica (B) nano-SSA

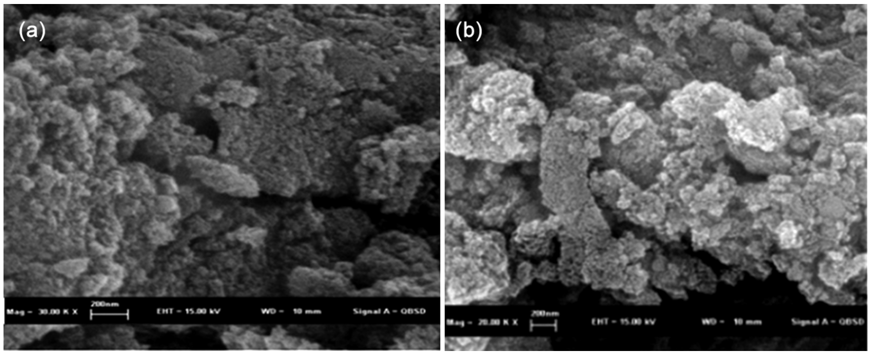


Fig. 2 — SEM images of (a) nano-silica (b) nano-SSA

Fig. 3 shows the characteristic diffraction peak for silica at around 2θ = 22°. Moreover, the XRD peaks of freshly prepared (Fig. 3(a)) and recovered (Fig. 3(b)) nano-SSA catalysts were showed identical positions with dissimilar intensities.

Nano-SSA is a bench-top catalyst, ascertain as versatile, reusable, and efficient for the promotion of many acid catalyzed organic reactions[22]. Furthermore, it can be stored at ambient temperature for several months without any special precautions as well as unaffected catalytic activity. Due to these overwhelming characteristics of nano-SSA, we sought to explore its heterogeneous acidic concert on synthetic reactivity of various anilines towards substituted amino thiazoles in the construction of azo scaffolds[3,11,26].

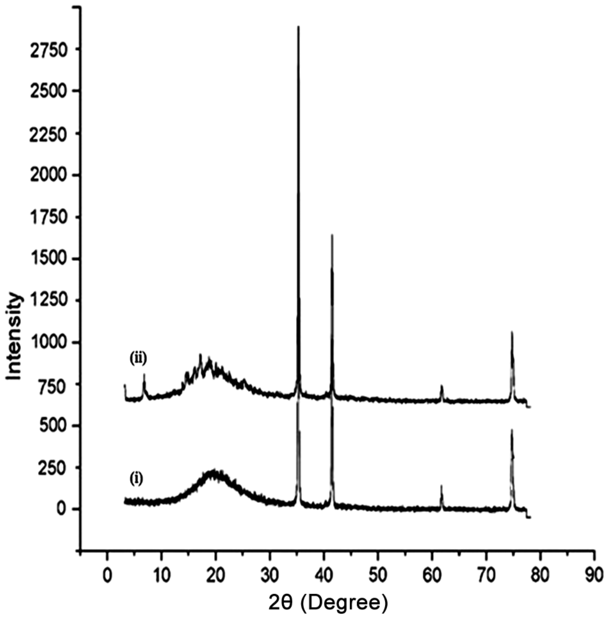
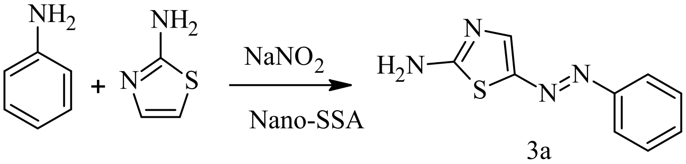


Fig. 3 — XRD of nano-SSA (i) fresh and (ii) recovered catalyst

The model diazotization reaction of an equimolar amount of aniline (10 mmol) and $NaNO_2$ with 2-amino thiazole (10 mmol) in the presence of nano-SSA on co-grinding with a mortar and pestle for 5 min. afforded the corresponding 2-amino-5-phenylazo thiazole (3a), in the excellent yield. Table 1 describes the performance of different amounts of nano-SSA under assorted conditions. (Table 1, entries 1-10) The increase in amount of catalyst from 0.01 to 0.05 gm (Table 1, entries 1-5) increases the conversion of product formation and it was worth to mention that 0.05 g of nano-SSA would be sufficient to achieve maximum product quantity. Further increase in amount of nano-SSA would not increase the yield remarkably (Table 1, entry 6). To our delight, on repetition of aforesaid condition with various amounts of nano-SSA under solvent-free condition (Table 1, entries 9-10) was found to be most effective in terms of reaction yield and rate. The solvent-free condition justifies, rigid, tight, and regular arrangement of molecules in the crystal structure of nano-SSA helps in effective formation of the azo dye[23]. Thus taking into consideration of aniline (10 mmol), $NaNO_2$ (10 mmol), 2-amino thiazole (10 mmol) and nano-SSA (0.05 gm) without any solvent is the preeminent reaction condition to promote the application of nano-SSA for the building of other azo derivatives.

With the optimized condition in hand, we intend to evaluate the scope of the protocol by reacting electronically and structurally diverse thiazoles. The obligatory thiazoles derivatives were prepared by fusion of thiourea with acetophenone[24a] and chloro acetone,[24b] respectively, as per reported procedures. On receipt of 4-phenyl/4-methyl -2-amino thiazole, it was quickly reacted with various diazonium salts of aniline derivatives in presence of nano-SSA, forming bright-colored 2-amino-5-arylazo thiazoles (Table 2, entries a-l). The reaction was clean, and the purification

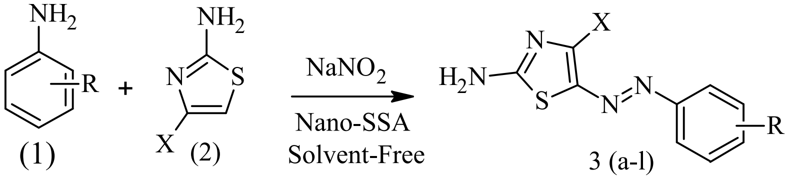
Table 1 — Optimization in nano-SSA quantity[a]

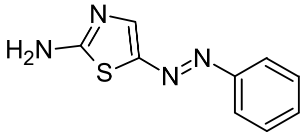
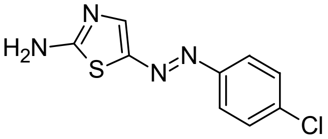


S. No.	Nano-SSA (g)	Solvent (mL)	Time (min)	Yield (%)
1	0.01	Ethanol	10	50
2	0.02	Ethanol	10	52
3	0.03	Ethanol	10	58
4	0.04	Ethanol	10	66
5	0.05	Ethanol	10	72
6	0.06	Ethanol	10	70
7	0.05	Methanol	15	65
8	0.05	Water	20	70
9	0.05	Solvent-free	5	89
10	0.04	Solvent-free	5	85

[a] Aniline (10 mmol), $NaNO_2$ (10 mmol), 2-amino thiazole (10 mmol), nano-SSA, Solvent (5-10 mL), grind with a mortar and pestle

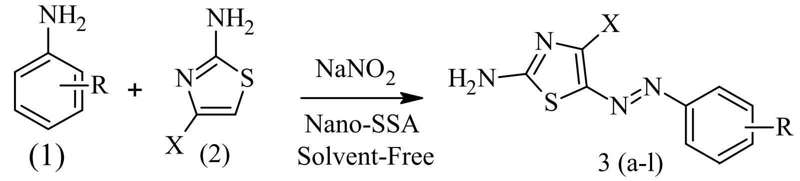
Table 2 — Synthesis of substituted 2-amino-5-phenylazo thiazoles[a]

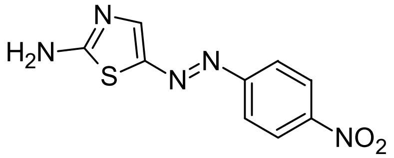
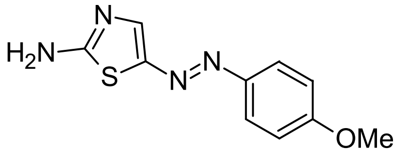
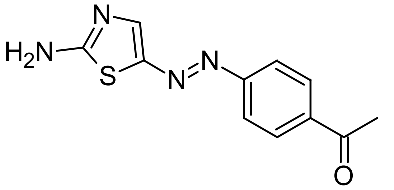
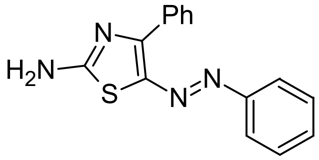
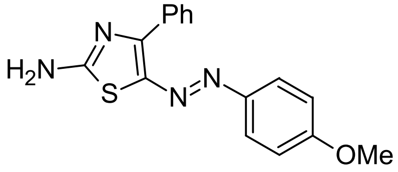
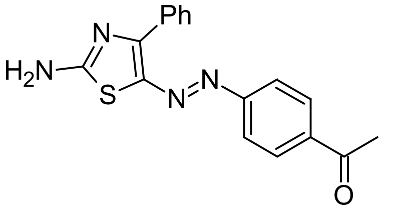


Entry	R (1)	X (2)	Products (3)	Yield (%)	mp (°C) [Lit. ref.]
a	H	H	 (3a)	89	270-271 (270–271) [Ref. 26a]
b	p-Cl	H	 (3b)	87	172-174 (168–171) [Ref. 26a]

(*Contd.*)

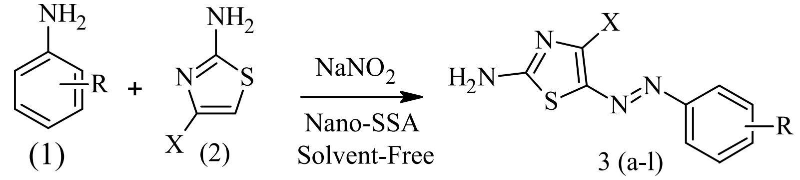
Table 2 — Synthesis of substituted 2-amino-5-phenylazo thiazoles[a] (*Contd.*)

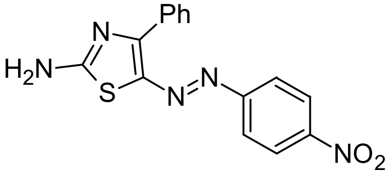
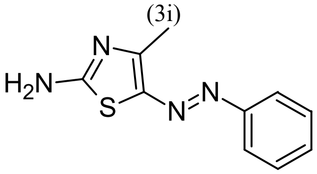
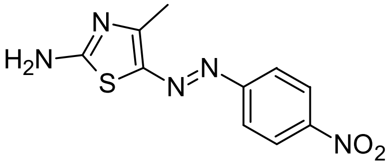
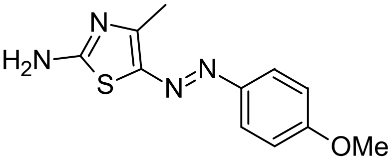


Entry	R (1)	X (2)	Products (3)	Yield (%)	mp (°C) [Lit. ref.]
c	p-NO$_2$	H	 (3c)	85	166-168 (162–164) [Ref. 26a]
d	p-OMe	H	 (3d)	90	110-112 (113–116) [Ref. 26a]
e	p-acetyl	H	 (3e)	91	153-154 (153–154) [Ref. 26b]
f	H	Ph	 (3f)	85	172-174 (175) [Ref. 26c]
g	p-OMe	Ph	 (3g)	86	252-254 (253-255) [Ref. 26d]
h	p-acetyl	Ph	 (3h)	82	252-254 (254–256) [Ref. 26e]

(*Contd.*)

Table 2 — Synthesis of substituted 2-amino-5-phenylazo thiazoles[a] (*Contd.*)



Entry	R (1)	X (2)	Products (3)	Yield (%)	mp (°C) [Lit. ref.]
i	p-NO_2	Ph	 (3i)	80	242-244 (245-247) [Ref. 26f]
j	H	CH_3	 (3j)	83	268-270 (270-271) [Ref. 26g]
k	p-NO_2	CH_3	 (3k)	82	168-170 (167-169) [Ref. 26g]
l	p-OMe	CH_3	 (3l)	88	210-212 (211-212) [Ref. 26g]

[a]Anilines (1), 10 mmol), $NaNO_2$ (10 mmol), amino thiazoles (2), 10 mmol), nano-SSA (0.05 gm) grind with a mortar and pestle

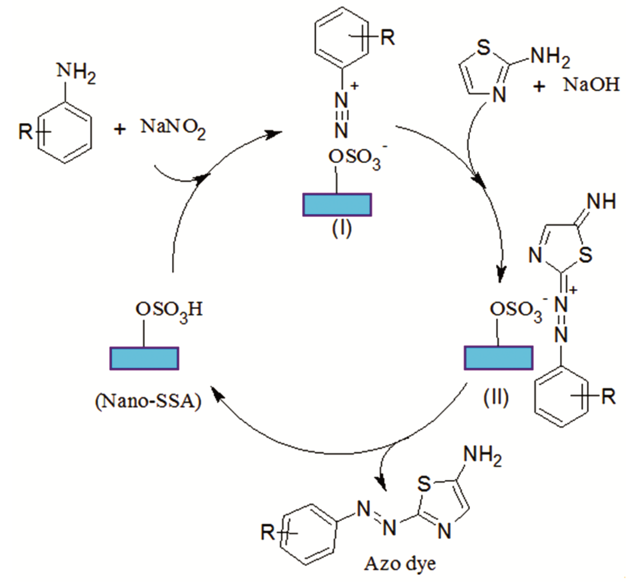
of the product is straightforward with excellent yields, especially with liquid aniline derivatives. The rate of formation of diazonium salts are faster with anilines containing electron-releasing groups (Table 2, entries d,g,l) as compared with the electron-withdrawing groups. (Table 2, entries b,c,i,k) On the other hand sterically hindered amino thiazole such as 4-phenyl-2-amino thiazole, owing to phenyl substituent's at 4-position yielding lesser yields and slower than the other simple derivatives. (Table 2, entries a-e and j-l) The structures of all resulted dyes were characterized by, FT-IR, ^{1}H-NMR, and elemental analysis.

Mechanism

From a synthetic perspective, possible mechanism commenced with *in situ* formations of stable aryl diazonium sulfate complex (I)[25] with substituted anilines followed by tandem reaction with amino thiazoles thereby providing facile access to azo derivatives *via* sequential intermediate (II) and hydrogen transfer and it was schematically described in Scheme 2. On the basis of literature, the formation of intermediate (I) was ascribed due to nucleophilic addition of lone pairs on the nitrogen atom of aniline with the adsorbed NO_2. Soon after base mediated coupling of amino thiazole yielded highly unstable intermediate (II), which on immediate hydrogen transfer produces, desired 2-amino-5-phenylazo-thiazole exclusively and regeneration of the catalyst takes place.

Recyclability Test

To check the catalyst sustainability in retaining its activity, the recyclability was assessed on a model reaction of aniline coupling with 2-aminothiazole. The catalyst was recovered by following steps such as



Scheme 2 — Plausible mechanism in nano-SSA catalyzed synthesis of Azo dyes

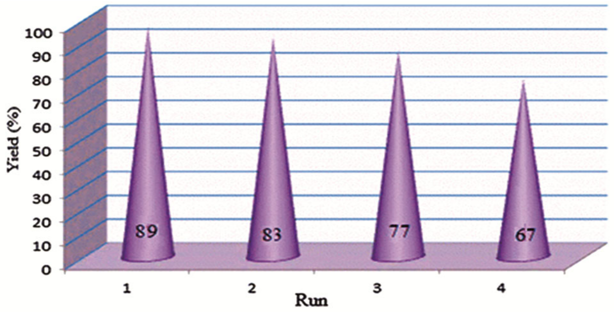


Fig. 4 — Recyclability study of nano-SSA

filtration, ethanol washing, treatment with water, and acetone and drying (vacuum oven at 60°C for overnight). Further, it was then subjected to the next catalytic cycles and found to be active without an appreciable reduction in the product 3a yield, under the established conditions. Thus, based on the above results, it was confirmed that the nano-SSA catalyst is having enough stability and can be reused up to four consecutive runs (Fig. 4).

Comparative study

In order to show the merit of nano-SSA in comparison with the other catalysts used for the synthesis of 2-amino-5-phenylazo-thiazole (3a) from aniline and $NaNO_2$ with 2-amino thiazole, we have summarized several results in Table 3. It is evident from these results that nano-SSA is a highly efficient catalyst for the synthesis of an azo derivative at ambient temperature and solvent-free reaction conditions.

Table 3 — Comparison of different catalysts for the reaction of aniline and $NaNO_2$ with 2-amino thiazole

S. No.	Catalyst (g)	Time of coupling reaction (min)	Solvent	Yield (%)
1	$Fe_3O_4@SiO_2$-SO_3H (0.2)	30	Ethanol	90 [26a]
2	Chitosan-SO_3H (0.2)	30	Ethanol	40 [26a]
3	Starch-SO_3H(0.2)	30	Ethanol	45 [26a]
4	Montmorillonite SO_3H (0.2)	30	Ethanol	94 [26a]
5	Conc. HCl (3)	120	Ethanol	84 [27]
6	Nano-SSA(0.05)	05	Solvent-Free	89 [Present Work]

Conclusion

In summary, we have developed the Nono-SSA catalyzed diazo coupling reactions of anilines and amino thiazoles in good to excellent yields. This methodology proceeds with high chemoselectivity even in the presence of other sensitive functional groups like nitro, halo and keto. This is an important advantage compared with known traditional homogeneous catalytic systems wherein, special cold conditions for stabilization of diazonium salt are required. Another important aspect of the present work is the catalyst stability and recyclability without losing activity. Finally, the broad applicability and the relatively mild reaction conditions make this procedure interesting for the synthesis of all kinds of diazo coupling reactions in fine and bulk chemicals.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/58776.

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